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Development of Aluminum-Based Coatings Produced by Cold Gas Dynamic Spraying

By

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Abstract

Cold Gas Dynamic Spraying (CGDS) has emerged as a promising coating technology able to produce coating layers for a wide variety of applications. In CGDS, fine particles are accelerated in a high velocity gas flow and undergo solid-state plastic deformation upon impact on the substrate. The distinctive feature of CGDS is that the process gas temperature is well below the melting point of the sprayed materials. The undesirable effects of high temperatures found in conventional thermal spray processes, such as oxidation, grain growth and thermal stresses, are therefore avoided. In response to the potential of CGDS, this study primarily explores and expands the range of applicability of CGDS and specifically addresses the development and characterization of aluminum-based coatings consolidated by the CGDS process.

The first part of this thesis is dedicated to particle in-flight velocity measurements. Two different particle in-flight velocity measurement tools, a Cold Spray Meter (CSM) and a Particle Image Velocimetry (PIV) system, are compared based on their operating characteristics and limitations.

In the second part of this work, Al-Co-Ce, Al-5083 and Al-12Si coatings are consolidated by the CGDS process. Blends of Al-12Si and silicon carbide and a composite powder consisting of Al-5083 alloyed with boron carbide are also sprayed to synthesize metal-matrix composite coatings. A microstructural characterization of these coatings is carried out to evaluate the porosity, thickness, defects and microhardness. The adhesion strength and the fatigue strength are respectively measured using the ASTM C 633-01 and the ASTM B 593-96 tests.

The relationships between the particle velocities, the coating microstructures and their properties are explained. The nozzle exit-to-throat area ratio, the gas stagnation temperature and the powder feed rate are factors that influenced the particle velocities and their effects on the coating properties are described. The effects of other parameters, such as the substrate traverse speed, the substrate surface roughness and the stand-off distance are also investigated.

Sommaire

La projection dynamique à froid (CGDS : Cold Gas Dynamic Spraying) est une technologie de revêtement prometteuse pour la réalisation de revêtements destinés à une vaste gamme d'applications. Le CGDS se distingue des autres techniques de projection thermique par sa température du gaz qui est bien en-dessous de la température de fusion des matériaux projetés. Par conséquent, les effets thermiques tels l'oxydation, la croissance des grains et les contraintes thermiques que l'on retrouve dans les procédés de projection thermique conventionnels sont évités. En réponse au potentiel du CGDS, cette thèse s'adresse au développement et à la caractérisation de revêtements à base d'aluminium produit par CGDS.

Ce travail traite en premier lieu de la prise de mesures de vitesses des particules. Deux outils de mesure, un Cold Spray Meter (CSM) et un système de vélocimétrie par images de particules (PIV : Particle Image Velocimetry), sont comparés selon leurs caractéristiques d'opération et leurs lacunes.

En deuxième partie, des revêtements d'Al-Co-Ce, Al-5083 et Al-12Si sont produits par CGDS. Des mélanges d'Al-12Si et de carbure de silicium et des particules-composites d'Al-5083 et de carbure de bore sont aussi utilisés pour développer des revêtements composites à matrice métallique. La porosité, l'épaisseur, les défauts et la dureté des revêtements sont évalués à partir d'une analyse de la microstructure de ces revêtements. Les mesures d'adhésion et de résistance à la fatigue sont effectuées selon les tests ASTM C 633-01 et ASTM 593-96, respectivement.

Les relations entre la vitesse des particules, la microstructure des revêtements et leurs propriétés sont expliquées en détail. Le rapport des aires de sortie et du col de la tuyère, la température de stagnation et le débit des poudres sont des facteurs qui agissent sur la vitesse des particules et leurs effets sur les propriétés des revêtements sont décrits. Les effets de la vitesse de passage du substrat, de la rugosité de surface du substrat et de la distance de projection sont aussi étudiés.

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Chapter 1 – Introduction

1.1 Background

The objective of any coating technology is to restore or to increase the performances and the properties of the part to be coated. As such, thermal spray coatings can be a cost-effective way to enhance the performance qualities of manufactured components. Thermal spray processes involve in a first step the heating of a material, in powder or wire form, to a molten or semi-molten state. The material is then propelled using a stream of gas toward a substrate. The particles strike the substrate, flatten, and form splats that conform to the irregularities of the surface. The splats subsequently solidify on the surface and incrementally build up to form a lamellar structure. The coating material may consist of a single element but is often an alloy or a composite. Metals, alloys, polymers, cermets, and ceramics are common materials that are applied by thermal spray processes. Depending on the application and the thermal spray process used, the coating thickness can vary between 25 μm and 2.5 mm (0.001 to 0.100 in) [1].

Due to the flexibility of thermal spray processes, a wide variety of engineering problems have been solved through the application of thermal spray coatings. The coating properties can be tailored for wear prevention, dimensional restoration, thermal insulation and control, corrosion resistance, oxidation resistance, lubrication, abrasive reactivity, sealing ability, biomedical activity and electromagnetic properties control [1]. These coatings are found in a substantial number of industrial sectors including aerospace, automotive, transportation, power generation, petrochemistry, pulp and paper processing, biomedical, metal processing, electronics, marine, ceramics and glass manufacturing, textile,

and consumer products. In 2004, the global thermal spray market was estimated at \$5.2 billion and about 60% of the overall market originated from the turbine industry [2]. The reported 10% increase per year in thermal spray sales since 1990 reflects the economic need and opportunities for thermal spray [3].

The properties of thermal spray coatings are significantly affected by the amount of defects present in the coated layer. These imperfections, which depend on the spray process and parameters as well as the materials sprayed, may comprise of pores, cracks, and oxides as shown in Figure 1.1. The origins of these defects are the outcome of poor deformation of partially melted particles and of particles much larger than the median, low velocity particle impacts, oxidation of metallic particles, and fragmented splats [5].

The latest developments in thermal spray rely on reducing the particle temperatures to limit the oxidation levels and on increasing the particle velocity to enhance their deformation upon impact. For example, plasma torches working with lower temperatures enable better particle acceleration and limit the surrounding air entrainment [3]. In high velocity oxygen-fuel (HVOF) spraying, the aim is to increase the combustion chamber pressures to achieve higher particle velocities and decrease the particle dwell time in the hot flame [6].

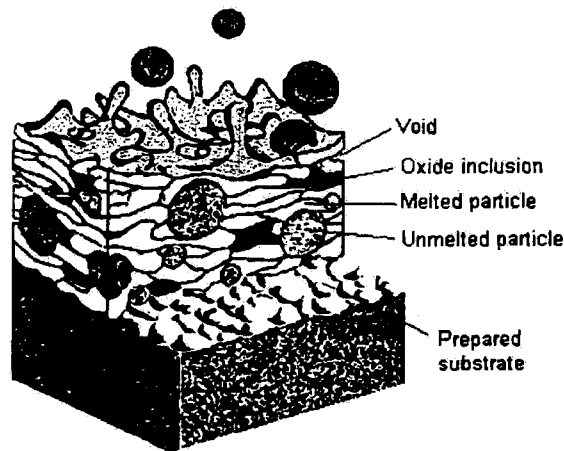


Figure 1.1 Schematic showing the typical microstructure of a thermal spray coating (from [4])

An emerging thermal spray process, the Cold Gas Dynamic Spraying (CGDS) process, has shown great promise in the application of coatings through high particle velocities at low temperatures. In conventional thermal spray processes, the particles are exposed to gas temperatures that typically range between 3000 and 25000°C, which are values well above the melting point of most materials. In CGDS, the absence of high temperatures enables the production of coatings with the same microstructural, mechanical, and chemical properties of the particle feedstock [7]. The prevention of grain growth, oxidation, and thermal shrinkage are some of the advantages of the CGDS process [7].

CGDS is particularly well suited for ductile materials such as aluminum and its alloys. Aluminum has become important in virtually all segments of the world economy as it comes second to iron in terms of global use [8]. In 2006, the worldwide production of aluminum reached 32 million metric tons [9] in comparison to the 1.2 billion metric tons of iron ore produced [10]. Structural components made from aluminum alloys are vital to the aerospace industry and very important in other areas such as transportation and building. For example, aluminum overtook iron to become the second most used material in new cars and trucks in

2006 [11]. These alloys are used extensively due to their ability to resist corrosion, their high strength to weight ratio, their reusability through recycling, and crash energy absorption capacities. The use of aluminum alloys in several automotive parts allows for weight reductions which directly translate into fuel economy.

1.2 Objectives and Problem Description

The present study was motivated by the potential of the CGDS process to develop engineered coatings with desired properties for specific applications. The primary research objective of this study is to explore and expand the range of applicability of the CGDS process to a wide variety of aluminum alloys and composite coatings. Although, in recent years, a number of studies have shown the capabilities of CGDS in producing pure aluminum coatings, few aluminum alloys have been investigated. Moreover, the mechanical properties of CGDS aluminum alloy coatings have not been evaluated yet and their microstructural characteristics in relation to the particle velocity are still poorly understood. There is, therefore, a need to synthesize aluminum-based coatings by CGDS and to examine the relationships between the particle velocities, the microstructures and the properties of these coatings. In order to achieve the desired goals, a number of interrelated studies will be undertaken, these being:

- 1) Implement and compare particle in-flight velocity laser diagnostic systems,
- 2) Explore the coating potential of the CGDS process,
- 3) Develop a series of CGDS coatings from several aluminum alloys such as:
 - a. Conventional coatings
 - b. Metal-matrix composite coatings

- 4) Characterize the microstructure of the coatings and correlate to the particle impact velocity, and,
- 5) Evaluate the mechanical properties of the coatings and correlate them to their microstructure.

1.3 Arrangement of the Thesis

The material to be presented in this thesis is organized in seven chapters. Chapter 1 contains introductory notes on the background of thermal spray processes and the CGDS technique. The motivation for the project is presented along with its general objectives. This thesis outline is also part of the same chapter.

Chapter 2 gives a brief description of commonly used thermal spray processes and situates CGDS amongst the other processes. Part of this chapter presents a literature review on previous work on the CGDS process. Several topics such as the background of the technology, the general process overview, the isentropic one-dimensional nozzle flow, the critical velocity and the bonding mechanism are discussed here. Characteristics of aluminum coatings produced by CGDS are also examined. The chapter ends with a list of advantages and limitations of CGDS.

Chapter 3 describes in detail the objectives of this research to provide a clear vision on the prospective opportunities of CGDS in the production of conventional coatings and metal-matrix composite coatings.

The method of investigation is outlined in Chapter 4. The CGDS facility, the particle in-flight velocity measurement systems, and the coating characterization techniques are described.

The particle velocities obtained by two different particle in-flight laser diagnostic systems are discussed in Chapter 5. The operating characteristics and the limitations of each system will be listed. The most practical particle measurement system for CGDS will then be selected.

In Chapter 6, the microstructural features and the mechanical properties of several aluminum-based coatings are presented and discussed. The microstructures are described and correlated to the particle velocities. Mechanical properties such as porosity, hardness, bond strength, and fatigue strength of the coatings are addressed and linked to the microstructures.

Finally, Chapter 7 summarizes conclusions from the results found within the present research and presents recommendations for future research. A complete list of references then follows.

Chapter 2 – Critical Assessment of the Relevant Literature Review

2.1 Preamble

This chapter deals with a literature survey of the broad topic of interest, namely the development of coatings through a relatively new material deposition process, the CGDS process. This section contains a review of some thermal spray processes, including CGDS.

2.2 Thermal Spray Processes

Thermal spray processes have historically been classified into three categories based on their method of heating the coating material: plasma, electric arc and combustion, as shown in Figure 2.1. Each process has its own characteristic process and particle temperatures and velocities. Several sub-categories for each of the major processes exist. The specific attributes of a few thermal spray processes, highlighted in Figure 2.1, lead to variations in the coating properties and situate CGDS amongst the other processes. A summary of the thermal spray processes and the microstructural features of coatings produced by several thermal spray processes will also be presented.

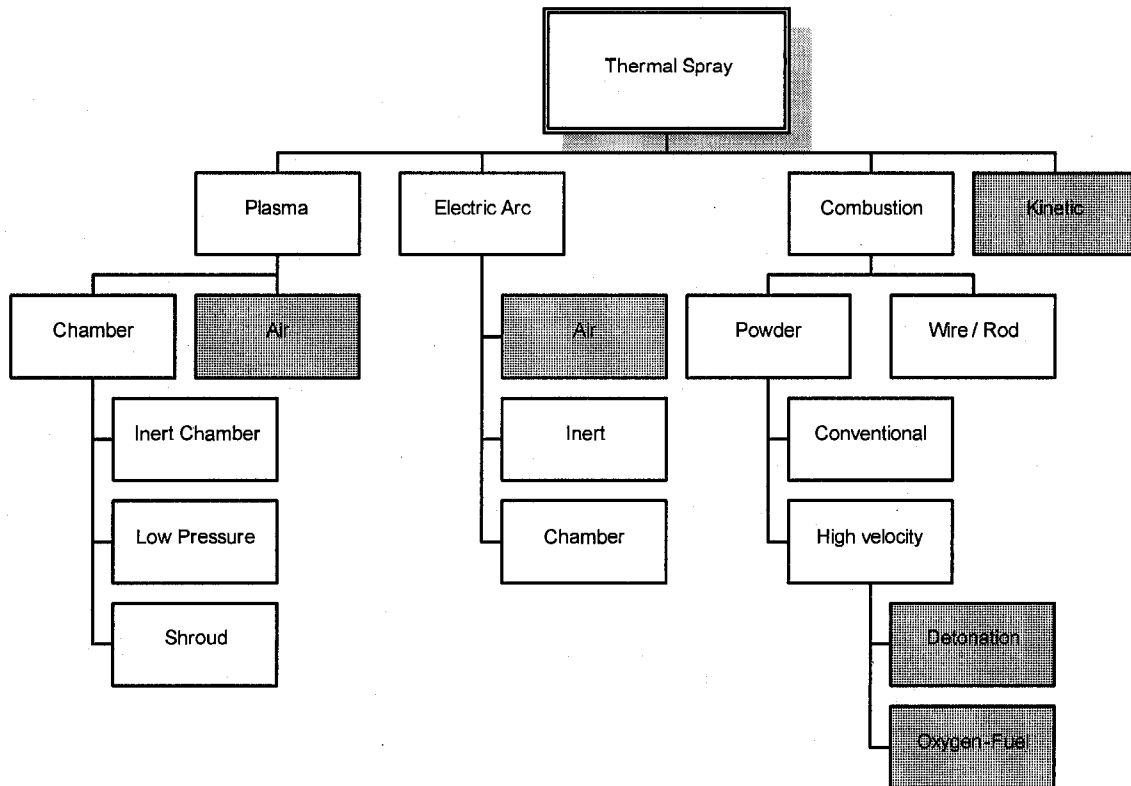


Figure 2.1 Thermal spraying processes (adapted from [12])

2.2.1 Plasma Spraying

In this technique, a mixture of gases, typically N_2 or Ar with additions of H_2 or He to improve the plasma gas thermal conductivity, is passed through a direct current electric arc generated between an anode and a cathode. The arc heats the process gases to temperatures ranging from 5000 to 25000°C [5], where they partially dissociate into a plasma of ions, electrons, atoms, and molecules. Besides direct current arcs, radio-frequency (RF) inductively-coupled or microwave discharges and alternate current arcs are also used as energy sources to generate plasmas in thermal spray devices. The ionized gas expands and accelerates through the nozzle of the gun. The coating material in powder form, suspended in an inert carrier gas, is injected in the plasma flame either externally through a port

mounted near the anode nozzle exit, or internally through the nozzle itself. The particles are rapidly heated and propelled in the plasma towards a substrate at velocities of 200 to 800 m/s [12]. Upon impact, the softened or molten droplets flatten, and undergo rapid solidification to form a coating. A schematic of the cross section of a plasma spray gun is shown in Figure 2.2.

Although plasma spraying is the most complex, it is the most flexible thermal spraying process because a wide variety of materials such as metals, ceramics, polymers, and composites can be deposited. Plasma spray coating bond strengths typically range from 10 to 45 MPa but can reach 80 MPa [14]. Porosity levels may vary from 1 to 40%, as dictated by the application [12]. The associated high equipment costs, complexity, induced thermal residual stresses, particle oxidation and non-uniform melting represent some of the disadvantages of the plasma spraying process.

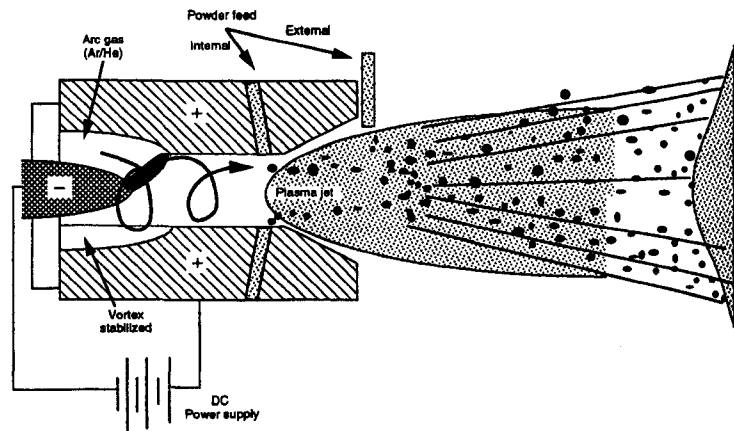


Figure 2.2 Cross section of a plasma spray gun (from [13])

2.2.2 Electric Arc Spraying

In the electric arc spraying process, illustrated in Figure 2.3, a direct current electric arc is struck between two electrically conductive and consumable wires. The electric arc formed between the wire tips, where the arc temperature may reach 3000 to 6000°C [14], produces molten spray material as the two wires are continuously fed together. The molten metal is atomized into fine particulates by compressed air or an inert gas supply. The process gas is also used to accelerate the particles toward a substrate, where the molten particles impact and solidify to build up a coating. The particle velocities associated with this thermal spray process approach 50 to 150 m/s [15].

The materials for electric arc spraying are limited to conductive materials which are ductile enough to be formed into wires. This process is particularly suited to spray at high deposition rates aluminum alloys, zinc, copper, and stainless steels. The bond strength is in the range of 10 to 40 MPa and the porosity varies from 5 to 20% [12].

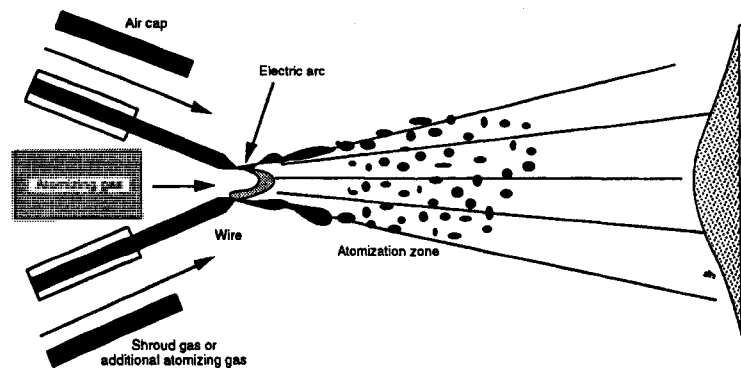


Figure 2.3 Operational principles of a twin wire electric arc spraying system (from [13])

2.2.3 Combustion Spraying

Combustion spraying processes rely on the heat generated by the combustion of fuel gases to form a high temperature jet. Powders, wires, or rods are introduced axially into the spray gun. In conventional combustion spraying, the combustion process is external and the molten particles are accelerated to relatively low velocities (< 100 m/s) by a compressed annular air jet.

The detonation spraying process relies on higher thermal and kinetic energy jets to improve the heat and momentum transfer to particles by confining the combustion gases within a tube. During the process, pulses of a mixture of fuel, oxygen, and powder are fed into a long barrel. A spark plug ignites the mixture, generating a detonation wave that can reach a maximum temperature of 4500°C [14]. The resulting detonation heats and accelerates the powder up to temperatures of 4500°C and velocities that can reach 900 m/s [14]. A pulse of nitrogen is used to purge the barrel after each detonation. This cyclic process of purging, injecting, and detonation is repeated at a frequency of 1 to 15 Hz [12, 14]. Successive firings overlap build up the coating. A detonation gun system is depicted in Figure 2.4.

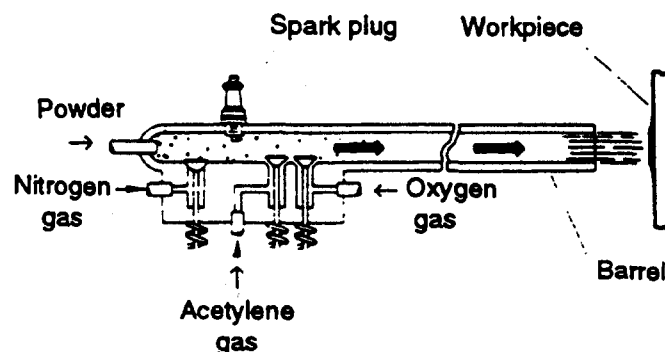


Figure 2.4 Detonation gun system (from [13])

The detonation spraying process is particularly well suited for producing WC/Co coatings. Compared to other thermal spray processes, detonation sprayed WC/Co coatings have a higher degree of retained carbides. The protective environment of the combustion gases and the short dwell time prevents decarburization (WC decomposition) and oxidation of the fine particles. Coatings with bond strengths above 80 MPa and porosities between 0.5 and 5% are possible [14].

The HVOF spraying process also confines the combustion but operates on a continuous basis (see Figure 2.5). In HVOF, the combustion of the fuel with an oxidant (typically oxygen) at high pressures generates a high velocity exhaust jet. The process fuels include acetylene, propane, propylene, hydrogen, and kerosene, and can generate flame temperatures of 3000°C [14], depending on the gas mixtures. The flame is forced through a converging-diverging (De Laval) nozzle and expands supersonically. The coating material in powder form, fed axially into the nozzle or through the side of the nozzle, is entrained in the flame and undergoes rapid heating and acceleration. The molten or semi-molten particles are propelled at high velocities, which can vary from 400 to 800 m/s.

The bond strengths and porosities of the coatings produced by HVOF are comparable to those of the detonation gun coatings. This process excels in the production of carbide cermet coatings and hard-facing applications. Possible grain growth and undesirable chemical reactions are among the shortcomings of HVOF, especially for spraying temperature sensitive materials.

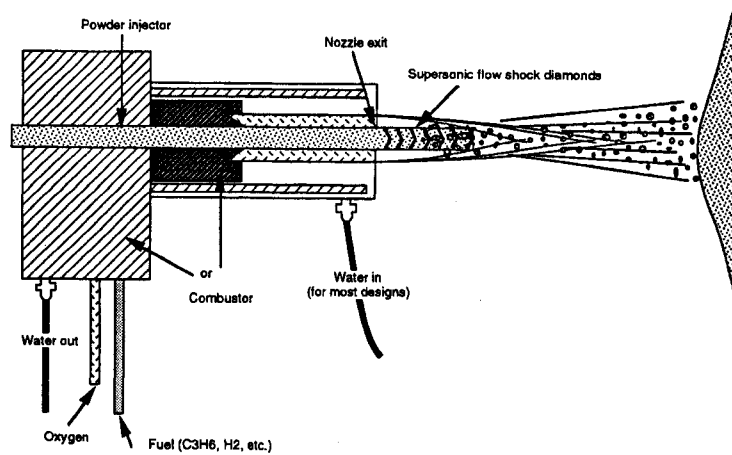


Figure 2.5 Cross section of a HVOF thermal spray gun (from [13])

2.2.4 Kinetic Spraying

The kinetic spraying processes include kinetic powder deposition, kinetic spraying, high-velocity powder deposition, cold gas dynamic spraying, or simply cold spray. All of these processes rely exclusively on the kinetic velocity transferred to powder particles. Although kinetic spraying represents an extreme case where no thermal energy is used to heat the powder, the process is recognized as a thermal spray process by the Thermal Spray Society, an affiliate society of the American Society for Metals (ASM International) [16]. Powder particles are accelerated to high velocities (400 to 1200 m/s) by a high velocity gas jet developed in a converging-diverging nozzle. Although the process gas may be preheated to temperatures between 25 and 700°C, the gas exit temperature is significantly lower than the gas preheated temperature due to its expansion in the spray gun.

The materials used in kinetic spraying include ductile materials such as metals and polymers. Brittle or hard materials such as ceramics may be deposited with a ductile matrix

material. Coatings with bond strength ranging from 20 to 70 MPa [17] have been reported while porosity values extend from 0.5 to 20% [12].

2.2.5 Summary of the Thermal Spray Processes

The main characteristics of the various thermal spray processes are summarized in Table 2.1. The deposition rates and deposition efficiencies were not included in the table since these quantities depend not only on the process but on the sprayed material as well. In thermal spray, deposition rates from 1 to 25 kg/h and deposition efficiencies ranging from 20 to 95% are achievable [12]. The differences in the process temperatures and particle velocities produce variations in the coating microstructures and properties such as the bond strength and porosity.

**Table 2.1 Characteristics of various thermal spray processes
(from [12-15])**

Spray Process	Process Temperature (°C)	Particle Velocity (m/s)	Materials	Coating Bond Strength (MPa)	Coating Porosity (%)
Plasma	5000 – 25000	200 – 800	Any material that melts without decomposition	10 – 45 and up to 80	1 – 40
Electric Arc	3000 – 6000	50 – 150	Conductive and ductile metals	10 – 30	5 – 20
Detonation	4500	Up to 900	Metals and cermets	Up to 80	0.5 – 5
HVOF*	3000	400 – 800	Metals and cermets	Up to 80	0.5 – 5
Kinetic	25 – 700**	400 – 800	Metals, polymers, ceramics in a ductile matrix	20 – 70	0.5 – 20

* HVOF: High Velocity Oxygen Fuel

** Preheated gas temperatures

In order to comprehend the microstructural differences in the thermal spray processes, coatings produced by electric twin wire arc (TWA), air plasma spray (APS),

HVOF, and CGDS processes using Ni-5Al feedstock materials (powder or wire) are compared in Figure 2.6. The reported in-flight average particle velocities and temperatures of each process are listed in Table 2.2. The coatings produced by TWA and APS display similar microstructural features. These coatings consist of build ups of several splats with numerous interlamellar pores. The metallurgical bonded areas are the result of remelting upon the arrival of subsequent droplets. The elemental distribution in the APS coating demonstrated that the core of the splats was predominately nickel. Aluminum and oxygen were found on the external boundaries of the splat [18]. In the case of HVOF, the coating contains fewer interlamellar pores than the coatings of TWA and APS and the boundaries between the splats are difficult to discern. The particles reached a semi-molten state and did not break into several fragments upon their impact on the substrate. Although the particle velocity was increased to 612 m/s, thermal energy was required to soften the particles and facilitate the splat formation. The CGDS coating demonstrates features of densely packed particles that have plastically deformed. The particle boundaries are clearly visible and no coalescence is observed in this case. The formation of oxides did not occur as a result of the absence of chemical reactions.

The gas temperatures and particle velocities associated with the conventional thermal spray processes, shown in Figure 2.7, clearly illustrate the distinctive feature of CGDS. The process is capable of producing coatings with preheated temperatures that are generally below the melting temperature of the coating material. It will be shown later in this chapter that the gas exit temperature is substantially lower than the gas preheated temperature. The undesirable effects of high temperatures on the coatings such as oxidation, evaporation,

melting, recrystallization, grain growth, and thermal stresses are eliminated. Advantages and some limitations of CGDS will be listed later in this chapter.

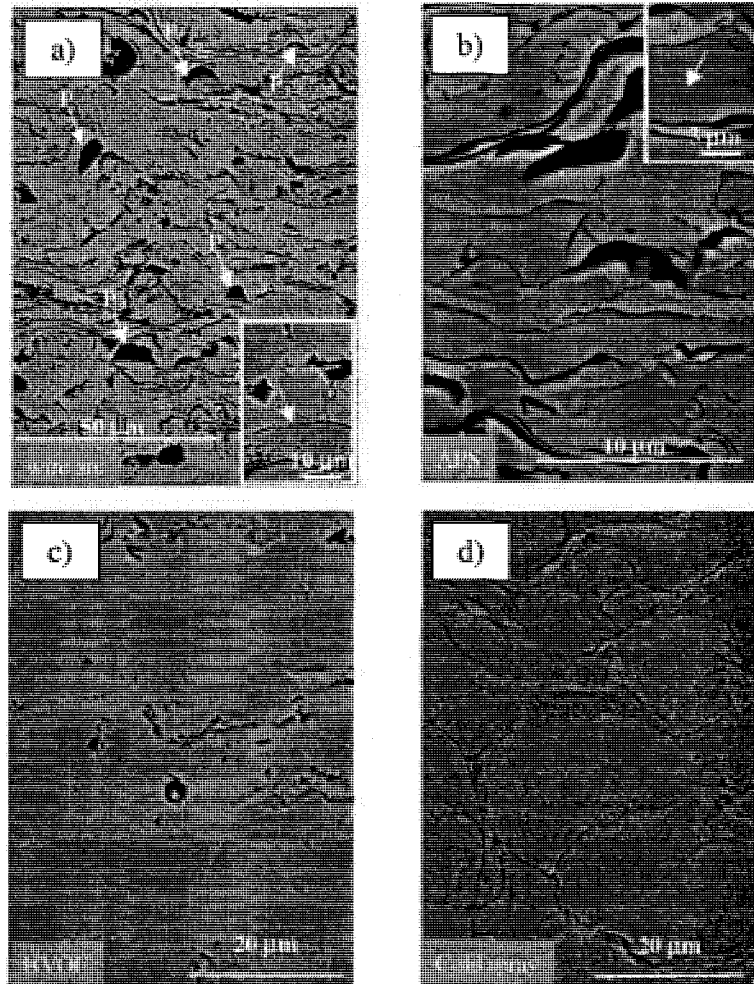


Figure 2.6 Cross-sectional images of Ni-5Al coatings produced by a) electric twin wire arc, b) air plasma spray, c) HVOF, and d) CGDS processes. The arrows point to pores formed with trapped air and the inset shows metallurgical bonded areas (from [18])

Table 2.2 Measured in-flight particle velocities and temperatures of the processes during the spraying of Ni-5Al (adapted from [18])

Process	Particle Velocity (m/s)	Process Temperature (°C)
APS	121	2340
TWA	87	2330
HVOF	612	1819
CGDS	700	N/A

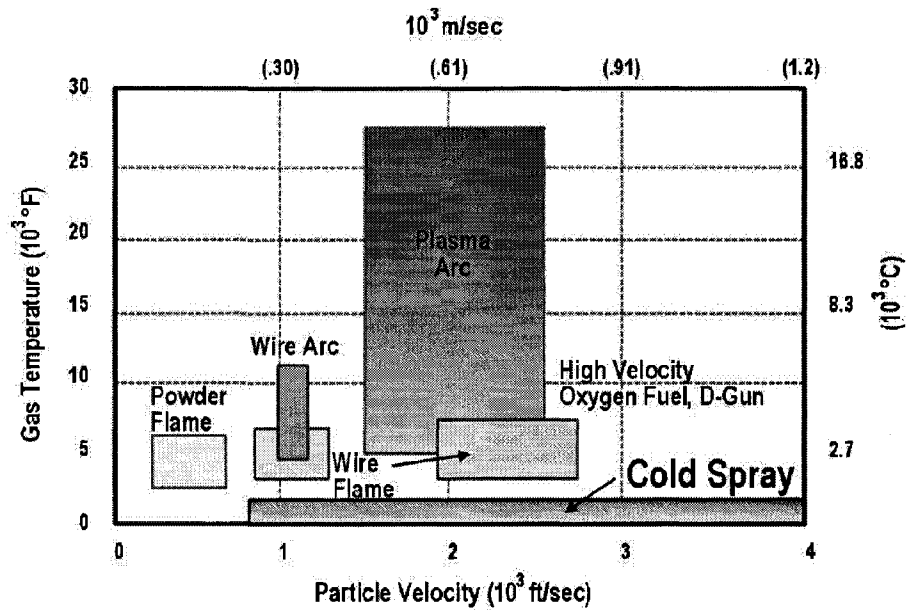


Figure 2.7 Temperature and velocity regimes for common thermal spray processes compared to the temperature and velocity in CGDS (from [19])

In the following section, the background, the general process overview, the isentropic one-dimensional nozzle flow, the critical velocity, and the bonding mechanism of CGDS are discussed in greater detail.

2.3 Cold Gas Dynamic Spraying (CGDS)

2.3.1 Background of the Technology

The Cold Gas Dynamic Spraying (CGDS) process, also referred to as cold spray, was developed in the mid-1980 at the Institute of Theoretical and Applied Mechanics of the Siberian Division of the Russian Academy of Science in Novosibirsk. While they were conducting experiments in a supersonic wind tunnel, the researchers observed that under certain conditions the fine metallic tracer particles injected in the flow stream deposited on the leading edges of the models [20-22]. As the flow velocity was increased, there was a transition from particle erosion of a target surface to a rapid build-up. Figure 2.8 illustrates the level of deformation undergone by a copper particle upon impact on a copper substrate. The Russian scientists recognized the potential of this finding as a new material deposition process, and developed a spray coating device based on this principle. They successfully deposited a wide range of pure metals, metal alloys, and composites onto a variety of substrate materials, and demonstrated the feasibility of cold spray for various applications [22]. A United States patent was issued in 1994 [7] and the European patent in 1995 [23].

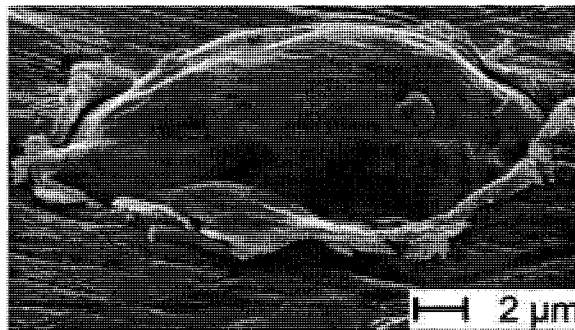


Figure 2.8 Image of a copper particle that impacted on a copper substrate (from [24])

2.3.2 General Process Overview

A schematic diagram of a typical CGDS system is shown in Figure 2.9. The process gas coming from a primary high-pressure gas supply is introduced in the system by regulating a control valve. The compressed gas may be preheated to a preset temperature. The gas is not heated to heat or soften the spray particles but to achieve a higher gas flow velocity which will result in higher spray particle velocities. The gas is introduced into a converging-diverging nozzle where it becomes supersonic as it expands in the spray gun. The gas cools as it expands, almost always exiting below the ambient temperature, hence the name cold spray. A secondary high-pressure gas supply, connected to a powder feeder, carries the spray particles to a mixing chamber. The spray particles are then injected in the process gas flow. The powder may alternatively be introduced downstream of the throat, where the pressure is lower as a result of the gas expansion. The high velocity gas stream exerts a drag force on the spray particles. The later are accelerated above a critical velocity and upon impact on the substrate, plastically deform and incrementally form a coating.

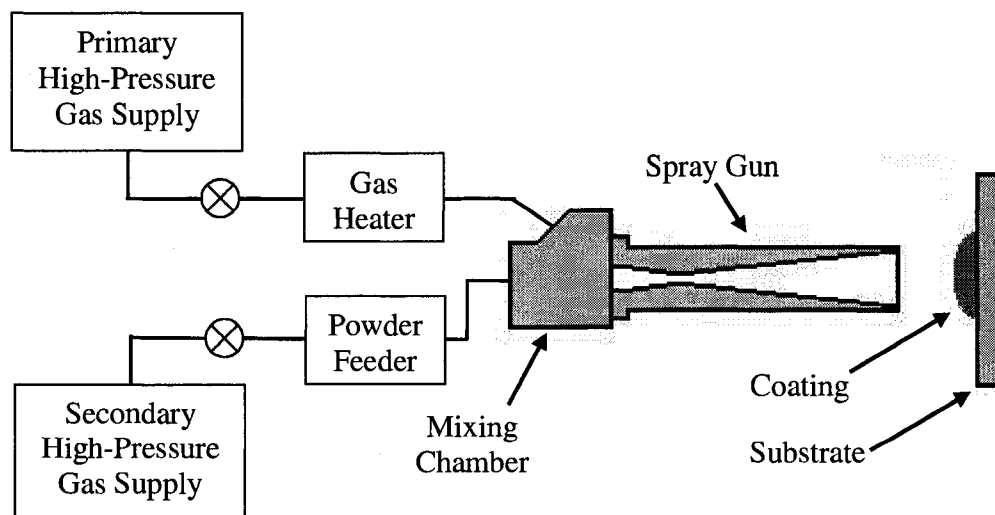


Figure 2.9 Schematic diagram of a CGDS system

2.3.3 Isentropic One-dimensional Nozzle Flow

In this section, the theory of isentropic one-dimensional flows of ideal gases in nozzles is reviewed. An isentropic flow is a flow that is both adiabatic and reversible. No energy is added to the flow and no energy is lost due to friction or dissipative effects. These concepts of gas dynamics are useful since they allow an understanding of the effects of operating parameters, such as pressure and temperature, and of geometrical aspects of the nozzle. In addition, the design of the nozzles used in CGDS relies on these same notions.

2.3.3.1 Flow through a Variable Area Section

An analysis of the flow through a variable area section can readily be conducted for a one-dimensional, steady, and isentropic flow. Under these assumptions, the continuity, energy, and Gibbs equations are combined to give:

$$\frac{dV}{V}(1 - M^2) = -\frac{dA}{A} \quad (2.1)$$

and

$$dp(1 - M^2) = \rho V^2 \frac{dA}{A} \quad (2.2)$$

where V is the flow velocity, M is the Mach number, A is the cross sectional area, p is the pressure, and ρ is the density. The Mach number is the ratio of the flow velocity to the speed of sound in the fluid, c , that is:

$$M = \frac{V}{c} = \frac{V}{\sqrt{kRT}} \quad (2.3)$$

where k , R , and T represent the specific heat ratio, specific gas constant, and static temperature, respectively. Equations 2.1 and 2.2 provide useful insight on the effects of area changes on the velocity and pressure under the subsonic and supersonic flow regimes. In the

case of a subsonic flow $M < 1$ and $1-M^2$ is positive. A diverging section ($dA > 0$) leads to a pressure increase and a velocity decrease. Conversely, a converging section ($dA < 0$) produces a pressure drop and a velocity increase. However, in the case of a supersonic flow $M > 1$ and $1-M^2$ is negative. An increase of pressure and a decrease in velocity are obtained in a converging section ($dA < 0$). On the other hand, a diverging section ($dA > 0$) will accelerate the flow and cause a pressure drop. The isentropic acceleration of a fluid from rest to supersonic speeds can only be accomplished by a converging section followed by a diverging section, a converging-diverging nozzle.

2.3.3.2 Definition of the Fluid Stagnation Properties

The fluid stagnation properties represent a reference condition where the fluid is brought to rest ($V = 0$) through an isentropic process. As a result, stagnation properties correspond to the ideal conversion of the fluid's kinetic energy and potential energy into pressure and internal energy.

At any point in the variable area section, the flow pressure may be described by its stagnation pressure, p_0 , or its local static pressure, p , and the flow temperature may be defined by its stagnation temperature, T_0 , or its local static temperature, T . Using the isentropic relationships, the stagnation temperature and stagnation pressure are:

$$T_0 = T \left(1 + \frac{k-1}{2} M^2 \right) \quad (2.4)$$

$$p_0 = p \left(1 + \frac{k-1}{2} M^2 \right)^{\frac{k}{k-1}} \quad (2.5)$$

Based on these relationships, the Mach number reached by the flow and consequentially, its velocity can be determined if the pressures and temperatures are known.

Alternatively, given the Mach number, the required pressure ratio p_0/p and T_0/T can be calculated to ensure that the appropriate flow conditions in the nozzle are reached.

2.3.3.3 Compressible Isentropic Flow in a Converging-Diverging Nozzle

A qualitative description of the flow development inside a converging-diverging nozzle can now be undertaken. The converging-diverging nozzle shown in Figure 2.10 is connected to a large reservoir where the stagnation properties p_0 and T_0 remain constant. For a given value of p_0 , the variation of the pressure and flow velocity in the nozzle will depend on the value of the back pressure, p_b . When $p_b = p_0$ (case a), there is no flow and the pressure remains constant in the nozzle. As p_b is reduced below p_0 (case b) a flow is initiated in the nozzle but the flow is subsonic and isentropic throughout. According to Equation 2.2, in subsonic flows the pressure decreases in the converging section but increases in the diverging one. The back pressure is now reduced sufficiently to make the flow reach sonic conditions at the throat, the smallest section of the nozzle. At this point, the flow rate through the nozzle has reached its maximum and the flow is said to be choked. Any further reduction of the back pressure will not change the flow pattern in the converging part of the nozzle or its flow rate. The pressure waves travel at the speed of sound and cannot propagate upstream into the nozzle to cause any flow adjustment.

Once the choked condition is reached, two possible isentropic solutions are possible for the flow in the diverging section: a subsonic flow (case c) or a supersonic flow (case f). In case c, p_b is too high and the flow decelerates in the diverging section. In case f however, p_b is small enough to render the flow in the diverging section supersonic.

Between cases c and f, the flow does not expand isentropically. As p_b is changed to a value between cases c and f, the flow accelerates as it enters the diverging section of the

nozzle and becomes supersonic. The downstream resistance is too large and a normal shock occurs in the diverging section (case d). Lowering p_b further causes the shock to move out of the nozzle and the gas adjusts to the back pressure externally (case e). The situations where the nozzle operates with a back pressure between cases c and f are said to be overexpanded because the pressure at some point in the nozzle is less than the back pressure. In situations where p_b is less than the one in case f, the flow can not expand to reach the back pressure. Flow adjustments take place outside the nozzle through expansion waves (case g). The nozzle is then said to be underexpanded.

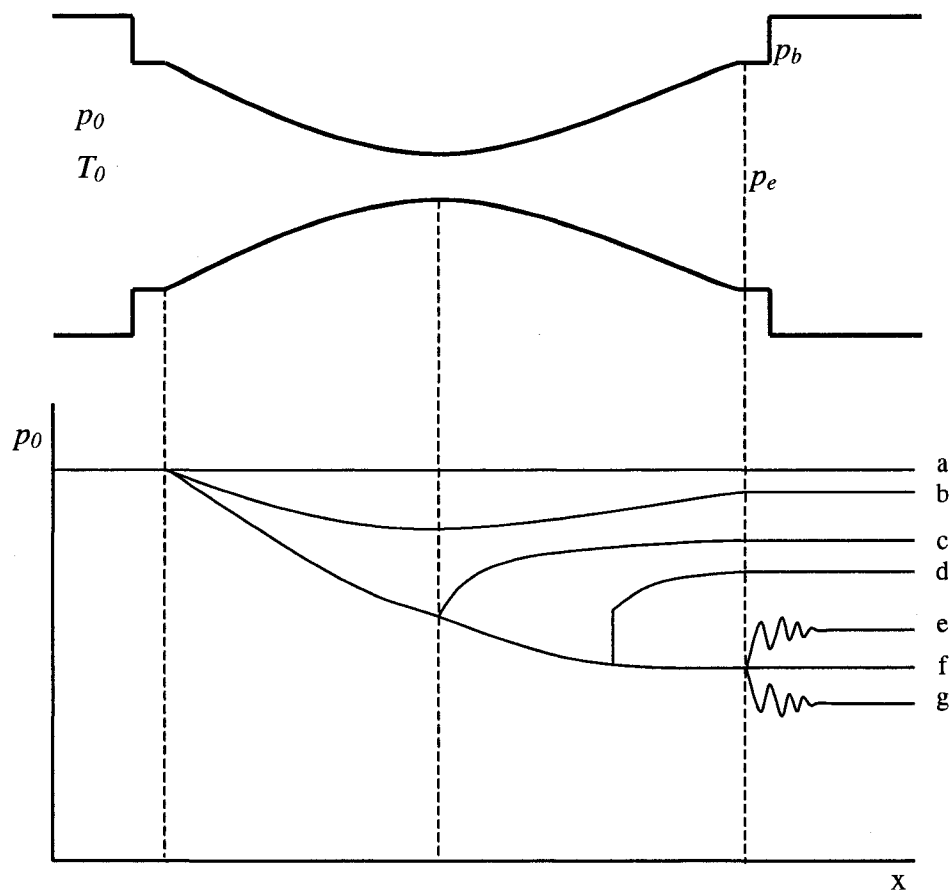


Figure 2.10 Pressure distribution for an isentropic flow in a converging-diverging nozzle

2.3.3.4 Design Parameters of CGDS Nozzles

Equations 2.4 and 2.5 provide property relations in terms of the local Mach number but do not offer insight on the geometrical features of a converging-diverging nozzle such as the throat area (A_t) and exit area (A_e). Combining the continuity equation and ratios of the fluid properties results in the following:

$$\frac{A}{A_t} = \frac{1}{M} \left[\left(\frac{2}{k+1} \right) \left(1 + \frac{k-1}{2} M^2 \right) \right]^{\frac{k+1}{2(k-1)}} \quad (2.6)$$

where A is the nozzle area at any position in the diverging section. For each Mach number, two solutions are possible: one subsonic and the other supersonic. It is the pressure ratio of the stagnation pressure to the static pressure, p_0/p , which determines whether the flow is subsonic or supersonic. In CGDS, the process is generally conducted at atmospheric pressure. To obtain a supersonic flow at the nozzle exit without shock waves in the nozzle, the exit pressure should then be greater than or equal to the atmospheric pressure. The stagnation pressure must be adjusted accordingly. In the case of a choked flow (sonic at the throat), the mass flow rate in the nozzle, assuming one-dimensional isentropic flow, can be determined using:

$$\dot{m}_{choked} = A_t p_0 \sqrt{\frac{k}{RT_0} \left(\frac{2}{k+1} \right)^{\frac{k+1}{k-1}}} \quad (2.7)$$

Increasing the stagnation pressure increases the mass flow rate because according to the perfect gas law, the fluid density augments with pressure. Increasing the stagnation temperature decreases the mass flow rate and increases the flow velocity in the nozzle since the speed of sound, c , is related to the local temperature according to Equation 2.3.

2.3.4 Critical Particle Velocity

As mentioned previously, Alkhimov et al. [22] were the first to recognize the existence of a minimum particle velocity at which deposition occurs. A critical velocity was then defined as the particle velocity which produced a notable increase of the deposition efficiency, as illustrated in Figure 2.11. The deposition efficiency represents the ratio of the mass of the deposited layer to the mass of sprayed powder.

The critical particle velocity is associated with the properties of the sprayed material [22, 24-26], substrate [26, 27], particle temperature [28-30], particle size [31, 32], and surface oxidation state [33, 34]. Typical orders of magnitude of the critical velocities of copper and nickel are 475 and 575 m/s, respectively. Measured critical velocities of several feedstock materials are reported in Table 2.3.

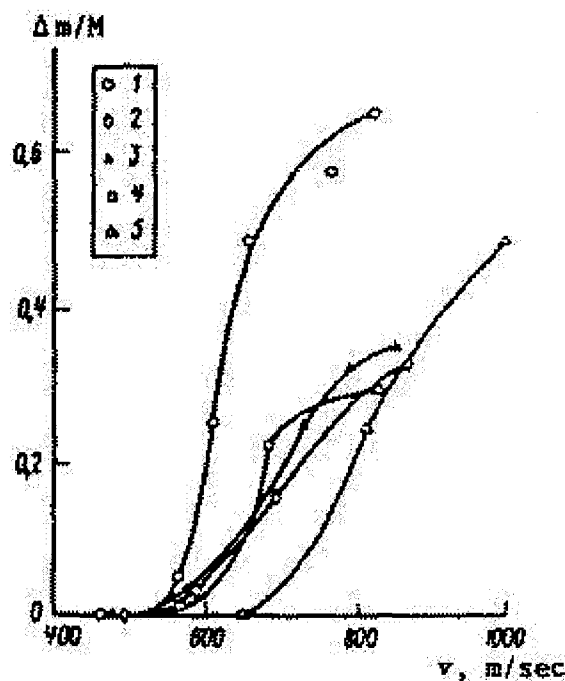


Figure 2.11 Deposition efficiency as a function of velocity for particles with an average diameter of 10 μm for copper (1), zinc (2), iron (3), nickel (4), and aluminum (5) powders (adapted from [22])

Table 2.3 Measured critical velocity of several feedstock materials with an average particle diameter of 10 μm (from [22])

Material	Critical Velocity (m/s)
Copper	450
Iron	475
Zinc	500
Nickel	575
Aluminum	650

Of the materials listed in Table 2.3, aluminum possesses the highest critical velocity. This may be attributed to the protective layer, alumina, which naturally forms upon exposure of aluminum to atmospheric air. Alumina possesses a high hardness, excellent wear and corrosion resistance but can cause a reduction of ductility [8]. Numerical studies have shown that the thickness of the surface oxide film restrained the particle deformation upon impact [33, 34]. Several critical velocities for aluminum feedstock powder have been reported, depending on the particle size examined. Values between 600 and 680 m/s have been measured for particles below 50 μm [19, 22, 25]. A critical velocity of 440 m/s was found for larger particles ($> 50 \mu\text{m}$) [31]. It was suggested that since the larger particles have more kinetic energy, there is more energy to break the oxides before plastic deformation can occur.

The nature of the substrate will only affect the particle critical velocity during the application of the first coating layer. The subsequent incoming particles will impact and build up on that initial coating layer. Van Steenkiste et al. [26] and Zhang et al. [27] produced aluminum coatings from a single pass of the nozzle over various types of substrates. In each study, the authors found that the coatings produced on steel substrates were thicker than the ones produced on aluminum substrates. The deposition onto an

aluminum alloy substrate was different and slightly more difficult due to the presence of oxides on the substrate's surface. The deposition efficiency was then dependent on the substrate type. A higher particle velocity would then be required to break the surface oxides and produce coatings on aluminum substrates.

The spraying angle, defined as the angle made between the substrate and spray gun, was also found to influence the build-up of the coatings and deposition efficiency of the process, as illustrated in Figure 2.12 [35]. The deposition efficiency decreases with the spraying angle due to a reduction of the normal component of the particle velocity. The optimal configuration is then obtained when the spray gun is held perpendicular to the substrate.

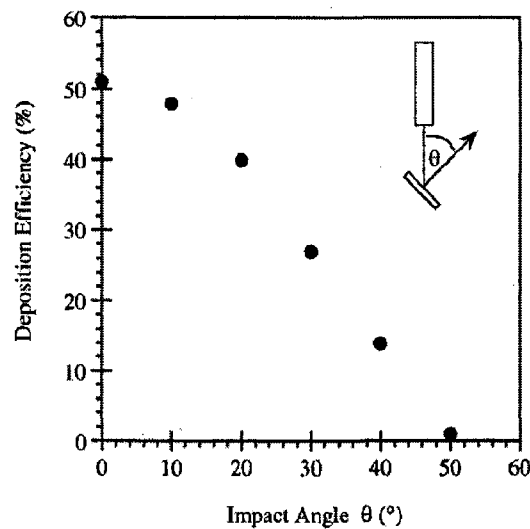


Figure 2.12 Deposition efficiency as a function of the spraying angle (from [35])

As shown in Table 2.1, lower particle velocities are required to form coatings when the particle temperatures are increased (by means of higher process temperatures). The particle material softens at high temperatures and requires less kinetic energy to deform upon impact on the substrate. In CGDS, increasing the particle temperature can only be

accomplished by increasing the gas stagnation temperature or by preheating the powder [30].

According to Equation 2.4, a higher gas stagnation temperature results in a higher gas static temperature and a larger local speed of sound (Equation 2.3) throughout the nozzle. This, in turn, is likely to accelerate the particles to higher velocities due to the enhanced momentum transfer caused by the higher gas velocity. It then becomes difficult to differentiate the increase in particle velocity from particle temperature at higher gas stagnation temperatures.

Numerical models have been used to evaluate the particle temperature variation inside the spray gun. The results using the FLUENT® code showed that a 15 μm copper particle exited the nozzle at temperature of -20°C when it was injected in a gas flow with a gas stagnation temperature of 320°C [28]. However, one-dimensional isentropic calculations by the same authors showed that increasing the stagnation temperature to 520°C increased the particle temperature to 227°C . Other models predicted that a 20 μm copper particle reached a temperature of 400°C for a gas flow stagnation temperature of 527°C [26].

Increasing the gas stagnation temperature does not necessarily increase the particle temperature significantly. The particles are injected in the spray gun at an initial velocity and are entrained in the process gas flow. Since the process gas also has a velocity, the gas temperature seen by the particles at the injection location is less than the gas stagnation temperature. The stagnation properties are only obtained through an isentropic deceleration of the gas to zero velocity. As the process gas accelerates in the converging and diverging sections of the spray gun, its temperature rapidly drops. At the same time, the particles quickly gain momentum and pass through the spray gun. The particles then spend a very

short time in contact with the gas and in the spray gun, lessening the chances of particle heating. Raising the gas stagnation temperature increases the gas temperature throughout the nozzle, augments the speed of sound and gas velocity, and accelerates the particles to greater velocities. As a result, the particles spend even less time in the nozzle.

Schmidt et al. [30] have used a numerical model to predict the particle temperature in a spray gun with a preheating chamber located upstream of the spray gun. It was reported that a 50 μm copper particle can reach an impact temperature of 600°C in a process gas temperature of 900°C. The authors did not provide correlations of the convection heat transfer used in the calculations and did not validate the predicted results with experimental values. Although the measured deposition efficiency of copper increased as the process gas temperature was raised up to 400°C, changes of the critical velocity of copper were not provided. The increase of the deposition efficiency may be partially attributed to higher particle velocities.

Raletz [36] was the only one to clearly demonstrate that preheating particles in CGDS shows not effects on the coating microstructure, as shown in Figure 2.13. It was also found that the porosity levels and measured hardness values of the deposits were not linked to the particle preheated temperatures. Any preheating of the particles is ineffective because they quickly dissipate heat to the gas stream expanding in the spray gun.

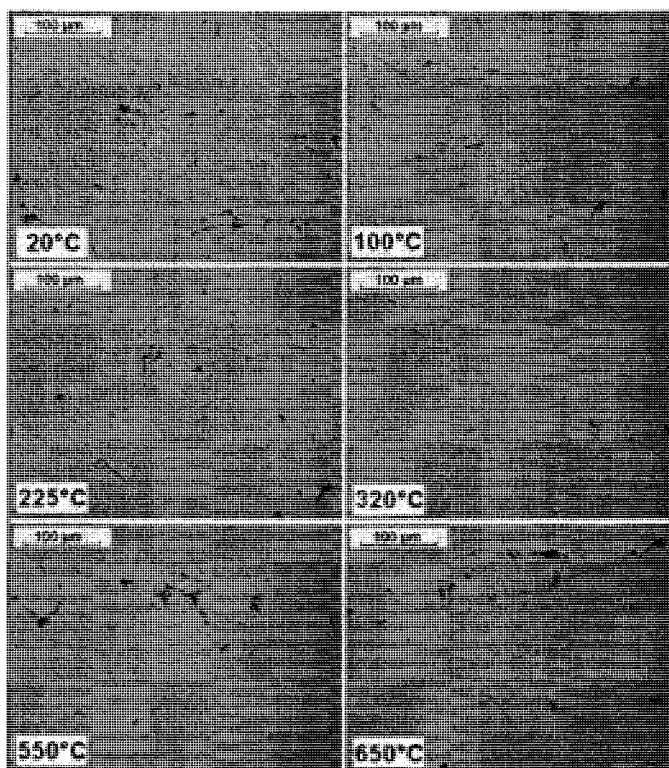


Figure 2.13 Images of nickel coatings produced by CGDS at different preheated particle temperatures (from [36])

Defining the particle critical velocity of various materials at several particle diameters has become a questionable issue. The feedstock powder available commercially and synthesized at the laboratory scale has a wide size range. The critical velocity of a material at a specific diameter becomes difficult to evaluate and irrelevant from an industrial point of view. The deposition efficiency could then be reported as a function of the measured particle velocity for a particular particle size range. For example, one could mention that a deposition efficiency of 50% was obtained at a particle velocity of 500 m/s for a particle size of $25 \pm 10 \mu\text{m}$.

2.3.5 Bonding Mechanism

The process of coating formation in CGDS is attributed to impact phenomena and the kinetic energy of the particles. Upon impact with the substrate, the kinetic energy of the particles is spent for plastic deformation and for local heat release. Assuming that the particles go through a deformation process akin to ductile materials, the deformation energy can be determined based on the total strain energy from a stress-strain diagram. Calculations demonstrate that 20% of the kinetic energy of a 25 μm aluminum particle impacting with a substrate at 600 m/s is used to plastically deform the particle. The other 80% is dissipated into heat. The impact forces cause particle deformation beyond the material's elastic limit and adhesion of the particles prevents them from bouncing off the substrate [7, 22]. However, this explanation merely describes the behavior of the particles on the substrate; it does not provide a mechanism through which the particles adhere to the substrate.

The particle-substrate and particle-particle bonding mechanisms are still not clearly understood, though they have been the focus of several numerical and experimental investigations. On the other hand, it has become widely established that bonding is the result of extensive plastic deformation. Various ductile materials, including metals and polymers, have been deposited by CGDS. Experiments with brittle materials, such as ceramics, have not been successful unless they are deposited with a ductile matrix material. This theory provides an explanation to the observed minimum particle velocity necessary to achieve deposition. The particle must possess sufficient kinetic energy to plastically deform upon impact with the substrate. Calculations have shown that the particle kinetic energy at impact is significantly lower than the energy required to melt the particle [31, 37]. This suggests

that the deposition mechanism is a solid-state process despite few evidences of local particle melting [41, 42].

Modeling the particle impact and bonding processes in CGDS is a controversial area due to the complexity of the deformation process. Experimental investigations of the process only show deformed particles and do not provide the temporal progression of the particle deformation. The simulations provide clues on the deformation process of particle impacts and of the effects of spraying parameters. In the next paragraphs, features of bonding mechanisms obtained through numerical and experimental investigations reported in the literature are examined.

The first bonding mechanism reported suggests that the intense plastic deformation disrupts the thin surface films, such as oxides, and provides intimate conformal contact under a high localized pressure [20]. The examination of craters created by impacting copper particles with a stainless steel substrate, showed in Figure 2.14, reveals the formation of a ring of jet-type morphology around the impact zone composed mostly of copper [37]. Computational modeling of the impact process also illustrated the severe plastic deformation of an impacting particle and of the underlying substrate as the particle impact velocity increased. The experimental and numerically-obtained impact morphologies created by a 700 m/s copper particle onto a stainless steel substrate are compared in Figure 2.14. The penetration depth of the particle and the splat size is over-predicted by the model. This is attributed to improper modeling of the strain rates and/or incorrect material properties. The copper particles may have mechanical properties different than the ones of bulk copper, as used in the model. The rapid cooling rates encountered during powder formation possibly lead to a finer grain size and possible superior mechanical properties. The edge around the

impact zone generated with the numerical model is composed mostly of stainless steel, in contrast to experimental observations. The oxide layer on the copper was not considered in the simulations. The level of oxidation on copper particles can have a significant effect on the critical velocity for particle deposition and on the coating formation process [29].

The peak local temperatures predicted by the model are below the melting point of the materials studied. The deformations of the particles and substrate under high pressure (estimated to be on the order of 5 GPa [37]) were then credited for the formation of a solid-state jet that may remove any surface impurities, thus providing clean contact interfaces between the particle and the substrate.

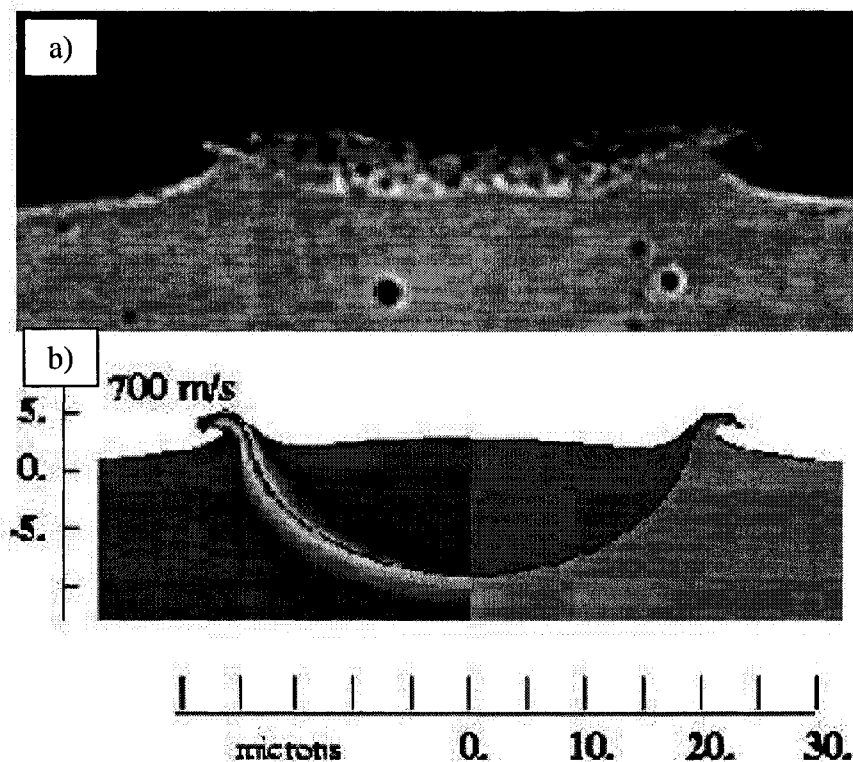


Figure 2.14 Cross-section of a splat created by the impact of a 700 m/s copper particle onto a stainless substrate obtained a) experimentally and b) numerically (adapted from [37])

Different numerical models have reported the formation of interfacial roll-ups and vortices as a result of substrate penetration by an impacting particle [38]. The evolution of a particle impact with a substrate at successive times, as shown in Figure 2.15, demonstrates the formation of interfacial roll-ups. During the deformation process, the material surrounding the particle-substrate interface adopts the behavior of viscous materials as a result of localized material softening [38]. The model also predicts that particle or substrate melting only occurred at particle velocities above 900 m/s. The condition for melting occurred only on 14% of the interfacial area and do not contribute significantly in the particle-substrate bonding. The interfacial instabilities consisting of rollups and material mixing may promote interfacial bonding by increasing the area for bonding and by creating mechanical interlocking of the two materials.

However, these interfacial instabilities and mixing, illustrated in Figure 2.16, have only been reported in a few experimental studies and are not always observed at the substrate-coating interface of CGDS coatings [39, 40]. For particles traveling faster than their critical velocity, the formation of an interfacial jet may not be a necessary condition for deposition to occur. For particle impacts with substrates of similar material, the jet may be morphologically less prominent. Deposition experiments of aluminum particles on steel substrates have shown limited deformation of the substrate during the spraying process [27, 41]. The deformation was mostly restricted to the aluminum particles. The oxide films on the aluminum particle were not taken into account in the numerical analysis of Grujicic et al. [38]. The presence of an oxide film on the surface of aluminum particles has been found by numerical investigation, to restrict the particle deformation and metal-jet formation [33].

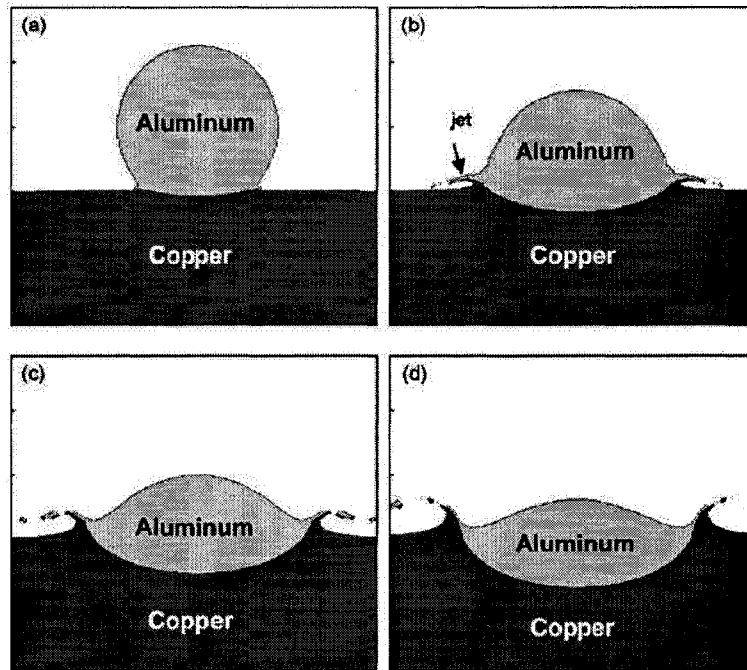


Figure 2.15 The impact of a 650 m/s aluminum particle onto a copper substrate at successive times: (a) 5, (b) 20, (c) 35 and (d) 50 ns (adapted from [38])

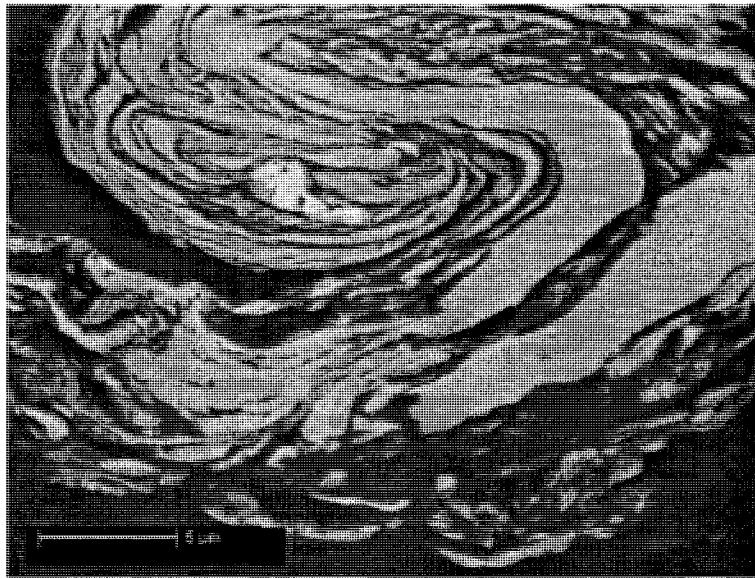


Figure 2.16 Image of the interfacial instabilities of a cold spray nickel coating (bright region) on an aluminum substrate (dark region) (from [39])

Other numerical analyses investigating the deformation of copper particles upon impact suggested that the bonding mechanism in CGDS is attributed to adiabatic shear instabilities [24, 43]. These instabilities occur in very narrow regions of a plastically deforming material as it undergoes a high strain rate. The heat generated during the plastic deformation is not dissipated by conduction but adiabatically increases the temperature and softens the material. The effects of heat conduction are negligible because of the short contact time during impact, estimated at 10^{-8} s [43]. The temporal evolutions of the strain, temperature, and stress in an element at the copper particle surface are illustrated in Figure 2.17. At particle velocities below the critical velocity, all temporal evolutions show a monotonic change with the particle-substrate contact time. At a particle velocity slightly above the critical velocity, the strain and temperature undergo an abrupt increase while the stress suddenly decreases to a zero value since the deformation mechanism changes from plastic to viscous flow. These results demonstrate that adiabatic shear instabilities in localized regions are triggered at a sufficiently high particle velocity. The minimum velocity that prompts any adiabatic shear instabilities for different particle materials onto various substrate materials corresponds to the critical velocity required in the CGDS process [24]. However, the simulation results were found to be dependent on the selected calculation parameters and size of the mesh elements [24, 29, 33]. Decreasing the mesh size in the areas of highly localized plastic deformations was found to decrease the minimum velocity required for the onset of shear instabilities [29]. The results obtained through numerical investigations are not reliable because of their mesh dependency.

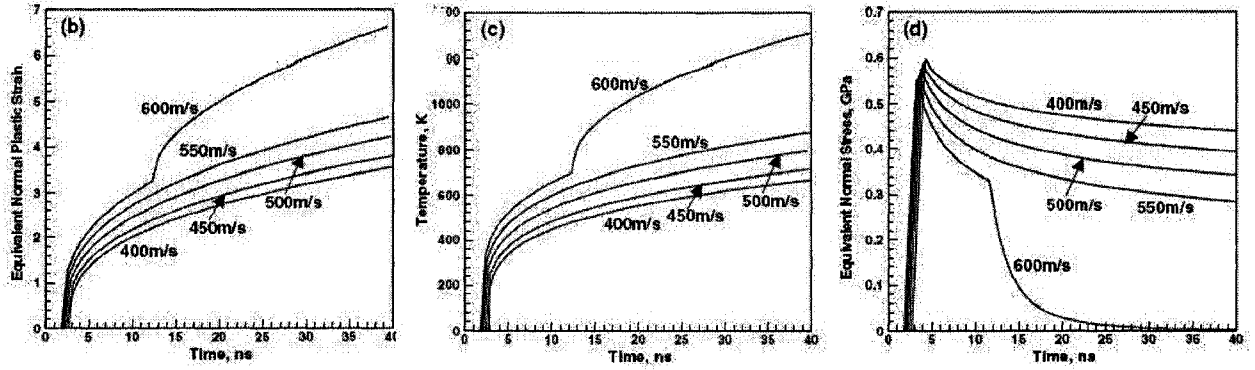


Figure 2.17 Temporal evolutions of the strain, temperature, and stress in an element at the particle-substrate interface during the impact of copper particles onto copper substrates (adapted from [43])

Adiabatic softening becomes the proposed mechanism for the formation of interfacial jets that clean the surface at the particle-substrate and at particle-particle interfaces. Intimate contact between these surfaces promotes metallurgical bonding. Experimental evidences of metallurgical bonding and of adiabatic shear bands can be obtained experimentally, as shown in Figures 2.18 and 2.19 [34, 44], 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.

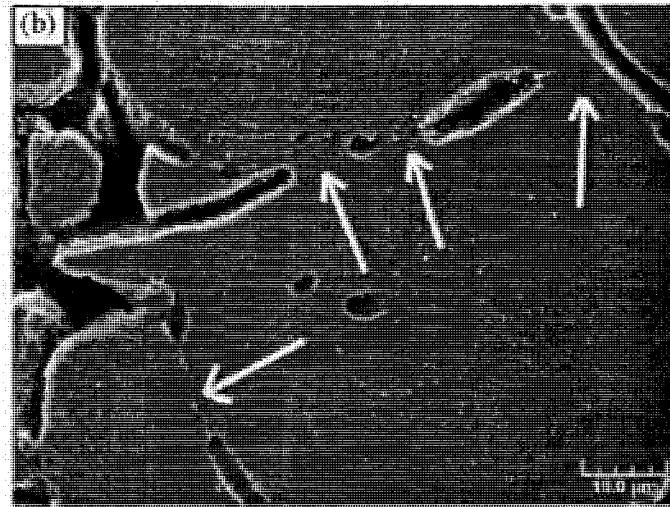


Figure 2.18 Evidence of metallurgical bonding (indicated by arrows) of a Ti-6Al-V coating in the etched state (from [34])

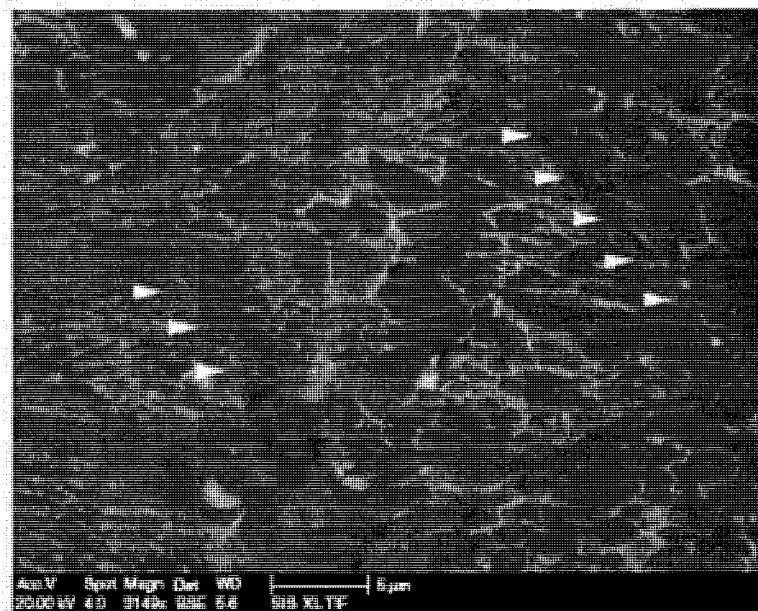


Figure 2.19 Evidence of shear instabilities (indicated by arrows) and heavily deformed microstructures in the interior of the particles in an Al-2618 coating (from [44])

The formulation of a bonding mechanism for the CGDS process is still lacking. Agreement on whether mechanical or metallurgical bonds (or a combination of both) are predominant has yet to be reached. Numerical models provide a decent qualitative view of the particle impact and deformation process. The micron-size particles, the strain-hardening mechanism as well as the short duration of the impact complicate the analysis. The interpretation of the microstructure from electron microscopy images relies heavily on the metallographic preparation of the samples. Sectioning, mounting, grinding, and polishing steps of sample preparation may induce artifacts into the coating and lead to inaccurate results [45].

In other thermal spray processes, the bonding mechanism is not well established but it is generally accepted that it is a combination of mechanical interlocking, metallurgical bonding, and weak physical forces [14]. Mechanical anchorage is thought to be mostly responsible for bonding of the particles to the substrate. Molten or semi-molten particles fill the asperities of a roughened substrate and solidify around these surface irregularities. In some cases, metallurgical interaction through diffusion or chemical reactions can occur when supplemental fusion or heat treatments are used. The high cooling rates limit the thermal interaction between the particles and the substrate. Weak physical bonding due to Van der Waals forces can occur when the surfaces in contact are clean and under a state of intensive plastic deformation. At last, factors such as the thermal spray process operating conditions, substrate composition and mechanical properties, and the nature of the sprayed material all influence the type and strength of the bond.

2.4 Characteristics of Aluminum Coatings Produced by CGDS

The characteristics of aluminum coatings produced by CGDS and reported in the literature are presented in this section. The porosity, hardness, bond strength, and corrosion behavior of aluminum coatings will be reviewed.

2.4.1 Porosity

The porosity of CGDS aluminum coatings, showed in Table 2.4, can vary from less than 0.5% to more than 12%, depending on the type of powder and deposition conditions. In CGDS, void reduction is the result of particle deformation. The continuous high velocity impacts of the particles produce a shot-peening effect and cause further plastic deformation in the deposited layers [31, 39]. The porosity of the coating microstructure is an important feature. Porosity can be detrimental to coating performance since it may reduce the corrosion and wear resistance, may act as sites of crack initiation and cause delamination.

Table 2.4 Porosity of aluminum coatings produced by CGDS (from [26, 46-48])

Aluminum	Porosity (%)
Pure	0.5 to 12
Al-2618*	5 to 10
Al-Mg*	1 to 6
Al-12Si	0.4 to 7.4

* nanocrystalline coating

2.4.2 Hardness

Hardness represents a measure of a material's resistance to plastic deformation. The coating hardness is often used for preliminary assessment of the coating quality and is an

important property in wear resistance. The hardness of aluminum coatings, listed in Table 2.5, is strongly dependant on the composition of the feedstock powder.

The microstructure of the feedstock powder also affects the hardness. Nanocrystalline coatings have a much higher hardness than crystalline coatings since these materials possess a finer grain structure as a result of the manufacturing process, with a greater amount of grain boundaries which impede the motion of dislocations.

Work hardening effects have also been observed by comparing the hardness of the feedstock powder particles and of the coating. It was suggested that particles exhibit work hardening upon impact which increases the dislocation density within the grains and hardness of the coating [46].

**Table 2.5 Hardness of aluminum coatings produced by CGDS
(from [39, 44, 46-51])**

Aluminum	Hardness (HV)
Al-5083*	261
Al-2618	150
Al-2618*	181
Al-Mg*	265
Al-12Si	110
Pure	34 to 52
Al-1100	84 to 275
Al-5083	138

* nanocrystalline coating

2.4.3 Bond Strength

The bond strength of coatings refers to the degree of adhesion of a coating to a substrate and can have strong effects on the operational performance. Few studies have reported the adhesion of aluminum coatings produced by CGDS and each of these studies used a tensile stud-pull test method. In this technique, studs with a diameter of 2.69 mm (0.106 in) are glued to the coating and the force required to pull the stud is measured. The strength of the coating is then defined as the force divided by the surface area of the stud. This testing method is a simple way to estimate the strengths of coatings but it is not a standard method to measure the bond strength of thermal spray coatings [17].

The reported values of cohesive strengths of pure aluminum coatings removed from their substrate range between 25 and 49 MPa [31], and from 33 and 35 MPa [49]. Adhesive strength values of 20 to 70 MPa have been obtained for Al-12Si coatings [17].

ASM International recommends evaluating the adhesion and cohesion strengths of coatings in accordance with the ASTM C 633-01 standard: Standard Test Method for Adhesion of Cohesion Strength of Thermal Spray Coatings [12]. This standard, described in section 4.4.3, will be used in this study.

2.4.4 Corrosion Behavior

Electrochemical studies performed on CGDS aluminum coatings have demonstrated that these coatings portray a similar corrosion resistance than bulk aluminum sheets [50, 52]. Sacrificial corrosion protection can then be achieved by means of CGDS aluminum coatings.

It was shown in one study that the corrosion resistance performance improved by changing the composition of the carrier gas [50]. The particles accelerated in a helium gas stream reach greater velocities and generate more plastic deformation than particles entrained in a gas mixture of helium and nitrogen. As a result, the highly stressed regions of the coating produced with helium acted as pitting initiation sites and slightly reduced the corrosion resistance of the coating.

2.5 Advantages and Limitations of CGDS

As it was mentioned in section 2.2.5, eliminating the undesirable effects of high temperatures on the resulting properties of the coatings and substrates offers significant advantages and new possibilities for CGDS. The advantages and some limitations of CGDS are discussed in this section.

2.5.1 Advantages

In CGDS, the initial microstructure of the feedstock powder is retained in the coating. The process offers the possibility of fabricating coatings and near net-shapes with the same microstructure as the powder. CGDS has also been applied to the fabrication of free-standing components [53].

CGDS becomes particularly suitable as a coating process with temperature-sensitive nanocrystalline and amorphous materials [54, 55], as well as oxygen-sensitive materials such as aluminum, copper, and titanium. The grain growth and chemical reactions that occur in conventional thermal spray processes do not take place in CGDS.

The peening action of the impinging particles causes plastic deformation of the underlying layers, thus generating compressive residual stresses. In addition, the tensile

stresses due to thermal shrinkage are avoided because the process temperatures remain well below the melting point of the sprayed material.

CGDS coatings may be applied to thin substrates (< 1 mm) without damaging the substrate [47]. The coating quality is also independent of the substrate thickness. Examination of CGDS coatings demonstrates that the depth of deformation of the substrate is below $50\text{ }\mu\text{m}$. Also, the process has the ability to build thick coatings and complex free-standing shapes and to form multilayer deposits.

The process is operationally safe since the lower jet temperatures significantly reduce the amount of thermal radiation and metal vapors. The process can also be operated under normal temperature, pressure, and humidity conditions. Finally, the particles are not heated or melt in the process and therefore, may be recycled and reused in subsequent coating cycles.

2.5.2 Limitations

Despite featuring several advantages, CGDS has a few limitations. Nozzle clogging or fouling has been encountered for prolonged spraying at high stagnation temperatures and powder feed rates. This phenomenon causes variations in the deposition rates and influences the coating properties [56-59]. The feedstock powder particles may be entrained in the slow moving gas of the boundary layer and stick to the nozzle wall. The accumulation of these particles obstructs the passage of the process gas and reduces the particle velocities.

Coatings on small inner bores, which are not in the line of sight of the spray gun, are currently not possible.

Finally, considerations should be given to the quality and microstructure of the powder. Since the coatings contain the same features as the feedstock powder, not only are

the microstructure and chemical composition of the feedstock powder maintained, its impurities will appear in the coating as well. The desired microstructure should first be achieved through an optimization of the powder fabrication process before attempting to produce coatings.

Chapter 3 – Description of the Research Objectives

3.1 Introduction

From a microstructural point of view, materials may come in various forms. They may be composed of a conventional, a nanocrystalline, or an amorphous microstructure or a combination of these forms. Composite materials constitute another class of materials in which two or more constituents with significantly different physical or chemical properties are combined to form a material with unique properties. The constituents do not dissolve into each other but rather retain their identities. Metal-matrix composites (MMCs) are a type of composite materials and are made by dispersing a reinforcing material into a metal matrix.

In this chapter, the aluminum alloys considered for the development of conventional and composite coatings and the reinforcement materials incorporated to the aluminum alloy matrices are described. Applications for each type of coatings are presented as well.

3.2 Development of Conventional Coatings

Currently, the vast majority of CGDS coatings are produced from powder particles having a microcrystalline microstructure. There are several reports from several authors on CGDS of pure aluminum [19, 21, 22, 25-27, 31, 32, 34, 42, 49, 52, 60-64]. Only a few aluminum alloy coatings produced by CGDS have been investigated such as Al-12Si [17, 41, 48, 59, 65, 66], Al-1100¹ [50, 67], Al-5083 [39, 51], and Al-2618 [44].

¹ The Al-1100 alloy contains a minimum aluminum content of 99%.

3.2.1 Al-5083 Coatings

The major alloying element in the 5083 aluminum alloy is magnesium, as shown in Table 3.1. This alloy possesses good welding characteristics and resistance to corrosion in marine atmospheres. Typical applications of Al-5083 include military and civilian transportation equipment, pressure vessels, and cryogenic equipment. More specifically, the hull of amphibious military vehicles, shown in Figure 3.1, is made from the Al-5083 alloy. These vehicles face a wide variety of terrains ranging from sand, gravel, mud, rocks, ice, snow, and water to name a few (see Figure 3.2). The hull is exposed to atmospheric and aqueous environments and solid obstacles. Abrasive wear then occurs, as some material will be removed from the surface as a result of cutting, friction, and rubbing against the debris on the hull's surface. The abrasive action may erode the film, leaving the bare metal exposed. Corrosion² pits then form and act as stress risers, defects difficult to detect and predict. A hard coating of the same material used on the hull would limit the effects of wear and provide corrosion protection.

Table 3.1 Chemical composition of the Al-5083 alloy

Element	Content (wt.%)
Mg	4.4
Mn	0.7
Cr	0.15
Al	balance

² Aluminum has a natural corrosion protection from its oxide layer, but may corrode if exposed to aggressive environments. Acidic (pH < 4) or alkaline (pH > 9) environments can destabilize the oxide layer and cause its dissolution. In acidic conditions, the aluminum oxide is more soluble than aluminum and pits may be initiated at weak sites (or local mechanical defects) in the oxide. In alkaline solutions the aluminum is attacked at locations where the oxide is perforated locally because aluminum is more soluble than aluminum oxide [68].

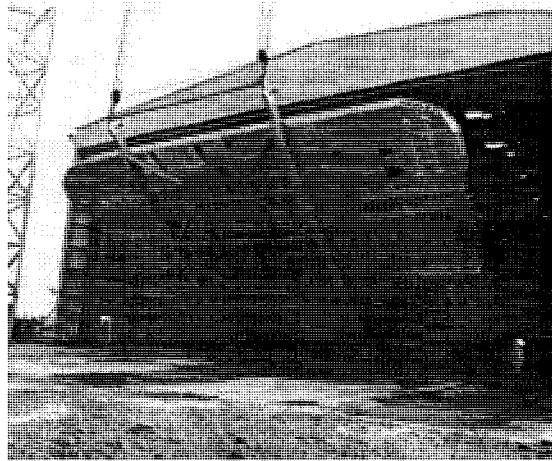


Figure 3.1 Hovercraft hull

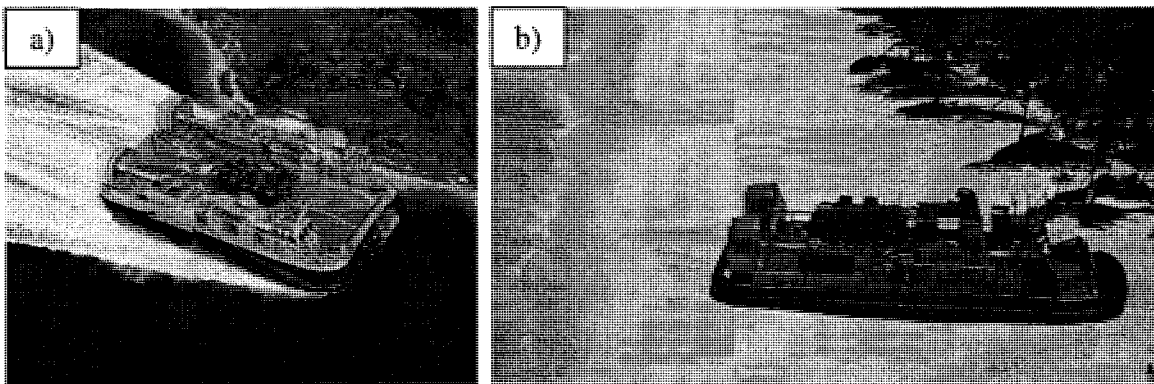


Figure 3.2 Military hovercrafts in operation along a) the shoreline and b) ashore (from [69])

Some of the characteristics of Al-5083 coatings have been the subject of a previous study [51]. The goal of this study is to continue the work of Mondoux [51] and assess the mechanical properties of Al-5083 coatings produced at several spraying conditions.

3.2.2 Al-12Si Coatings

Aluminum-silicon (Al-Si) alloys are well-known casting alloys with high wear resistance, low thermal expansion coefficient, good corrosion resistance, and improved

mechanical properties over a wide range of temperatures. These alloys are essential to the automotive and aerospace engineering sectors because Al-Si alloys allow the casting of complex shapes.

Abradable coatings of Al-12Si with additions of polymer or boron nitride composites are frequently used in the low temperature sections of compressors found in gas turbine engines. The coatings act as abradable seals to control and minimize the gas path clearance between the blades and the stator. The additives weaken the coating's matrix material by acting as sites of particle release. The coatings are also used during refurbishing to repair any excessive clearance produced during service. A reduction of the clearance distance between the blade tip and the casing increases the engine efficiency and reduces fuel consumption.

The purpose of this investigation is to produce Al-12Si coatings and evaluate their mechanical properties. An understanding of the effects of the CGDS process parameters on the Al-12Si coating characteristics will provide opportunities to produce abradable CGDS coatings.

3.2.3 Al-Co-Ce Coatings

In their amorphous forms, Al-Co-Ce alloys exhibit enhancements to corrosion resistance compared to their crystalline counterparts. The addition of cobalt, a late transition element, and cerium, a rare-earth element, to an aluminum matrix, improves its glass formability and its corrosion protection abilities. The presence of cobalt in the solid solution is necessary to maintain the amorphicity of Al-Co-Ce alloys. However, lower cobalt contents are desirable since the open circuit potential increases slightly in alloys with high cobalt content [70]. The addition of cerium also improves the amorphicity of the alloy and

offers sacrificial cathodic protection by decreasing the open-circuit potential [71]. When used as metallic coatings for aluminum components, an amorphous Al-Co-Ce alloy can act as a sacrificial anode and provide resistance to halide-induced pitting [71, 72].

Amorphous materials are characterized by their lack of defects such as grain boundaries and dislocations typically found in crystalline materials. It has been shown that the areas of high local stresses and precipitation around the grain boundaries of crystalline materials promote the preferential nucleation of pits and leads to pitting corrosion [73]. The absence of grain boundaries in aluminum-based amorphous alloys has resulted in improved mechanical properties as well as significant enhancements in corrosion resistance compared to their crystalline counterparts [74], such as a superior pitting resistance due to the limited number of pitting nucleation sites [75].

Although the corrosion behavior of Al-Co-Ce alloys has been explored [70-72], their fatigue performance as a coating has not yet been investigated. Such coatings could be used as cladding material to provide corrosion protection of the high strength aluminum alloy used on aircraft skin structures [76]. Aircraft flight cyclic pressurization generates stresses on the aircraft skin and affects its fatigue life. One of the objectives of this work is to demonstrate the feasibility of producing Al-Co-Ce coatings using a crystalline feedstock powder and the CGDS process and study the fatigue behaviour before using an amorphous Al-Co-Ce feedstock powder.

3.3 Development of Metal-Matrix Composite Coatings

MMCs constitute a class of materials that have made a major industrial impact in fields as diverse as aerospace, automobiles, and electronics. These materials can be tailored to yield superior properties by incorporating a controlled amount of reinforcements within a

metal matrix. Alloys reinforced with ceramic particulates can offer property enhancements such as increased hardness, improved wear resistance, better thermal stability, and superior yield strength [77, 78]. Among the various matrix materials available, aluminum and its alloys are widely used in the fabrication of MMCs. This is mainly due to the low density, high strength, and good corrosion resistance of aluminum alloys. These alloys are also cheaper than other low density alloys such as those using magnesium or titanium and can be produced by various processing techniques, such as extrusion, forging, casting, and powder metallurgy.

Major fabrication methods of reinforced aluminum materials include casting, extrusion, thermal spray deposition, and powder metallurgy [79]. It has been shown that defects such as porosity, shrinkage, oxide inclusions, clustering of the reinforcement particles, and degradation of the reinforcement significantly influence the bulk and coating properties [79-81]. In addition, the low temperature ductility and poor toughness generally encountered are drawbacks that limit the performance and applications of such composites. As a result, composite coatings are a viable method to improve the surface properties of components without producing any significant change in their ductility [82, 83].

Few studies have looked at the characteristics of reinforced aluminum alloy coatings produced by CGDS. It has been shown that deposits of hard materials such as silicon carbide (SiC) and alumina (Al_2O_3) incorporated in a ductile aluminum matrix can be successfully produced by CGDS [84]. The thickness of the Al-SiC composite films could reach 50 μm when spraying on silicone substrates [84]. It has also been shown that changing the content of SiC particulates within an aluminum matrix produces predictable changes in thermal properties such as the thermal conductivity and coefficient of thermal expansion [85].

Composite coatings using an aluminum matrix with reinforcing particles of diamond, tungsten, silicon carbide, aluminum nitride or boron carbide have also been produced using CGDS [86, 87].

3.3.1 Al-12Si + SiC Coatings

It has been reported that the addition of relatively inexpensive silicon carbide (SiC) particles to an aluminum alloy matrix results in increased strength [81], elastic modulus [81], and wear resistance [88], while providing good corrosion resistance. Al-SiC composite coatings produced by plasma spraying have yielded properties that are characteristic of bulk composites [82]. The SiC particle distribution and volume fraction in plasma sprayed composite coatings depend on the quality of the feedstock powder which is being used for spraying. In feedstock powders prepared by blending SiC with aluminum alloy particles, SiC particles are preferentially lost compared to the aluminum alloy particles [89-91]. The large difference in melting temperatures between the SiC and the aluminum alloy along with the poor wettability of SiC by aluminum explain this behavior [89-91]. During the plasma spraying process, aluminum particles are melted by the plasma gas and solidify upon impact on the substrate. However, the SiC particles remain in their solid state and are entrapped in the sprayed material or bounce off the surface of the deposit. Excess amount of SiC particles must then be added to the feedstock to compensate for the SiC lost during spraying. It was reported that increasing the SiC content in the feedstock powder beyond some value does not augment the SiC volume fraction in the coating [90, 91]. This is attributed to the fact that less liquid aluminum is available, in proportion, to retain the SiC particles and to fill the voids in the coating. Plasma spraying of Al-SiC composite powders prepared by the mechanical alloying process has been found to produce coatings with uniformly distributed

and fine reinforcements within an aluminum matrix [82, 89, 92]. In the mechanical alloying of composite powders, the particles of each constituent are added in a rotating ball mill and are continuously grinded. The repeated fracturing reduces the particles to a smaller size and cold welding produces agglomerates of aluminum particles with fragments of SiC [82, 89, 92]. The SiC particulates are incorporated and homogeneously dispersed within the aluminum matrix. This improves the wettability of SiC by aluminum and augments the fraction of SiC entrapped in the coatings [93].

Al-SiC composites have emerged as an important class of high-performance structural elements in the electronic and aerospace industries. Al-SiC materials have been used as base plates and heat sinks for power modules. The incorporation of SiC within the aluminum matrix strengthens the material and lowers the coefficient of thermal expansion. A reduction of weight, vibration fatigue and thermal cycling were obtained without reducing the thermal dissipation [94]. These composites have been used to decrease the deflection, increase the life and reduce the maintenance costs of the ventral fin of F-16 aircrafts [78]. Elimination of skin cracking and an increase of the allowable load were achieved using Al-SiC on F-16 fuel access door covers [78].

The objective of this study is to develop aluminum alloy coatings with dispersed SiC particles using CGDS. Several mass fraction combinations of an aluminum alloy and SiC reinforcements will be created and subsequently sprayed. The effect of various ratios and sizes of particulate ceramic, based on the coating microstructure and hardness, will be explored.

3.3.2 Al-5083/B₄C Coatings

Boron carbide (B₄C) has some attractive properties, such as an extremely high hardness (HV = 30 GPa) and a low density (2.52 g/cm³). It is one of the hardest known materials, ranking third behind diamond and cubic boron carbide [95]. This covalent ceramic offers neutron absorption capabilities, wear resistance, and impact resistance. Nuclear applications of Al/B₄C materials include shields and containment of nuclear waste [78]. In the form of coating, Al/B₄C can provide wear resistance [96].

The fabrication of Al/B₄C materials using liquid phase approaches requires temperatures exceeding 1000°C to completely melt the aluminum and wet the B₄C [80]. At these temperatures, chemical reactions between the B₄C and the aluminum alloys cause the formation of various undesirable and brittle phases, including Al₄C₃ [80, 97]. Such reactions are strongly dependant on the processing parameters, such as the consolidation temperature, time and oxygen content. Al/B₄C materials have also been manufactured by powder metallurgy processing [98, 99]. The blended aluminum alloy and B₄C powders are compacted and subsequently processed using hot working methods such as extrusion, forging, and rolling [99]. However, the composites fabricated by powder metallurgy methods have exhibited weak interface bonding between the ceramic and the aluminum. Debonding at the Al/B₄C interface has been found to occur in response to an applied load, which has resulted in the deterioration of the mechanical properties [99].

As was mentioned earlier, the incorporation of a ceramic phase to an aluminum matrix by mechanical alloying is an alternative approach to produce MMC powders. Conducting the alloying process at cryogenic temperatures results in a reinforcement phase uniformly distributed in a nanocrystalline matrix [100]. It has been reported that the

cryomilling process forms a clean interface between the B_4C powder and the aluminum matrix [101]. The low temperatures associated with the cryomilling process also prevented the formation of brittle phases that usually occurred in liquid phase processes [101].

The objective is to explore the possibility of producing coatings from an Al-5083/ B_4C composite powder produced by cryomilling. Near net-shape nano-composite parts for high performance applications may then be produced by CGDS.

Chapter 4 – Experimental Equipment, Measurement Methods, and Procedures

4.1 Introduction

This chapter outlines the experimental equipment, the measurement methods, and the procedures that were elaborated to produce and evaluate aluminum-based coatings. The CGDS facility and its main components are described. The methods used to measure the particle in-flight velocities are presented. This chapter ends with a description of the coating characterization tools used to evaluate the properties of the coatings.

4.2 Cold Gas Dynamic Spray (CGDS) Facility

At the onset of the current research, modifications to the existing system were required to upgrade the facility for accessibility, repeatability, and process control. The existing system was designed and developed by Mondoux [51] and has been used to examine the feasibility of spraying various materials. A new CGDS facility was developed at the University of Ottawa. The facility now comprises of a redesigned spraying chamber, spray guns, a powder feeder, driving and feeding gas supplies, and a gas heater. The following sections describe the components of the facility, schematically represented in Figure 2.9.

4.2.1 Spraying Chamber

Previously to the research presented here, CGDS was conducted in the spray chamber shown in Figure 4.1. The spray gun is positioned horizontally while the substrate is moved with a single-axis displacement system. The apparatus was only capable of producing coating traces on top of each other. A two-axis displacement system was then required to produce coatings over surfaces, such as bond strength specimens and bending fatigue specimens.

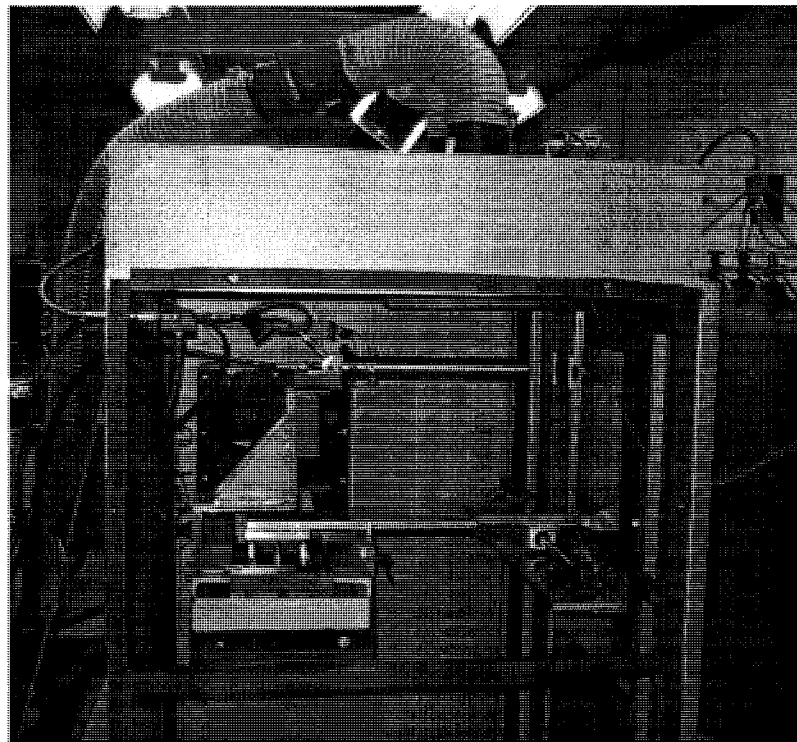


Figure 4.1 Previous spraying chamber

The new spraying chamber consists of a smaller enclosure equipped with several access doors and a ventilation duct. A picture of the setup is shown in Figure 4.2. In this arrangement, the spray gun is positioned vertically to improve accessibility to the substrate

and spray gun. A two-axis displacement system moves the substrate over the x-y plane, a plane perpendicular to the spray gun axis. The mechanism consists of linear slides driven by stepper-motors and controlled by a National Instrument LabView™ user interface.

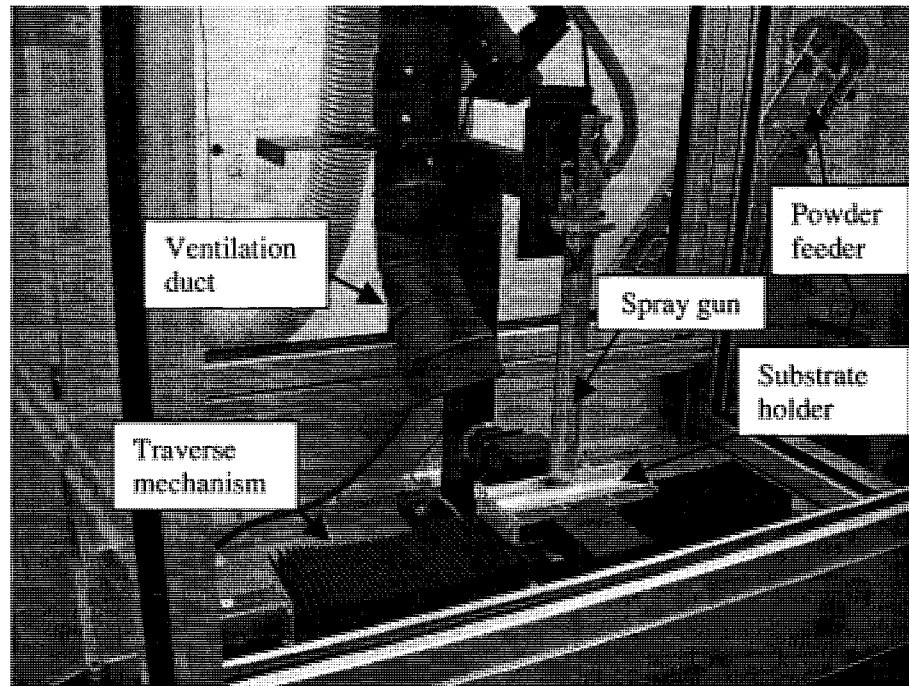


Figure 4.2 New spraying chamber

4.2.2 Spray Guns

The spray guns consist of two axisymmetric converging-diverging nozzles, which were developed at the University of Ottawa. These nozzles were designed using a modeling-based design process [51]. Several numerical models were elaborated to obtain a nozzle geometry that would produce a calculated particle exit velocity above 900 m/s for an aluminum powder particle of 20 μm . The physical dimensions of the nozzle such as the throat and exit diameters and diverging length, as well as the inlet pressure were varied to determine their effects on the particle velocity. Based on the simulation results, the nozzles

were fabricated with a throat diameter of 2 mm and a diverging length of 250 mm. The exit diameters are 6.3 and 7.3 mm, corresponding to exit-to-throat area ratios of 10 and 13, respectively. The complete details of the simulations are available in Mondoux [51]. The spray guns were designed to operate at a pressure of 1020 kPa since the powder feeder is limited to 1200 kPa.

A manifold bolted at the gun inlet consists of a mixing chamber with two injection ports (see Figure 4.3). The powder is injected axially while the driving gas is introduced at an angle.

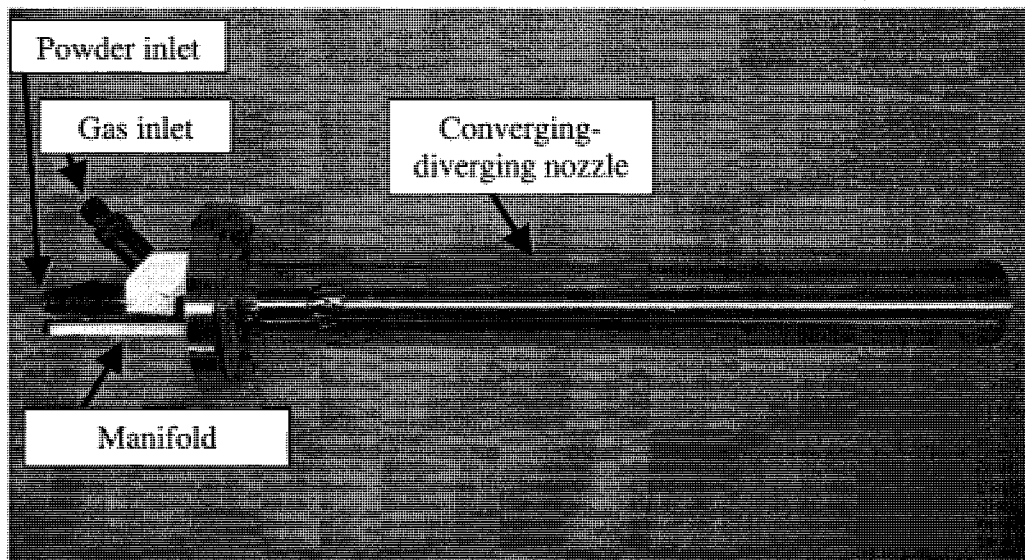


Figure 4.3 Spray gun with manifold

4.2.3 Powder Feeder

The powder is injected in the manifold by means of a commercial powder feeder (Model 1264, Praxair Surface Technologies, Concord, NH, USA). The powder feeder shown in Figure 4.4 consists of a powder carrier wheel and a tamper assembly contained at the base of a sealed canister. During operation, the canister is pressurized and the slots in the powder

wheel are filled with powder. As the powder wheel rotates past an exit port, the powder is metered by a feeding gas supply into the powder hose and carried to the manifold and into the process gas stream. The tamper assembly helps feed the powders that have a tendency to clog by tamping powder into the slots of the powder wheel.

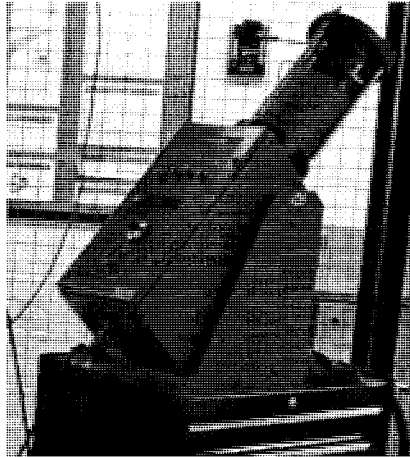


Figure 4.4 Powder feeder

4.2.4 Driving and Feeding Gas Supplies

Helium was chosen as both driving and feeding gases for the current study. Due to its relatively low molecular mass (4 g/mol), a much lower molecular weight than nitrogen (28 g/mol), helium has a sound velocity greater than any gas, except hydrogen. As a result, at the same gas temperature, helium yields greater gas velocities than nitrogen for a specific nozzle design [20]. Helium is also a noble gas and the least reactive of all elements. Chemical reactions between the process gas and the powder particles entrained in the system are thus avoided. A high-pressure powder feeder would allow the use of nitrogen as the process gas.

As the driving gas is passed through the spray gun, the canister of the pressure feeder also pressurizes to a pressure equal to the nozzle inlet pressure. A feeding gas supply set to

a slightly higher pressure than the nozzle inlet pressure is then required to push the powder particles into the driving gas.

4.2.5 Gas Heater

The pressurized process gas coming from the high-pressure gas supply is preheated to the desired stagnation temperature using a gas heater which consists essentially of an electrically resistance-heated tube. A stainless tube with a length of 3.91 m and an inner diameter of 17.5 mm (Figure 4.5) is connected to a 30 kW power supply. The heat generated within the tube is then transferred to the process gas passing through the tube without any gas contamination. Sensors are used to monitor the pressure and temperature of the flow passing through the gas heater during the spraying operations.

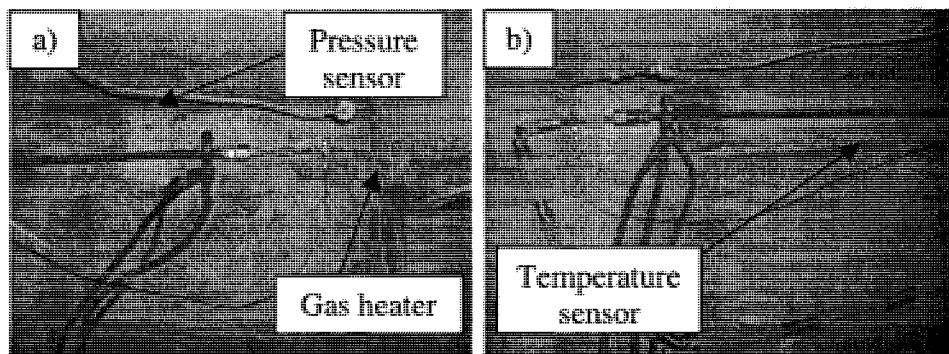


Figure 4.5 Photographs showing a) the inlet and b) outlet of the gas heater

4.3 Particle In-Flight Velocity Measurements

As mentioned previously, in-flight particle velocity measurements are essential to monitor the performance of the nozzle and the behavior of the powder particles. Two systems for velocity measurement have been used.

4.3.1 Cold Spray Meter (CSM)

The Cold Spray Meter (CSM) (Tecnar Automation Ltd, St-Bruno, Québec, Canada) is a laser in-flight diagnostic system and its operational principle is shown in Figure 4.6. While a continuous laser illuminates a measurement volume, a dual-slit photomask captures the signal (see Figure 4.7) generated by individual particles passing in front of the sensor. The signal from the photosensor is then amplified, filtered, and analyzed by a detection module. The in-flight diagnostic of each individual particle that crosses the measurement volume is performed by determining the time between two peaks of the particle signal. The particle velocities are then obtained by dividing the distance between the two-slits by the particle's flight time [102].

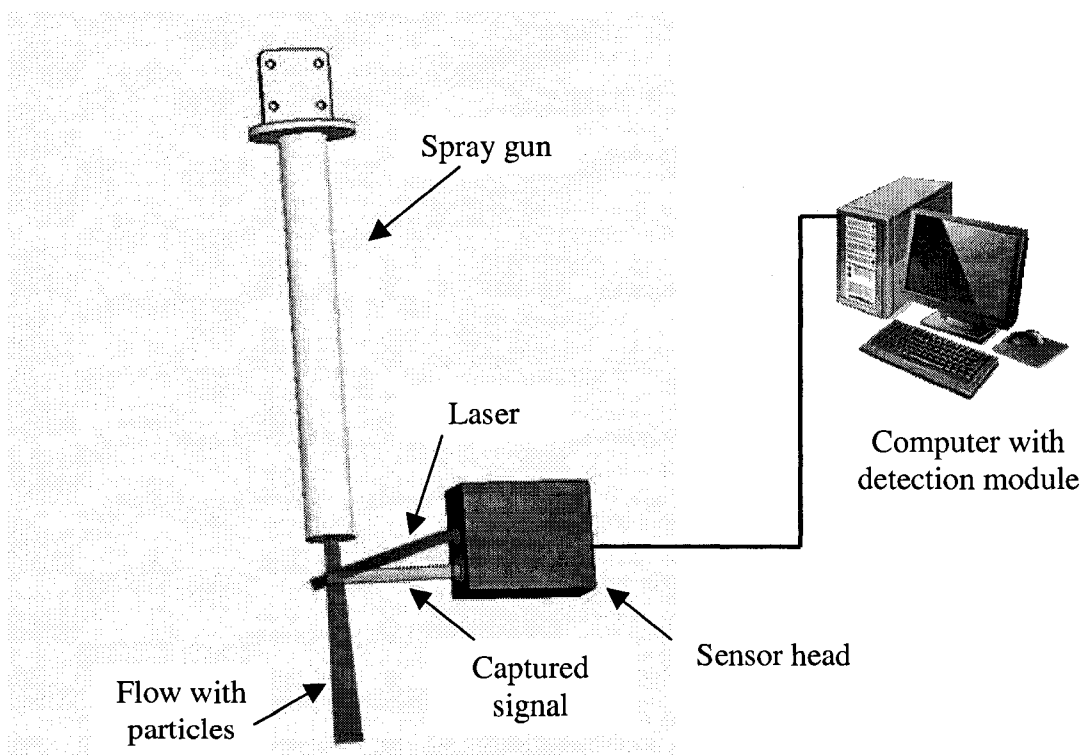


Figure 4.6 Operating principle of the Cold Spray Meter (CSM)

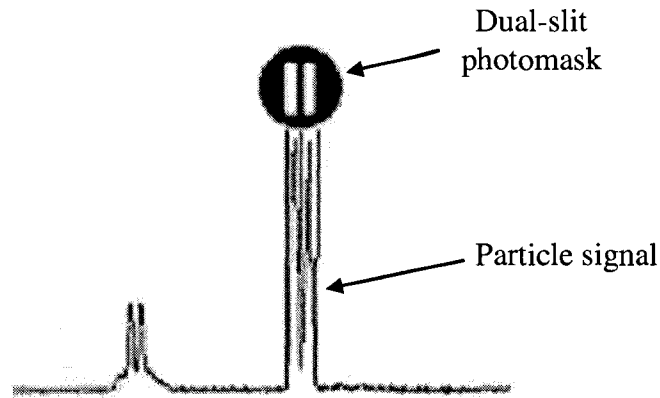


Figure 4.7 CSM dual-slit photomask and particle signal (from [102])

4.3.2 Particle Image Velocimetry (PIV)

Particle Image Velocimetry (PIV) is a non-intrusive measuring technique that can provide whole field instantaneous velocity maps over global two or three-dimensional domains. In principle, the PIV technique consists of taking two images closely separated in time and calculating the distance tracer particles traveled within this time lapse. From the known time lapse and the measured displacement, the velocity can be calculated. In PIV the fluid motion is made visible by adding small tracer particles to the fluid flow. A PIV setup requires four basic components, as shown in Figure 4.8:

- 1) An optically transparent test-section containing the flow seeded with tracer particles,
- 2) A light source (pulsed laser) to illuminate the region of interest,
- 3) A recording hardware consisting of a charged-coupled device (CCD) camera, and,
- 4) A computer with suitable software to process the recorded images and extract the velocity information from the tracer particle.

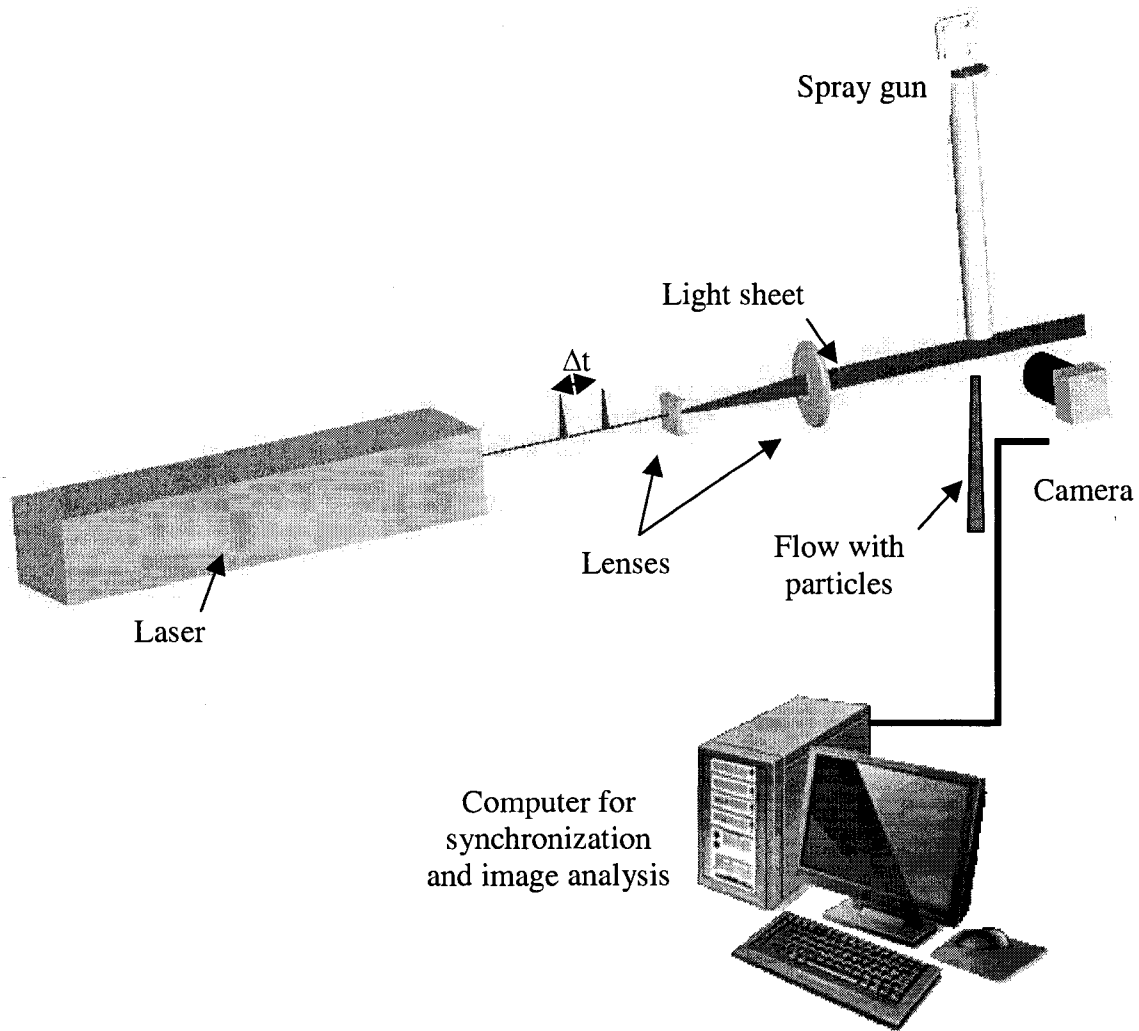


Figure 4.8 Components of a PIV setup

In contrast to CSM, PIV does not require the matching of individual particles. The region captured by the camera, the measurement window, is divided into small interrogation regions, as shown in Figure 4.9. The average motion of small groups of particles contained within each interrogation region is determined by cross-correlating the interrogation areas from two images. The cross-correlation function is effectively a pattern matching routine which approximates the average displacement of the particles in each interrogation region. The correlation produces a signal peak, identifying the average displacement in the

interrogation region. A velocity vector map over the whole target area is obtained by determining the particles average displacement of each interrogation area.

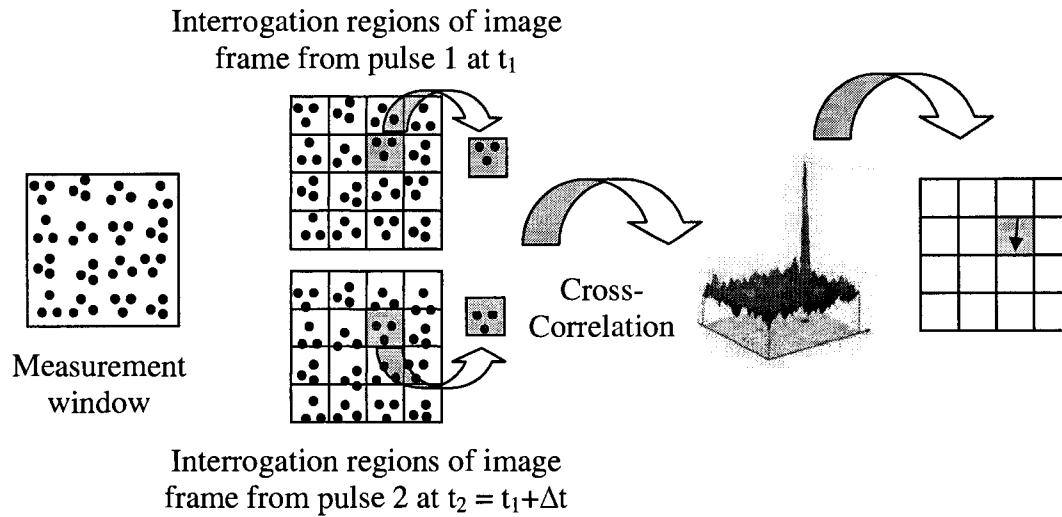


Figure 4.9 Image frame analysis of PIV

In the context of measuring flow velocities, the tracer particles are considered ideal if they exactly follow the motion of the fluid, do not alter the flow and do not interact with each other [103]. However, since we are interested in particle velocities, the particles themselves will be used as tracer particles.

4.3.2.1 Laser and Light Sheet Optics

The laser unit consists of a New Wave Solo PIV dual cavity Nd-YAG laser (New Wave Research, Fremont, CA, USA) capable of generating two consecutive 120 mJ pulses at a wavelength of 532 nm.

A cylindrical lens followed by a spherical lens was used to reshape the laser beam in a light sheet. The cylindrical lens expanded the laser beam in the vertical direction while the spherical lens controlled the thickness and the height of the laser sheet.

4.3.2.2 CCD Camera

The recording device used with the PIV system is an Imager Pro (LaVision Inc., Ypsilanti, MI, USA) CCD camera with a frame resolution of 1600 by 1200 pixels. The Imager Pro camera uses a two frame-straddling technique and is capable of achieving a minimum time separation of 0.2 μ s (200 ns) [104]. The camera is also fitted with a 532 nm bandpass filter to suppress the background light during the recordings.

4.3.2.3 Processing Unit

A processing unit was required to synchronize the laser and camera to ensure that the camera captured an image at the same instant that a laser pulse was emitted. The processor used in this study was a LaVision FlowMaster processor. The processing unit allowed the user to adjust several parameters such as the pulse time separation (Δt), size of the interrogation areas, and options for the cross-correlation routine.

4.4 Powder and Coating Characterization

4.4.1 Microscopic Observation

Observation of a specimen using optical imaging enables the detection of defects such as cracks and pores. Scanning electron microscopy (SEM) is commonly used to investigate the microstructure of materials. This type of microscope uses electrons rather than light to observe the microstructure of the sample surface at different magnifications. Prior to a microscopic observation, the specimens were prepared by standard metallographic techniques, as described in Appendix A. The coatings were sectioned and mounted in a resin in order to preserve the coating microstructure during the subsequent grinding and polishing

steps. SEM images of the coating cross-section were used to detect interlamellar cracks and to evaluate the coating porosity and thickness. The porosity and volume fraction of the SiC phase were obtained using the Clemex image analysis software [105]. A quantitative separation of the coating's structural elements was performed based on the grey level distribution of the SEM images. The porosity, SiC particles and nozzle fragments that appear in the coatings (see Figure 4.10) could be distinguished based on differences in the grey scale levels. Porosity, SiC and nozzle fragments were converted into different background colors while the aluminum matrix remained in its original color, as illustrated in Figure 4.11. The percent areas of the marked regions within the analysis frame (see Figure 4.11) could then be measured independently.

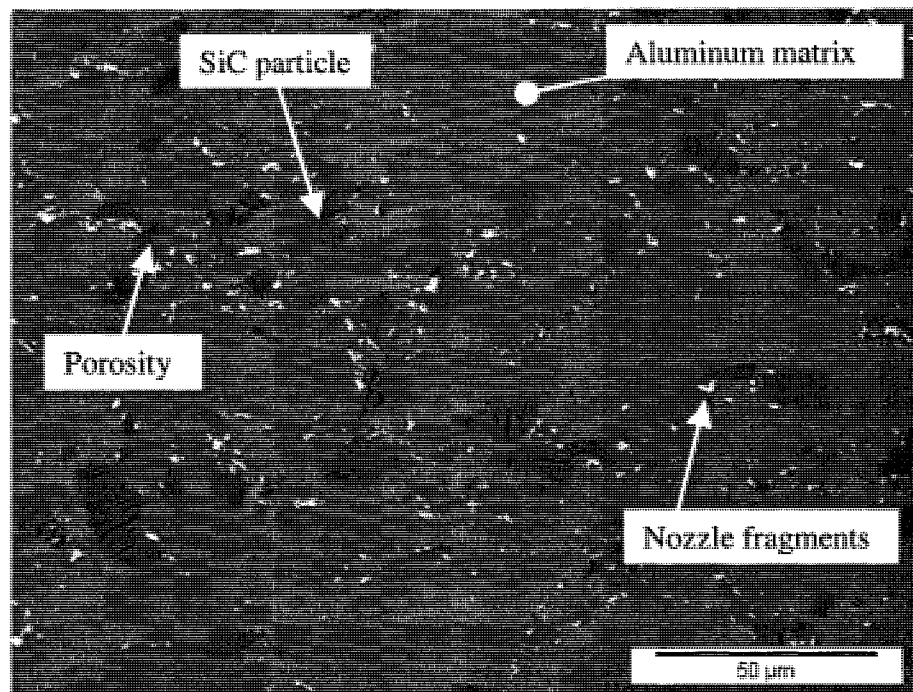


Figure 4.10 SEM of a SiC-reinforced Al-12Si coating produced by CGDS showing the constituents of the coating



Figure 4.11 Constituents of Figure 4.10 identified by pixels of different colors

4.4.2 Particle Size Distribution

The particle size distributions were obtained with a particle size analyzer (Coulter LS, Fullerton, CA). This device uses the interaction between light and particles to determine the particle size. A beam of laser light shone through the cell is diffracted by particles within the sample and the diffracted light is collected by a series of detectors. The distribution of light falling on the sensors enables the size distribution of the sample. The particles of a given size scatter light through a given angle; the angle increasing with decreasing particle size.

4.4.3 X-Ray Diffraction Analysis

X-ray Diffraction (XRD) is a material characterization technique used to identify the crystalline phases present in materials. X-rays of a fixed wavelength are projected into a sample and penetrate the surface. The interaction of the incident rays with an array of planes of atoms in the sample produces interference and a scattered ray. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. The signal is processed and converted into peaks in intensity as a function of the angle. The peaks in intensity are based on the interatomic spacing, which is characteristic for each material. Identification of the phases or compounds is achieved by comparing the relative intensities of the various peaks and their peak position with standard spectra within databases.

The structural properties such as strain state, grain size, phase composition, and orientation can be measured. In this study, the feedstock powder and coatings were analyzed by XRD. The measurements were carried out using a Philips X'Pert PW 1830 generator diffractometer with Cu K α radiation at 50 steps per degree and a count time of two seconds per step. The diffraction patterns were then compared to determine if any microstructural changes in the material occurred during spraying.

4.4.4 Bond Strength

Bond strength evaluations were conducted using the ASTM Standard C 633-01 [106]. The coatings were produced on grit-blasted standard test samples having a 25.4 mm diameter and an overall length of 38.1 mm. Typically, several passes at 50% overlap were carried out to cover the entire surface of the sample. The top portion of the coating were then machined flat and glued to an uncoated test sample. Figure 4.12 illustrates the bond

strength specimen and test fixture. The adhesive (Master Bond EP-15, Hackensack, NJ, USA) was used for bonding the test specimens. The assembled parts were cured at 170°C for 90 minutes in a V block device that ensures a proper alignment. The arrangement was then placed in the fixtures of the tension testing machine (Instron model 4482 equipped with a static load cell of 100 kN), as shown in Figure 4.13. An increasing tensile load was applied at a constant rate of cross-head travel speed of 0.021 mm/s (0.050 in/min), according to the standard specifications [106]. The machine registered the maximum load applied before rupture occurred.

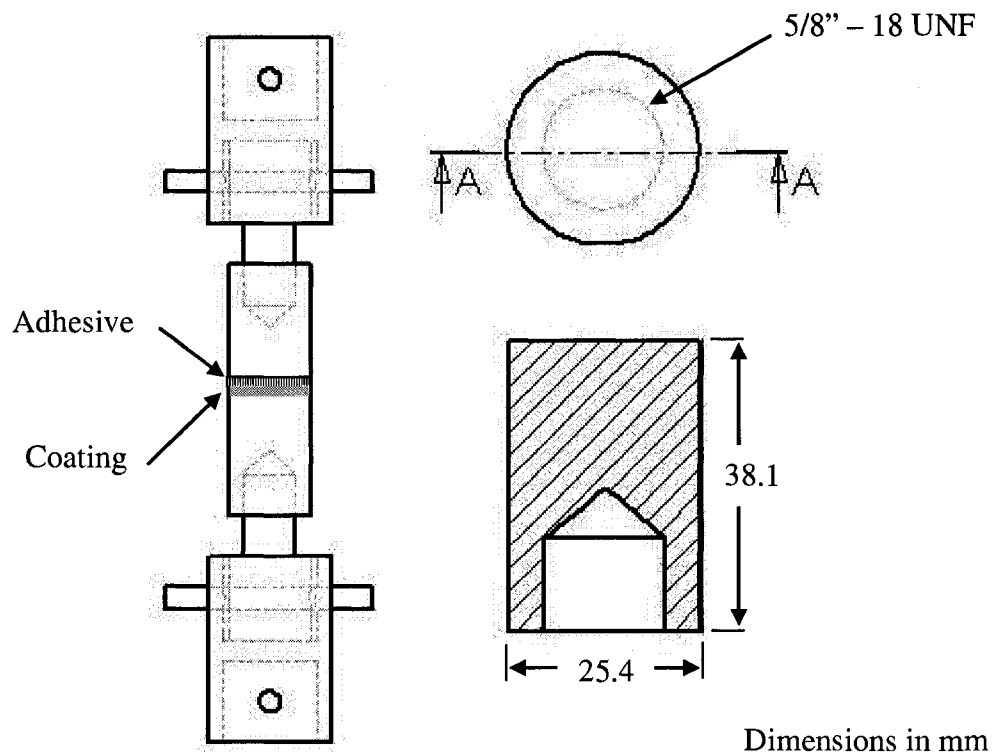


Figure 4.12 ASTM C 633-01 bond strength specimens and test fixture

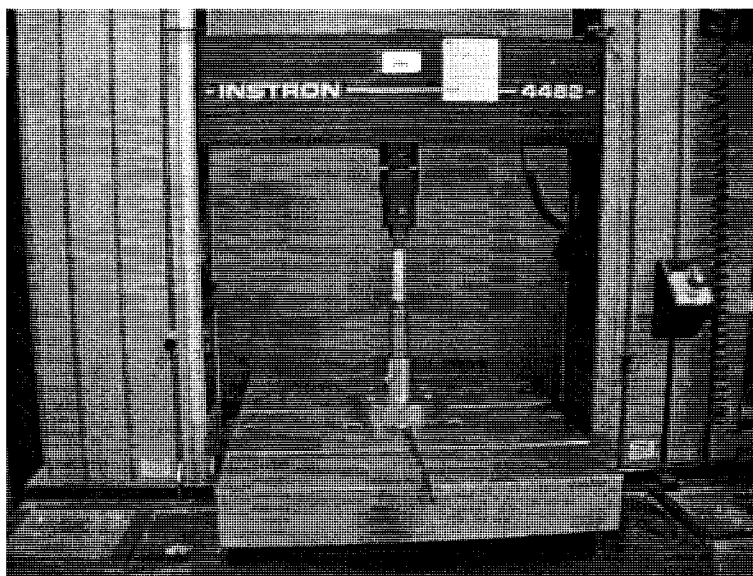


Figure 4.13 Bond strength specimen arrangement in a tension testing machine

4.4.5 Fatigue Strength

The effects of the coatings on the bending fatigue behavior of substrates were examined following the ASTM Standard B 593-96 [107]. This test is used to measure the ability of a material to withstand cyclic stresses without developing cracks or other evidence of mechanical deterioration. The test specimens were supported in the same manner as a cantilevered beam at one end and subjected to an alternating load at the other end, as depicted in Figure 4.14. The fatigue test specimen shown in Figure 4.15 included a triangular shape intended to produce a constant stress along the length of the test section of the specimen. This triangular region was grit-blasted on one side only and several passes at 50% overlap were used to cover this portion of the specimen with a coating. In the current study, the samples were tested at various stress levels using the fatigue strength tester shown in Figure 4.16. The number of cycles was automatically recorded until complete sample failure, characterized by the separation of the specimen into two pieces.

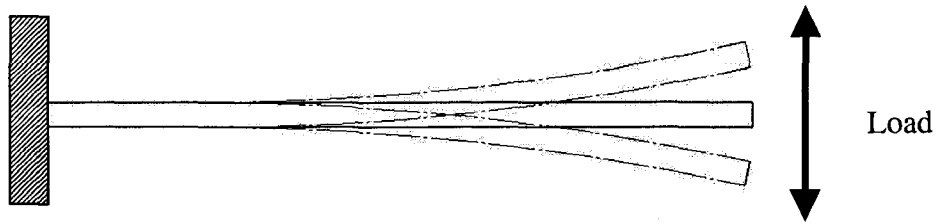
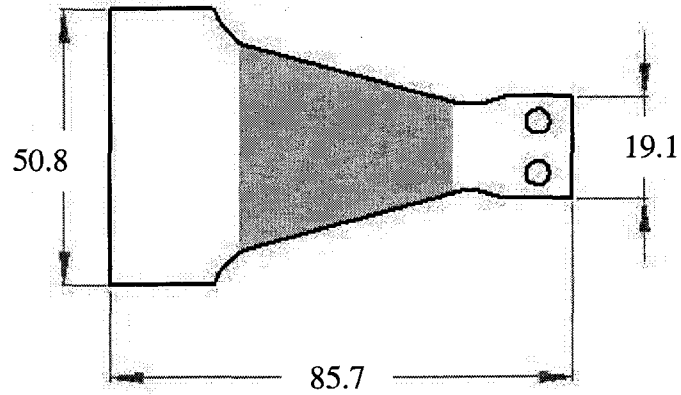


Figure 4.14 Cantilevered beam subjected to an alternating load



Dimensions in mm

Figure 4.15 Fatigue strength specimen. The grey region corresponds to the coated area

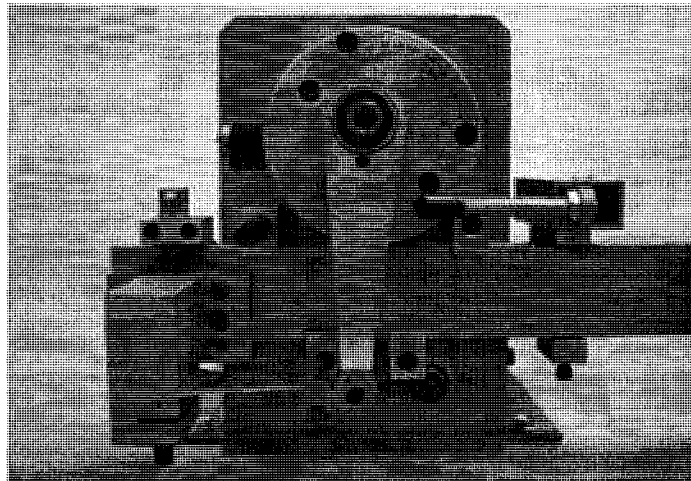


Figure 4.16 Fatigue strength tester

4.4.6 Hardness

The hardness of the coatings was tested on polished cross sections of coatings using a Vickers micro-hardness tester (Struers Duramin-1 micro-hardness tester), shown in Figure 4.17. In this test, a diamond indenter shaped as a square pyramid is forced into the material. The two diagonal widths of the indentation are measured using a microscope at a magnification of 1000X. The calculation of the Vickers hardness is calculated as follows:

$$HV = 1854.4 \frac{P}{d^2}, \quad (4.1)$$

where HV , P , and d represent the hardness value, the applied load to cause the indentation (in grams), and the average measured width of the indentation (in μm), respectively. In the conventional Vickers hardness testing method, also referred to as Vickers macro-hardness testing, the applied load ranges from 1 to 120 kgf. The tip of the indenter penetrates deep into the specimen and hardness values for the bulk material can be obtained. For coatings and surface properties, the indentation levels used in macro-hardness testing become too large, the measurements are highly variable and do not identify the individual features. Micro-hardness testing is well suited for testing thin materials, small parts, and individual microstructures since the load on the indenter does not exceed 1 kgf and the resulting indentation is smaller than the one used in the macro-hardness tests. The indenter can be precisely located at discrete locations of the coating to determine the local hardness. A micro-hardness indentation mark left on an aluminum alloy coating is illustrated in Figure 4.18.

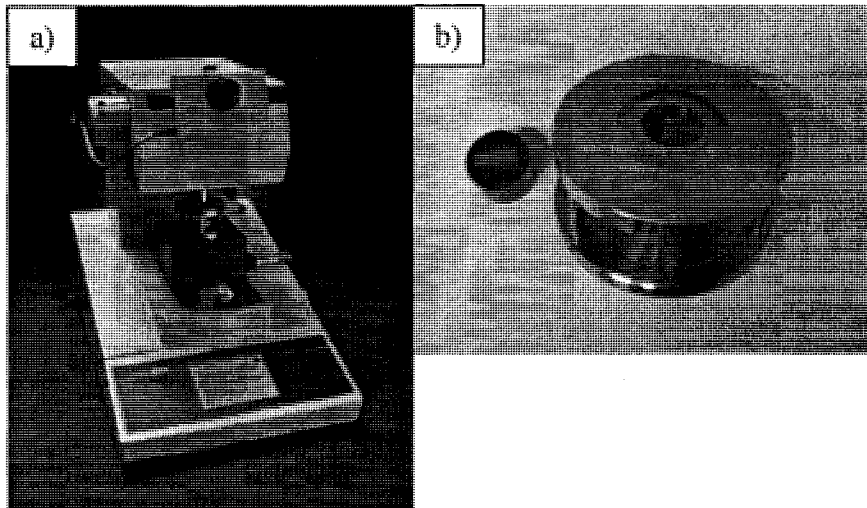


Figure 4.17 Photographs of a) the micro-hardness tester and b) a specimen and the specimen holder for the tester



Figure 4.18 Image of a micro-hardness indentation in an Al-Co-Ce coating

4.4.7 Substrate Surface Roughness

The substrate surface roughness was evaluated with a portable profilometer (Model Surftest SJ-201P, Mitutoyo), as shown in Figure 4.19. The instrument uses a stylus to measure the heights of the peaks and valleys, with a resolution of $0.01\ \mu\text{m}$, as a function of

position. The roughness measurements were used to characterize substrates that were grit-blasted and substrates that were not blasted.

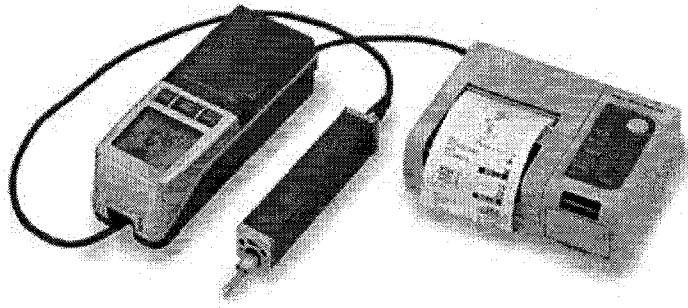


Figure 4.19 Photograph of the profilometer

Chapter 5 – Particle In-Flight Velocity

Measurements

5.1 Introduction

As it was outlined in section 2.3.4, previous studies have identified that CGDS is mainly governed by the particle impact velocity. It becomes important to establish relationships between the latter, the process operating parameters and resulting coating characteristics and properties, as it is outlined in Figure 5.1. Consequently, one should be careful when considering process parameters or operating conditions such as the stagnation pressure and temperature, driving and feeding gas compositions, and spray gun geometry as correlating parameters. These factors directly influence the particle velocities and are means of achieving the required particle impact velocity. Ultimately, the particle velocity should be monitored and used to correlate the coating properties such as thickness, hardness, porosity, and adhesion strength to the processing conditions. Subsequently, the coating properties could be predicted based on the process operating parameters, given that the operating parameters-particle impact velocity relationships are known. Particle velocity measurements are also essential to validate numerical models. These models are used to design the spray guns meant to accelerate the particles to an exit velocity superior to the critical velocity of the sprayed material. The effects of exit-to-throat area ratio, length of the diverging section, stagnation pressure and temperature, gas composition, and presence of shock waves on the particle velocity can be determined numerically. The nozzle design can then be optimized for specific particle average diameter and material, as well as desired coating properties.

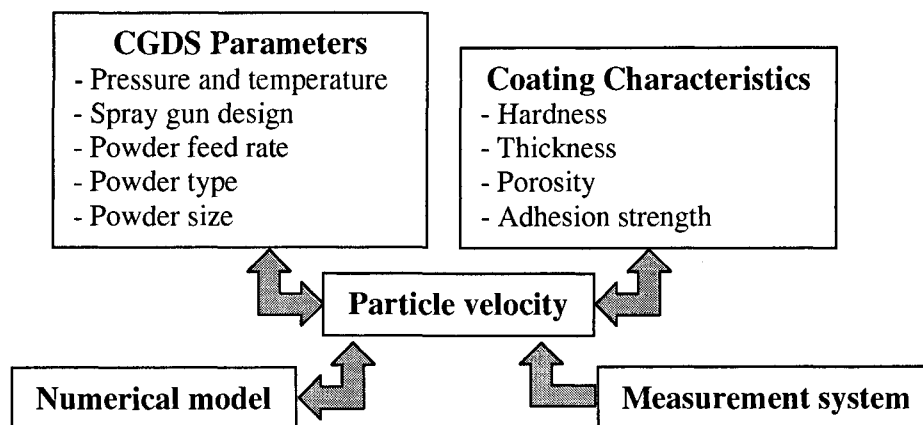


Figure 5.1 Links between the particle velocity, operating parameters and coating characteristics

The objective of this chapter is to select the most suitable particle velocity measurement technique. The implementation and operating characteristics of two different particle in-flight laser diagnostic systems are described. The particle velocities obtained by each system are presented and compared.

The CSM was conveniently inserted on the substrate holder of the new spraying chamber, as shown in Figure 5.2. The PIV system required more space and could not be installed in the new spraying chamber. It was then decided to build a separate setup, as illustrated in Figure 5.3. However, this setup could not accommodate a gas heater.

The effect of the particle size distribution of copper particles on the particle in-flight velocity was investigated using the CSM and the PIV technique. Copper particles were chosen because they were readily available and because the critical velocity of copper could be reached without gas pre-heating. As it was shown in Figure 2.11, copper possesses a lower critical velocity than aluminum. The tests were then conducted at operating conditions that consolidated copper coatings. The feedstock powder (Cu-103, Praxair Surface Technologies, Indianapolis, IN, USA), shown in Figure 5.4, has a size ranging from 16 to 45

μm . It was sieved into four size ranges: 16 to 25 μm , 25 to 32 μm , 32 to 38 μm , and 38 to 45 μm .

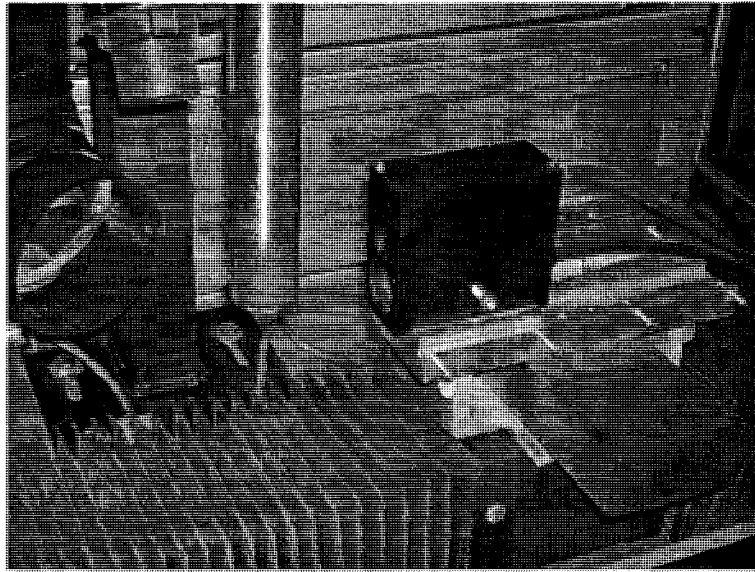


Figure 5.2 CSM on the substrate holder of the new spraying chamber

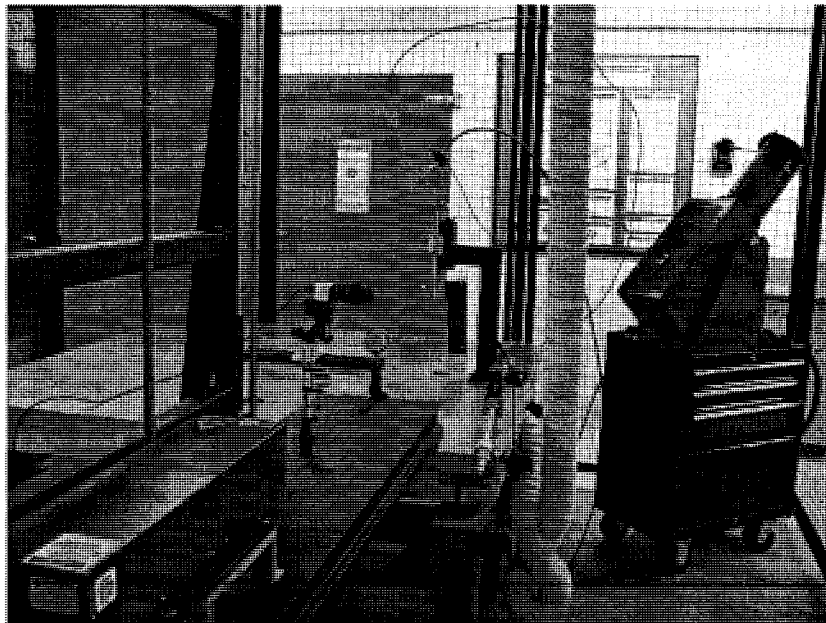


Figure 5.3 Photograph of the PIV setup (the enclosure was removed for clarity)

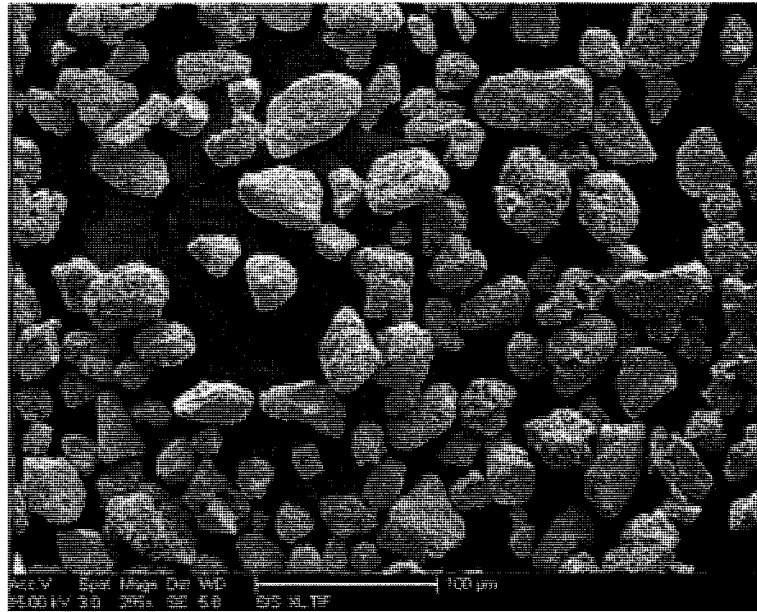


Figure 5.4 Morphology of the as-received copper powder

5.2 Cold Spray Meter (CSM) Measurements

The CSM velocity measurements were taken along the spray gun axis, 10 mm downstream from the spray gun exit. In order to avoid particle build-ups and rebounds that could obstruct the sensor field of view, particle velocity measurements were performed without the presence of a substrate. Particle velocity measurements with a substrate could not be performed adequately because the substrate reduced the space available for diagnostic and caused poor particle illumination. Particle rebounds that obstructed the sensor field of view and reflections of the laser beam off the substrate and nozzle are factors that affected the measurements with a substrate.

The resulting average particle velocities obtained for the bulk and for the four size ranges are shown in Figure 5.5. These averages were computed from a minimum particle count of 1000 particles. The results indicate a slight decay of the centerline velocity as the

particle average size increases. The momentum transfer between the gas and a particle, or the particle acceleration (a_p), is inversely proportional to the particle size, d , that is:

$$a_p = \frac{\frac{1}{2} \rho V_{rel}^2 A_p C_D}{V_p \rho_p} \propto \frac{1}{d}, \quad (5.1)$$

where V_{rel} is the relative velocity between the gas and the particle, A_p is the particle projected surface area, C_D is the drag coefficient, V_p is the particle volume, and ρ_p is the particle density. A smaller particle average size leads to higher accelerations and higher particle impact velocities. The larger particles experience smaller accelerations and consequently, reach lower particle velocities.

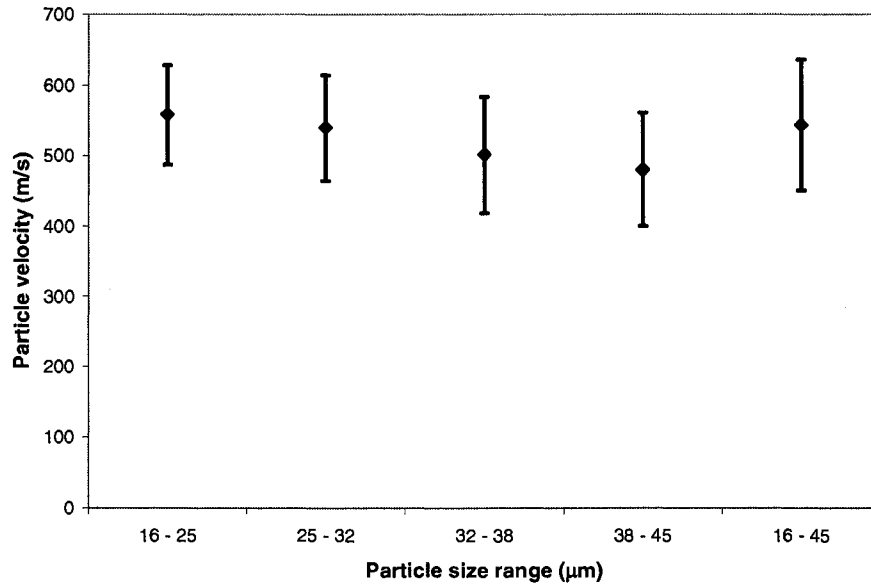


Figure 5.5 Average particle velocities (with standard deviations) of copper particles of different size obtained with the CSM

5.3 PIV Measurements

The particle velocity measurements with the PIV system were also conducted without a substrate to avoid reflections that could damage the detection array of the CCD camera. Particle velocity measurements of the bulk feedstock powder, ranging in size from 16 to 45 μm , could not be performed adequately. The wide particle size distribution caused saturation of too many pixels of the camera. Reducing the power level of the laser to lower settings lessened saturation but diminished the number of particles that could be captured by the camera. This produced an insufficient number of particles per image pair for meaningful statistics.

Sieving the bulk feedstock in various size ranges helped in reducing this effect but the irregularities in particle shapes affected the measurements. The irregularities in the particle morphologies caused non-uniform reflections and saturated pixels of the camera. The axial velocity profiles along the spray gun centerline are shown in Figure 5.6 for the four particle size ranges. The profiles were extracted from the data of the velocity field obtained by PIV. The effects of the particle size range on the particle in-flight velocity are not as clear as with the CSM measurements. A slight decrease of the centerline particle velocity is noticed as the mean particle size increases and with the axial distance from the spray gun exit. At 10 mm from the nozzle exit, values of 506, 470, and 445 m/s were obtained for the 16 to 25 μm , 25 to 32 μm , and the 38 to 45 μm size ranges, respectively. The tests for the 32 to 38 μm particles were conducted at slightly higher driving gas pressures and therefore, the resulting particle velocities do not follow the observed trend. An increase of the operating pressure produced an increase of the stagnation pressure and of the

stagnation density. The gas density throughout the nozzle flow was then slightly higher, which lead to larger particle accelerations (see Equation 5.1) and higher particle velocities.

The radial distribution of the axial particle velocity at a 10 mm distance from the spray gun exit, shown in Figure 5.7, also demonstrates the effects of particle size. There are significant velocity variations around the core of the velocity profile, even a few millimeters from the spray gun centerline. For example, at a radial distance equivalent to the nozzle exit radius, the particle velocity has dropped to approximately 200 m/s. The radial decrease of the particle velocity is also apparent in the cross-section of the coating shown in Figure 5.8. The center of the coating is thicker than the edges because a large number of particles have reached the critical velocity. The decrease of the particle velocity in the radial direction reduces both the deposition efficiency and the coating thickness near the edges. The radial velocity profiles at 5, 10, 15 and 20 mm for the four particle size ranges are given in Appendix B.

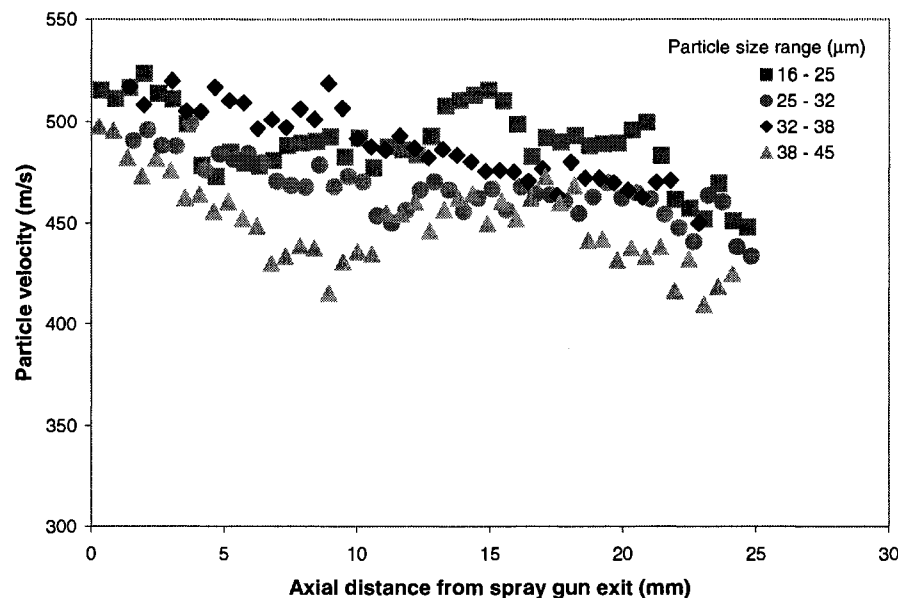


Figure 5.6 Particle axial velocity along the spray gun axis for various particle size ranges obtained by PIV

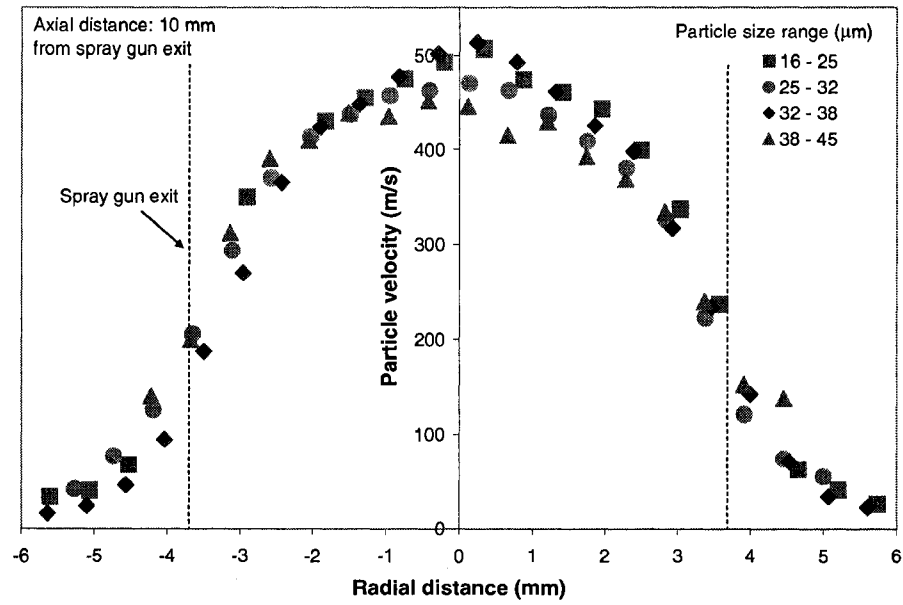


Figure 5.7 Radial distribution of the axial particle velocity at 10 mm from the spray gun exit for several particle size ranges obtained by PIV

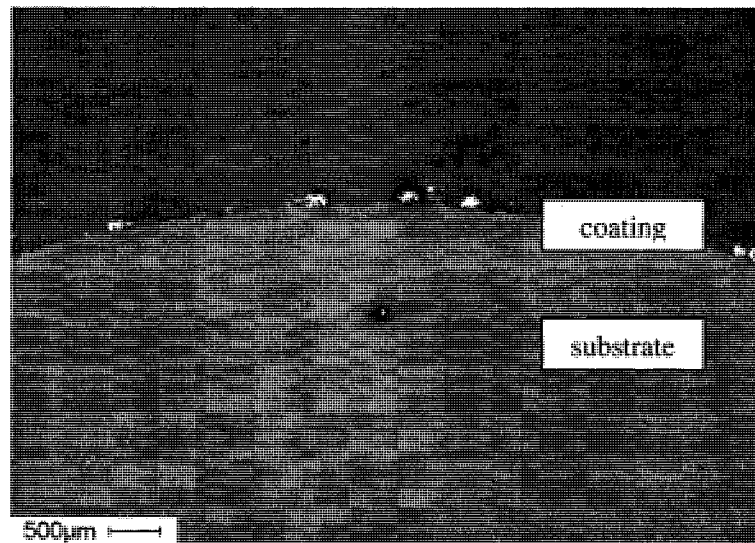


Figure 5.8 Cross-section of an Al-12Si coating showing the effects of the non-uniform axial particle velocity profile

5.4 Comparison of the CSM and PIV systems

Two different laser diagnostic systems were successfully implemented. In the CSM, the particle velocities are obtained by determining the time required for individual particles to cross a small control volume. In PIV, the displacement of a group of particles, measured from images taken at a very short time interval, is used to calculate the velocities.

The differences in the actual measured particle velocity values between the CSM and the PIV measurements are listed in Table 5.1. The results indicate that the particle velocities measured by the CSM are on average 10% higher than the ones from PIV. This may be due to minor differences in the operating conditions and in the setup. A separate CGDS setup was used to perform the PIV measurements. Neither the previous nor the new spraying chambers provided sufficient access to accommodate a PIV system. The post-processing routines used for the vector calculations in PIV may have been too restrictive in removing spurious vectors. The allowable vector range selected for the calculations may have eliminated too many of the high velocities associated with the smallest particles. Slight differences in the gas stagnation pressure would affect the particle velocities. For example, an increase in pressure would have augmented the density of the gas, which directly affects the drag exerted on the particles and their velocities.

Table 5.1 Comparison of the measured particle velocities

Particle size range (μm)	Particle velocities (m/s)		Difference (%)
	CSM (Figure 5.5)	PIV (Figure 5.6 at 10 mm)	
16 – 25	558	506	9
25 – 32	539	470	13
38 – 45	480	445	7

The CSM is advantageous in that real-time measurements can be obtained following a short set-up time. Real-time measurements of the particle velocities are useful and yield instantaneous feedback. The effects of the operating parameters on the particle velocities and on the coating properties can be readily examined and quantified. The particle velocities at the beginning and at the end of spraying runs can be monitored to detect problems in the spray gun or in the system, thus minimizing the down time. The CSM could then be used in an industrial setting to monitor the spraying process. The system was also found not to be sensitive to the particle morphology and could be installed in tight locations. Much less expensive than PIV, the CSM uses a laser with a lower power supply and does not require elaborate analysis routines to extract the particle velocities. On the other hand, the CSM only gives the average velocities of particles passing through a small region captured by the sensor head. As a result, the velocity map of an entire flow region can only be obtained by moving the sensor head in the flow field, which prolongs the spraying time.

PIV is a powerful method by which detailed velocity fields of a large region can be obtained instantaneously. Information relating to the flow field, such as vorticity, streamlines, and velocity vectors, can then be extracted from the data. This analysis would be valuable in the design and optimization of nozzles for CGDS. The particle velocity distribution as well as flow visualization of the field could be investigated. However such details of the flow field are not particularly useful in this study on CGDS, as only the particle velocities are of interest. In order to perform PIV measurements, lengthy calibration procedures of the flow field captured by the camera and alignment of the light sheet must first be performed. Real-time velocity measurements can not be achieved, which is a considerable shortcoming from an industrial perspective. An extensive analysis must be

conducted to remove the saturation regions of the images, perform the cross-correlation routines, and to eliminate the false vectors. A PIV system requires much more space than the CSM, can not be implemented in tight areas, and was found to have considerable sensitivity to the particle morphology. Particles with sharp edges and rough morphologies generated reflections that caused pixel saturation of the CCD. A similar effect was also observed in experiments conducted when the powder feed rate was increased. Velocity measurements at high powder feed rates could not be conducted appropriately by PIV.

Based on the ease of implementation and usability, it is then decided to perform the particle velocity measurements with the CSM for the remainder of this study.

Chapter 6 – Microstructural Features and Mechanical Properties of Aluminum-Based Coatings

6.1 Introduction

This chapter focuses on the microstructural features and mechanical properties of aluminum-based coatings produced by the CGDS process. The characteristics of conventional Al-Co-Ce, Al-5083 and Al-12Si coatings will be discussed in detail. An in-depth description of Al-12Si + SiC and Al-5083/B₄C composite coatings will then follow. The properties of the aluminum-based coatings produced by CGDS are summarized in tabulated form in Appendix C. All the coatings presented in this chapter were produced from a single pass of the substrate in front of the spray gun with the exception of the coatings for the fatigue and the bond strength specimens. These coatings were applied using several passes at a 50% overlap.

6.2 Al-Co-Ce Coatings

6.2.1 Powder Description

The Al-13Co-26Ce powder was prepared by gas atomization. The as-atomized particles have a spherical morphology, as illustrated in Figure 6.1. The particle size distribution, outlined in Figure 6.2, indicates that the powder has an average diameter of 12 μm . About 90% of the particles have a size below 23 μm . The small size and tight

Acc.V Spot Magn Det ASD
1200V X0 50000 00 00
50 μm

Particle diameter (μm)	Volume fraction (vol. %)	Cumulative size distribution (vol. %)
0	0.0	0
2	0.5	5
4	1.5	15
6	3.0	30
8	4.0	45
10	4.5	60
12	4.8	75
14	5.0	85
16	5.1	92
18	5.0	96
20	4.8	98
25	4.1	100
30	1.2	100
35	0.2	100
40	0.0	100
45	0.0	100

88

6.2.2 Parametric Study

A parametric study of three spraying parameters was first undertaken to examine the effects of the nozzle exit-to-throat area ratio, gas stagnation temperature, and powder feed rate on the coating microstructural features. The nozzle exit-to-throat area ratio and gas stagnation temperature are parameters that directly influence the process gas velocity and consequently, the particle velocity. The powder feed rate controls the amount of powder that can be injected and accelerated in the high velocity gas flow. A particle loading effect can occur when the gas flow becomes saturated with powder particles due to a high powder feed rate. As a result, the momentum transfer between the gas flow and the particles is not sufficient and the particles are not accelerated above the required critical velocity. This parametric study was performed to obtain appropriate spraying conditions that will be used to evaluate the fatigue behavior and bond strength of Al-Co-Ce coatings. The coatings were produced using single passes of the spray gun over grit-blasted aluminum substrates at a spraying distance of 10 mm and a substrate traverse speed of 2 mm/s.

6.2.2.1 Effect of Nozzle Exit-to-Throat Area Ratio

The cross-sectional SEM images of Figure 6.3 depict the Al-Co-Ce coating produced by CGDS with nozzles having exit-to-throat area ratios of 10 and 13 with identical diverging sections of 250 mm long (as described in section 4.2.2). The gas stagnation temperature and powder feed rate were set at 200°C and 6 g/min, respectively. In both coatings, the outline of individual particles is difficult to discern even if the back-scattering (BSE) mode is used. The coatings exhibit levels of plastic deformation suggesting that the particles were accelerated beyond the alloy critical velocity for both nozzles. Increasing the nozzle area ratio reduced the coating porosity from 2 to 0.5% while the coating thickness remained

approximately constant at 200 μm . No significant changes in the coating microhardness were observed. Microhardness values of 226 ± 12 and 229 ± 11 $\text{HV}_{500\text{g}}$ were obtained for the coatings produced with the nozzle having an area ratio of 10 and 13, respectively.

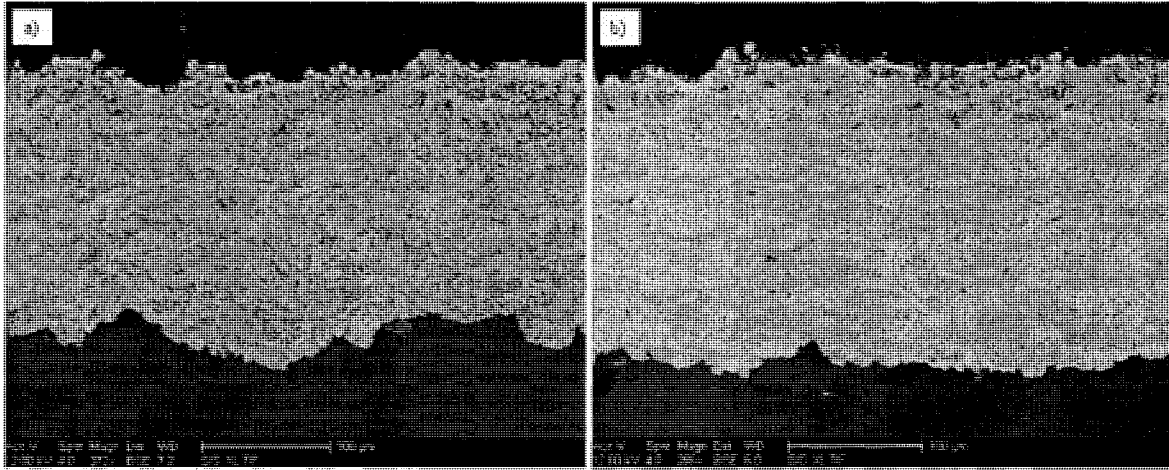


Figure 6.3 SEM images of the cross-section of CGDS Al-Co-Ce coatings for nozzle exit-to-throat area ratios of a) 10 and b) 13

Under similar conditions, the gas dynamics theory predicts that the gas undergoes a greater expansion in a nozzle with a greater exit-to-throat area ratio and thus, higher gas velocities are expected in the latter nozzle [108]. This behavior has been observed by monitoring the gas static pressure along the length of the nozzle using static pressure taps [109]. It was observed that the gas static pressure along the nozzle axis decreases more in the case of a nozzle with a greater exit-to-throat area ratio, confirming that the gas is expanded to a larger extent in this nozzle. The results from a validated two-dimensional numerical analysis of the nozzle indicate that increasing the nozzle exit-to-throat area ratio by 30% (from 10 to 13) increased the gas velocity by approximately 6% [51]. According to the model, this increase in the nozzle exit-to-throat area ratio increased the nozzle exit Mach number from 2.25 to 2.63. However, a greater expansion in a nozzle causes a larger drop of the gas static temperature, which reduces the local gas speed of sound, thus explaining the

limited increase of velocity of the gas despite a higher local Mach number [108]. The numerical results have also shown that a larger exit-to-throat area ratio produces a slightly higher gas velocity at every radial position inside the nozzle [51]. The particle velocity measurements, shown in Figure 6.4, demonstrate that increasing the nozzle exit-to-throat area ratio by 30% changes the average particle velocity from 530 ± 110 to 549 ± 93 m/s. A close examination of the particle velocity distributions reveals that for the nozzle with an area ratio of 10, 45% of the particles have velocities between 500 and 650 m/s. For the same velocity range, this proportion increases to 55% for the nozzle with an area ratio of 13. This shows that more particles have higher impact velocities and more particles will undergo extensive plastic deformation. The lower limit of 500 m/s was chosen as it is believed that this value is close to the critical velocity of these particles.

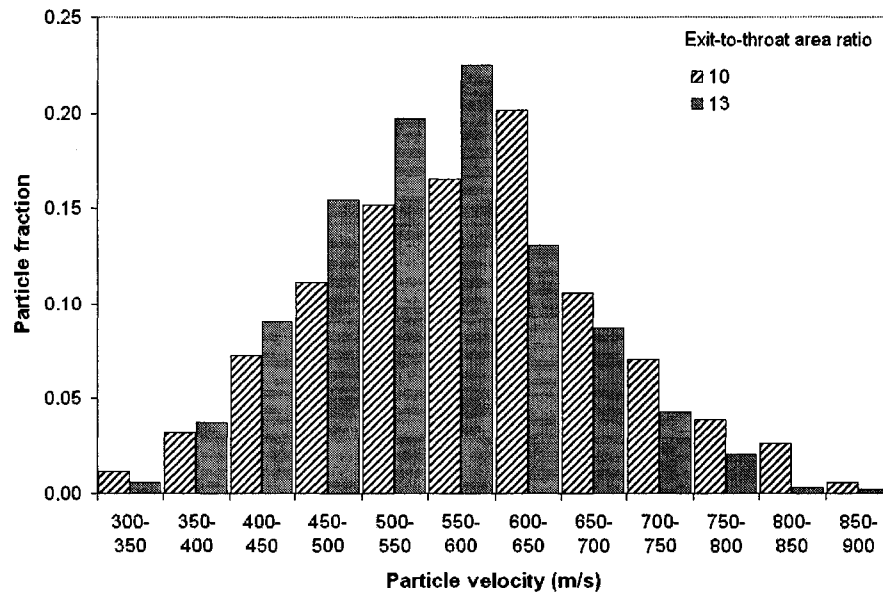


Figure 6.4 Histograms of the Al-Co-Ce particle velocities for nozzle exit-to-throat area ratios of 10 and 13

It is important to note that these velocity measurements were taken along the centerline of the nozzle and do not reflect the radial distribution of the particle velocity but rather, represent the average particle velocity at the nozzle centerline. Based on the numerical results, the nozzle with a larger exit-to-throat area ratio generated a broader particle velocity profile due to the reduced area occupied by the boundary layer. It is rationalized that the different microstructural features found in the coatings of Figure 6.3 may be the result of a change in both the average particle velocity distribution and in the profile of the particle velocity at the nozzle exit. In addition, the velocity measurements were performed without a substrate at the nozzle exit. The presence of a perturbation such as a substrate generates abrupt changes in the flow properties through shock waves. It is also envisioned that the structure and strength of the compression and expansion waves, which are dependent on the nozzle geometry, influence the velocity of the fine particles (average diameter of 12 μm) [109]. Flow visualization of the CGDS process has demonstrated that shock waves, entrainment of ambient air, and jet flapping all influence the flow pattern and velocity of the feedstock powder particles [61]. The difference in the average particle impact velocity is possibly greater than what is suggested by the velocity measurements performed without the presence of a substrate.

An increase of the particle velocities enhances the plastic deformation of the particles upon impact and reduces the porosity of the coating by allowing the particles to conform to the existing shape of the coating. A close examination of the coating produced with a nozzle area ratio of 10 shows particles deformed to a lesser degree with voids and pores surrounding these particles than in the coating produced with the larger nozzle area ratio. Densification of the previously deposited layers of material due to the impact of

impinging particles, similar to what is found in shot peening, was also observed in both coatings. This is confirmed by the observation that the top layers of the coatings are more porous than its bottom layers. The top layer consists of deformed particles that have not been exposed to the impingement of other incoming particles. Accordingly, the porosity in this region of the coating is greater than elsewhere in the coating. The reduction of the amount of voids and pores in the coating produced with the larger nozzle area ratio is then attributed to the amount of compaction. The measured increase in the particle impact velocity not only enhances the plastic deformation of the particles upon impact but also, intensifies the continuous compaction of the previously deposited layers of material by the incoming particles.

The fact that the coating thickness is not affected by the increase of the nozzle area ratio suggests that the latter did not influence the process deposition efficiency since the same powder feed rate was used for both nozzles. The defect-free interface observed between the substrate and coating indicates that a sufficient particle impact velocity was reached for deposition to produce an intimate bond. Although a slight enhancement of the particle plastic deformation was observed in the coating produced with the nozzle area ratio of 13, the microhardness measurements were not significantly affected by the level of plastic deformation or additional work hardening resulting from the spraying process.

6.2.2.2 Effect of Gas Stagnation Temperature

SEM images of Al-Co-Ce coatings produced at stagnation temperatures of 200°C and 370°C are shown in Figure 6.5. The nozzle with a larger area ratio was used since the coatings produced with it had a lower porosity and more visible particle plastic deformation. A powder feed rate of 6 g/min was used to produce these coatings. Both coatings display

substrate-coating interfaces free of defects and cracks, and of comparable porosity levels of less than 0.5%. The coating thickness was increased from 200 to 400 μm by raising the gas stagnation temperature. A higher gas stagnation temperature results in a higher gas temperature throughout the nozzle. Since the gas velocity at any location in the nozzle is a function of the local Mach number (determined by the nozzle geometry as per Equation 2.6) and local speed of sound (which is a function of the gas static temperature as per Equation 2.3), increasing the gas stagnation temperature increases the gas velocity throughout the nozzle [108]. This, in turn, is likely to accelerate the particles to higher velocities due to the enhanced momentum transfer caused by the higher gas velocity. The increased coating thickness indicates that a larger portion of the particle distribution has reached the velocity required for plastic deformation upon impact. The histograms of the measured particle velocity obtained for gas stagnation temperatures of 200 and 370°C are presented in Figure 6.6. Increasing the gas stagnation temperature from 200 to 370°C increased the average particle velocities from 549 ± 93 to 599 ± 103 m/s. For that same increase of the gas stagnation temperature, the proportion of particle having velocities above 600 m/s changed from 29 to 50%. Despite an increase of the average particle velocity, the degree of the particle plastic deformation in both coatings is comparable since the interfaces of undeformed particles are difficult to outline. These results suggest that particle velocities above 550 m/s seem to undergo similar levels of plastic deformation to form dense and defect-free coatings.

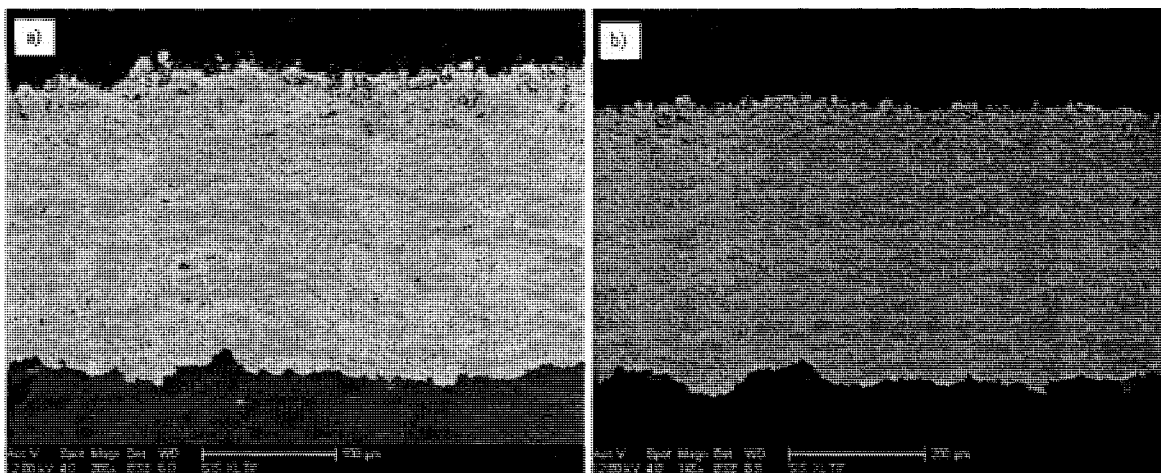


Figure 6.5 SEM images (at different magnifications) of the cross-section of CGDS Al-Co-Ce coatings produced at a) 200 and b) 370°C

At both gas stagnation temperatures, the top layer consists of deformed particles that were not exposed to the impingement of particles throughout the spraying process. The reduction of porosity in the underlying layers of deposited material is the result of a gradual compaction caused by the repeated impact of incoming particles on the coating. No apparent reduction of the porosity and no significant change in the microhardness were noticed by varying the gas stagnation temperature. Microhardness values of 229 ± 11 and 231 ± 10 HV_{500g} were obtained for the coatings produced at 200 and 370°C, respectively.

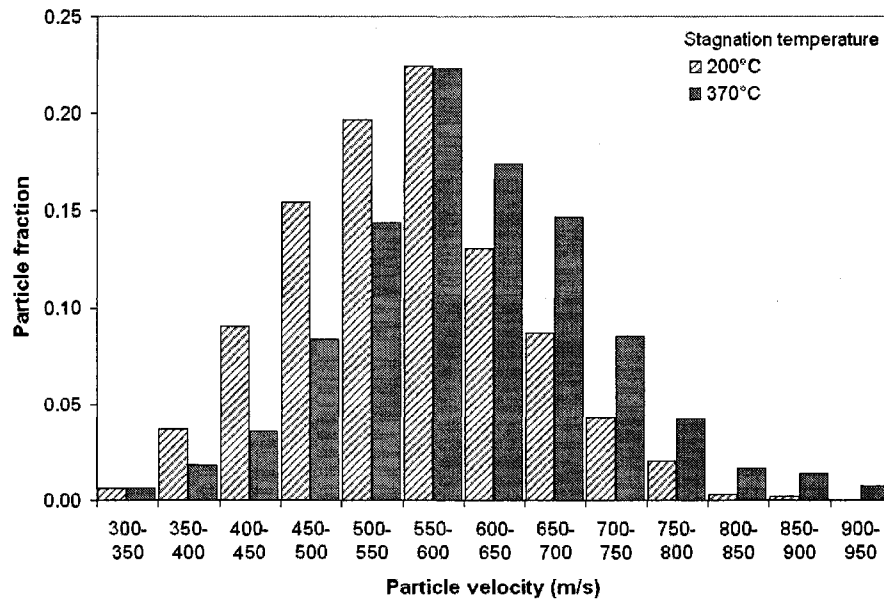


Figure 6.6 Histograms of the Al-Co-Ce particle velocities at gas stagnation temperatures of 200 and 370°C

6.2.2.3 Effect of Powder Feed Rate

The effect of powder feed rate was evaluated on coatings produced using the nozzle with an area ratio of 13 and a gas stagnation temperature of 370°C. The coatings produced with this nozzle had lower porosity levels and more detectable particle plastic deformation. This specific value for the gas stagnation temperature was chosen since the results of section 6.2.2.2 demonstrated that thicker coatings are obtained with a higher gas stagnation temperature. Changing the feed rate of Al-Co-Ce powder initiated a significant effect on the resulting coating thickness, as shown in Figure 6.7. The coating thickness decreased from 400 to 200 μm by decreasing the powder feed rate from 6 to 3 g/min. At both feed rates, the coatings demonstrated dense and compact microstructures with substrate-coating interfaces free of cracks. The porosity in both coatings was evaluated at less than 0.5%. The similarities between the coatings suggest a comparable plastic deformation at both feed

rates. A particle loading effect on the main flow in which the particle velocities are reduced below their critical velocity was not experienced. The measured particle velocity histograms of Figure 6.8 show that the particle velocities were not affected by the powder feed rate. Mean particle velocities of 605 ± 104 and 599 ± 103 m/s were obtained at powder feed rates of 3 and 6 g/min, respectively. For the same values of powder feed rates, the coating microhardness were 229 ± 13 and 231 ± 10 HV_{500g}.

It is interesting to note that increasing the powder feed rate produced a similar effect than raising the gas stagnation temperature of the process. Similar values of thickness, porosity, and hardness were measured for the coatings produced at 6 g/min and 200°C at 3 g/min and 370°C with the nozzle with an area ratio of 13. An increase in the process gas stagnation temperature only accelerated more particles above the critical velocity without affecting the microstructure of the coating.

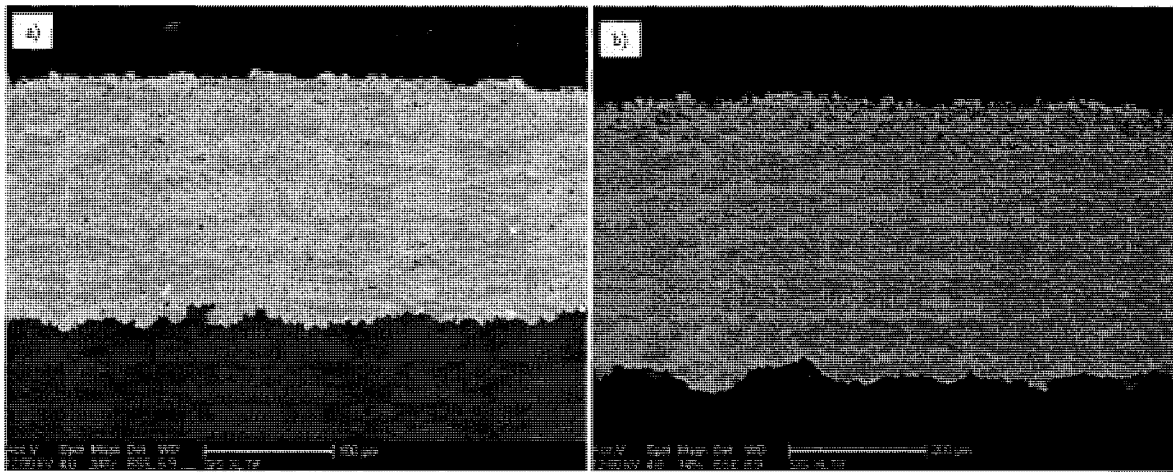


Figure 6.7 SEM images (at different magnifications) of the cross-section of CGDS Al-Co-Ce coatings produced with a gas stagnation temperature of 370°C and at feed rates of a) 3 and b) 6 g/min

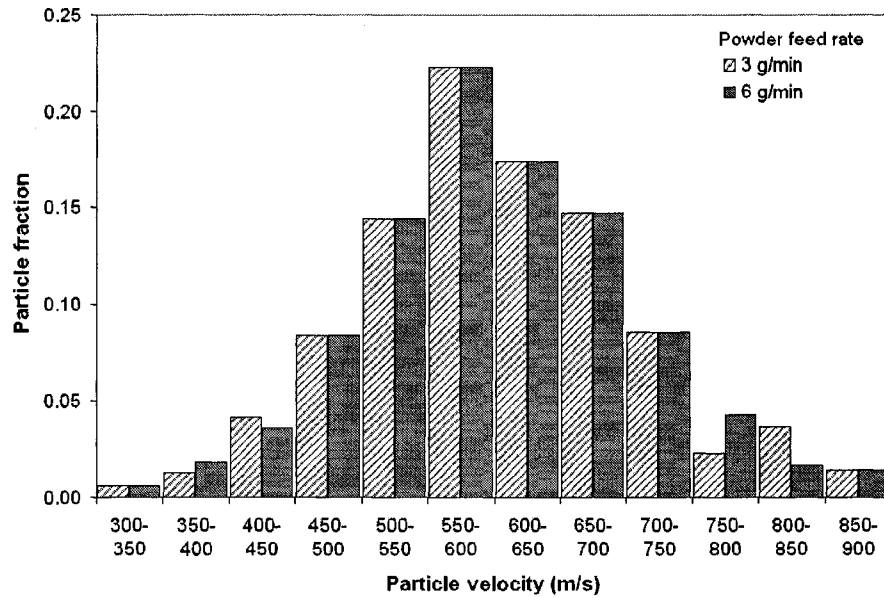


Figure 6.8 Histograms of the Al-Co-Ce particle velocities at powder feed rates of 3 and 6 g/min and at a gas stagnation temperature of 370°C

6.2.2.4 Summary of the Parametric Study for the Al-Co-Ce Coatings

The results of the parametric study for the Al-Co-Ce coatings are summarized in Table 6.1. Based on these results, it was possible to select optimized parameters to conduct a comprehensive analysis of the mechanical properties of Al-Co-Ce coatings. A dense coating with a minimum thickness of 200 μm was required for the purpose of using Al-Co-Ce coatings as cladding material. The nozzle with an area ratio of 13, with a gas stagnation temperature of 200°C, and a powder feed rate of 6 g/min were found to yield coatings that met the requirements. However, the top layers of these coatings were less dense than their bottom portion. The coating produced with the nozzle with an area ratio of 13, with a gas stagnation temperature of 370°C, and a powder feed rate of 6 g/min were very dense and thick enough for the application. However, nozzle clogging has been encountered for

prolonged spraying at this stagnation temperature and powder feed rate when using aluminum alloy powders, such as Al-5083, Al-2618, and Al-12Si. Some of the feedstock particles may be entrained in the slow moving gas in the boundary layer and stick to the nozzle wall. The accumulation of these particles could obstruct the passage of the process gas and reduce the particle velocities. It was then decided to reduce the gas stagnation temperature to an intermediate value of 320°C and set the powder feed rate to 4 g/min to conduct a comprehensive analysis of the mechanical properties of Al-Co-Ce coatings and to minimize the possibility of nozzle clogging.

Table 6.1 Results of the parametric study for the Al-Co-Ce coatings

Nozzle exit-to-throat area ratio	Gas stagnation temperature (°C)	Powder feed rate (g/min)	Particle velocity (m/s)	Thickness (μm)	Porosity (%)	Micro-hardness (HV _{500g})
10	200	6	530 ± 110	200	2	226 ± 12
13	200	6	549 ± 93	200	0.5	229 ± 11
13	370	6	599 ± 103	400	0.5	231 ± 10
13	370	3	605 ± 104	200	0.5	229 ± 13

6.2.3 Fatigue and Bond Strength Evaluations

Stress levels of 200, 275, and 350 MPa (30, 40, and 50 ksi, respectively) at a frequency of 30 Hz and a mean stress of zero were used to test the fatigue behavior of the coated samples. Two to three specimens were tested at each stress level. The results of the bending fatigue tests for the Al-Co-Ce coated specimens are presented in Figure 6.9. The fatigue behavior of the coated test samples is compared to uncoated AA 2024-T3 and Alclad specimens. At all three stress levels, the specimens with CGDS deposited Al-Co-Ce outperformed the bare and Alclad coated specimens. At a stress of 350 MPa, the Alclad and

Al-Co-Ce coated specimens failed at about the same number of cycles. However, as the stress amplitude decreases, the Al-Co-Ce coatings significantly improve the fatigue performance of the substrates. At 200 MPa, the Al-Co-Ce coatings outlasted the bare and Alclad specimens by over an order of magnitude. The fatigue curve for the coated samples indicates that the Al-Co-Ce coatings give rise to a significant increase in fatigue properties of the coated substrates in comparison with the uncoated substrates at all stress levels. It is important to note that during the tests, delamination of the Al-Co-Ce coatings from their substrates did not take place and failure occurred outside the coated area, as shown in Figure 6.10. The Al-Co-Ce coatings remained completely attached to the substrates for all tests. As a result, the fatigue life of Al-Co-Ce coatings is larger than the one obtained by the fatigue tests.

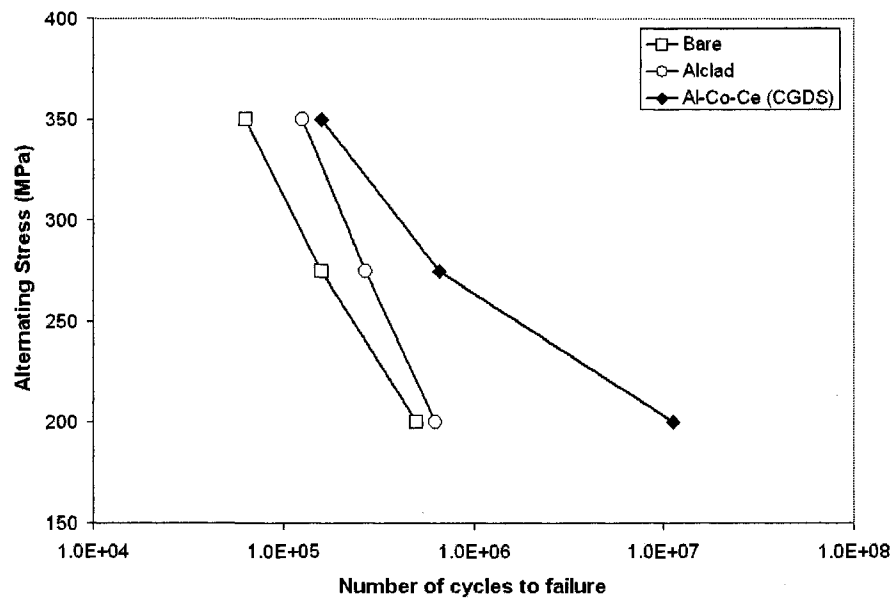


Figure 6.9 Mean number of cycles prior to failure as a function of the amplitude of the alternating stress for the bare, Alclad and CGDS Al-Co-Ce coating on AA 2024-T3 specimens.

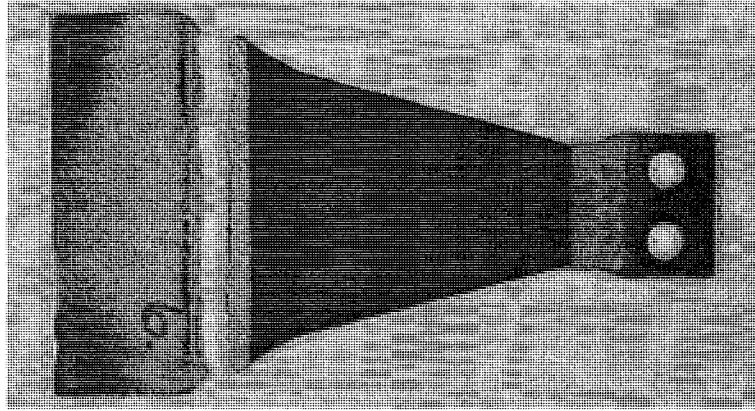


Figure 6.10 Photograph of a bending fatigue strength specimen with an Al-Co-Ce coating after the test. Failure occurred outside the coated area

The adhesion level of the Al-Co-Ce coatings to their substrates was evaluated through bond strength tests. The coatings produced on standard adhesion strength specimens failed at an average strength of 61 ± 4 MPa. The failures occurred partly in the coating (cohesive) and partly in the bonding agent. Figure 6.11 illustrates the mixed failure mode between the glue and the coating. Consequently, the adhesive strength of the Al-Co-Ce coatings is larger than the reported value since the coating remained attached to the coated specimen. These bond strength results for the Al-Co-Ce coatings are significantly greater than typical values obtained for CGDS coatings. Cohesive strengths of 33 and 35 MPa [49] and 25 to 49 MPa [31] have previously been obtained by performing cohesive strength tests on pure aluminum coatings removed from their substrates.

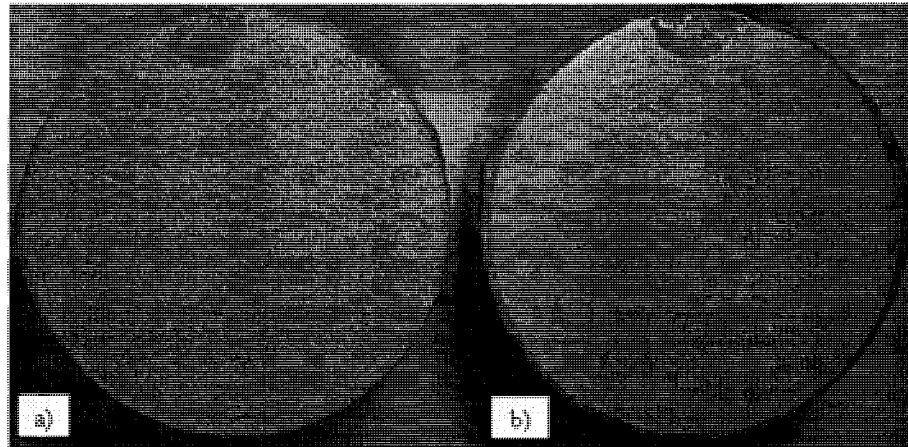


Figure 6.11 Photograph of the bond strength specimens with a) the bonding agent and b) the remainder of the Al-Co-Ce coating after the bond test

The fatigue results can be rationalized on the basis of two important factors: the existence of residual compressive stresses and the high adhesion of the coatings to the substrate. In CGDS, compressive stresses are induced in the coatings. The high velocity impacts of particle cause plastic deformations of the underlying layers and generate compressive residual stresses [18]. These stresses can play a significant role in improving the fatigue behavior of materials by delaying crack initiation and propagation. However, the stresses that exist within a cold spray coating are only beneficial if the coating remains attached to the substrate. Hence, the appropriate adhesion of the coatings to the substrates also contributed in improving the fatigue properties of the AA 2024-T3 substrates.

6.2.4 Microstructure of a Tested Fatigue Specimen

The cross-section of the coated region of a tested bending fatigue specimen is shown in Figure 6.12. The coating remained well adhered to the substrate during fatigue testing, which confirms the absence of any delamination of the coating from the substrate. The coating remained structurally intact as neither damages nor cracks as a result of the fatigue

test were found in the coating. Figure 6.13 shows the XRD patterns for the Al-13Co-26Ce powder and a CGDS coating. These results demonstrate that no microstructural changes occurred during the spraying process. The observed peak broadening in the XRD pattern of the coating was initiated by the residual stresses that were produced during spraying. Residual stresses may be classified in two categories based on the volume over which stresses are homogeneous [110]. Macro stresses are approximately constant over a large number of grains and initiate a line shift to a different angle of the diffraction pattern. The stresses that are uniform over distances on the order of a few grains are called micro stresses. Micro stresses cause diffraction line broadening due to changes in the range of the average distance separating the planes in a crystal for the same diffraction angle. Compressive stresses reduce the distance which widens the diffraction profile whereas tensile stresses contract the pattern as a result of larger spacing. Dislocations, defects, vacancies, and contractions are sources of micro stresses [111]. The extensive particle plastic deformation and the repeated impact of rapidly moving particles throughout the deposition process may have generated the compressive micro stresses detected at the surface of the coating by reducing the distances between the planes. The XRD pattern of the coating shows no evidence of macro stresses. However, the subsequent layers of material beneath the surface may reveal the presence of macro stresses that would contribute to the beneficial residual stresses induced in the coating.

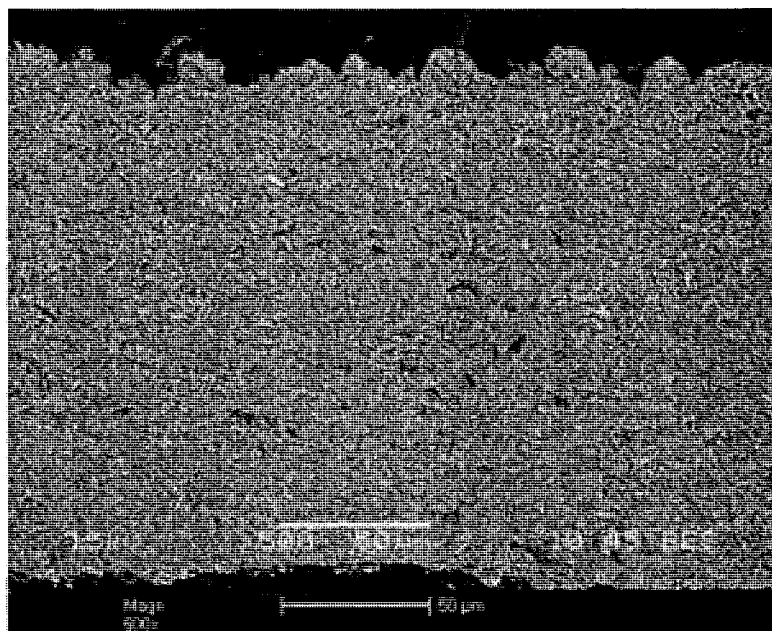


Figure 6.12 SEM image of the cross-section of an Al-Co-Ce coating produced on a fatigue strength specimen

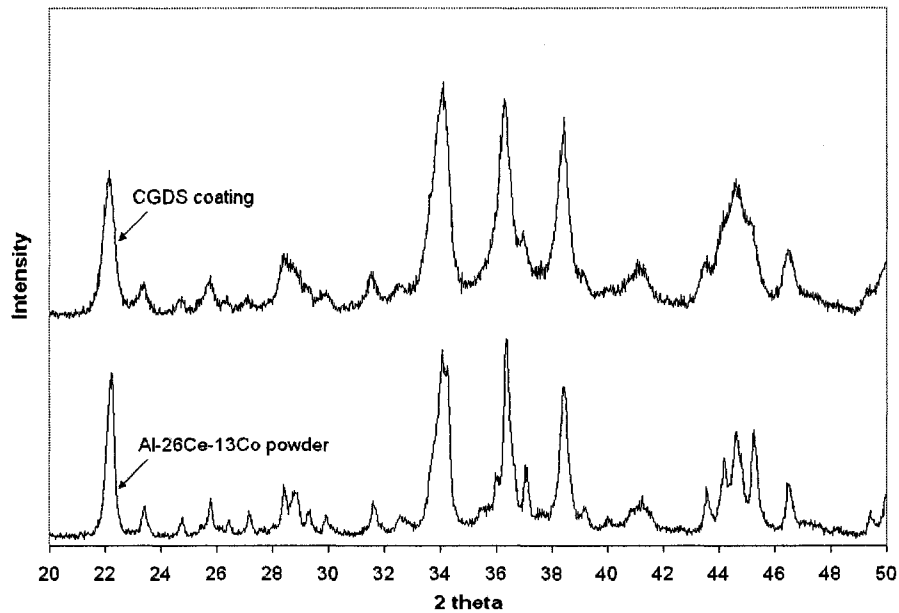


Figure 6.13 XRD patterns for the Al-13Co-26Ce powder and a CGDS coating

6.3 Al-5083 Coatings

6.3.1 Powder Description

The Al-5083 powder consisted of commercially available atomized particles and was passed through a 325-mesh sieve to obtain particles with a diameter less than 45 μm . The particles, shown in Figure 6.14, have a spherical morphology.

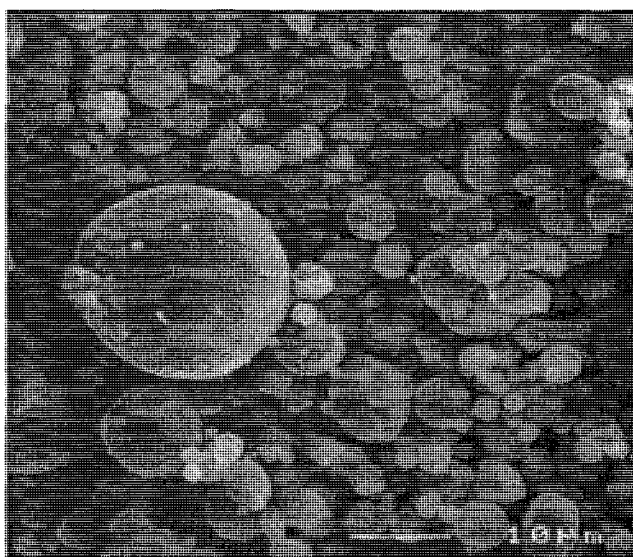


Figure 6.14 Morphology of the as-atomized Al-5083 powder particles

6.3.2 Coating Preparation

The coatings were produced with a spray gun using an exit-to-throat area ratio of 13 on grit-blasted aluminum substrates. The effects of gas stagnation temperature and powder feed rate on the coating properties were evaluated. The spray gun with an exit-to-throat area ratio of 10 was not used because at that time, this nozzle was not fitted with suitable seals for high temperatures. As a result, leakage occurred between the nozzle and manifold. As it

will be mentioned later, the Al-5083 powder caused nozzle clogging and it was decided to leave the nozzle with an area ratio of 10 aside.

6.3.3 Effect of Gas Stagnation Temperature

Cross-sectional SEM images of Al-5083 coatings produced at gas stagnation temperatures of 250 and 370°C and at a powder feed rate of 3 g/min are shown in Figure 6.15. The coatings consist of deformed particles and this indicates that the particles were accelerated beyond their critical velocity. The cracks at the coating-substrate interface originate from the metallographic preparation of the samples. The coating produced at 250 and 370°C have thicknesses of 300 and 400 μm respectively, and similar porosity levels of 1%. Microhardness values of 117 ± 8 and 124 ± 4 $\text{HV}_{300\text{g}}$ were obtained for the coatings produced at gas stagnation temperatures of 250 and 370°C, respectively. As it was explained in section 6.2.2.2, raising the gas stagnation temperature increases the gas velocity throughout the nozzle and more particles reach the critical velocity. The histograms of the measured particle velocities for gas stagnation temperatures of 250 and 370°C, presented in Figure 6.16, demonstrate this effect. Increasing the gas stagnation temperature from 250 to 370°C changed the particle velocity from 521 ± 145 to 559 ± 135 m/s.

While spraying Al-5083 feedstock powder at a feed rate of 3 g/min and stagnation temperatures of 250 and 370°C, nozzle fouling was experienced. Particles accumulated on the walls of the spray gun and caused partial blockage, obstructing the passage of the process gas and interfered with the momentum transfer between the gas and particles. As a result, nozzle clogging may have affected the particle velocity and may have caused variations in the thickness, porosity and hardness of the deposits. As mentioned in section 2.5.2, nozzle clogging after prolonged use is a limitation of CGDS. Spray guns with

replaceable converging and diverging sections made from polybenzimidazole, a synthetic fiber with a high melting point, have been found to solve this problem [58].

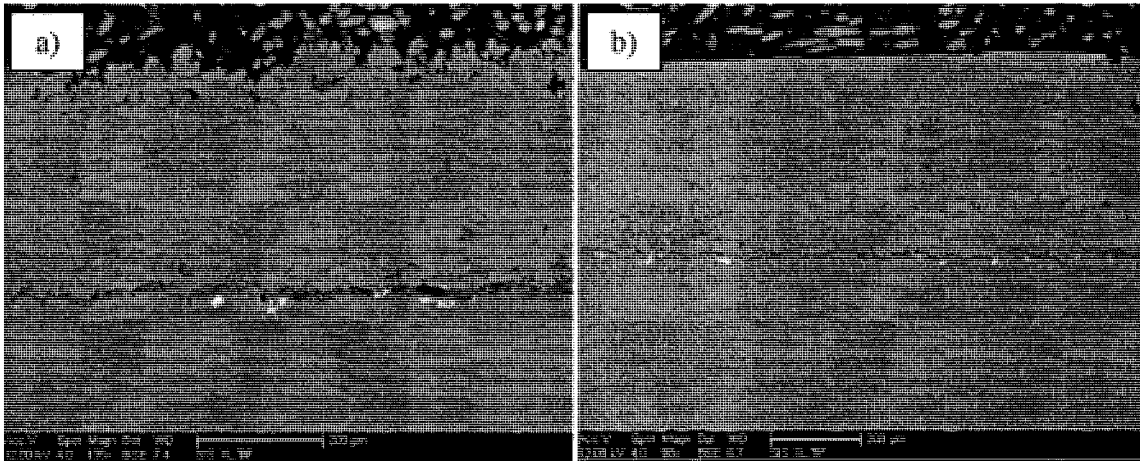


Figure 6.15 SEM images (at different magnifications) of Al-5083 coatings produced at stagnation temperatures of a) 250 and b) 370°C and at a powder feed rate of 3 g/min

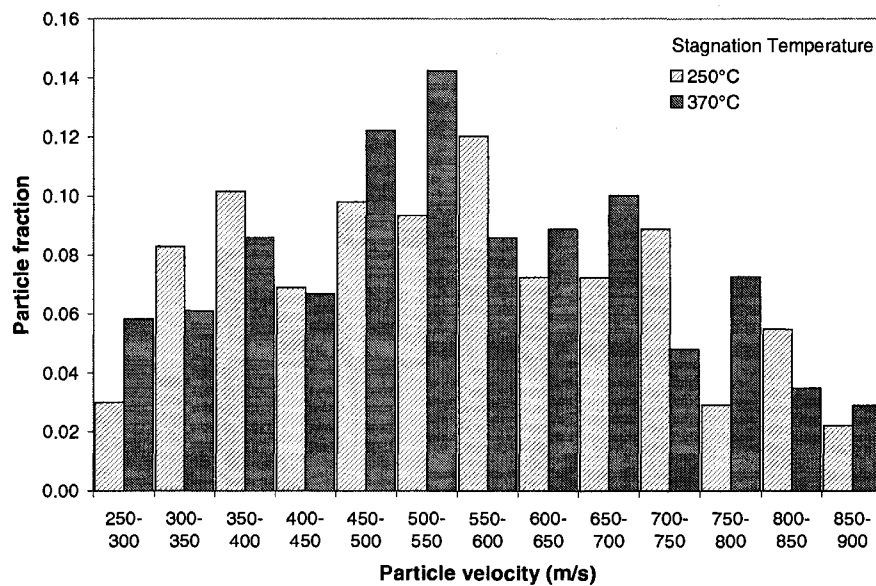


Figure 6.16 Histograms of the Al-5083 particle velocities at gas stagnation temperatures of 250 and 370°C and at a powder feed rate of 3 g/min

6.3.4 Effect of Powder Feed Rate

The effect of powder feed rate was evaluated on coatings produced at a gas stagnation temperature of 370°C. As shown in Figure 6.17, the coating thickness increased from 250 to 400 μm and the porosity levels from 0.2 to 1% as the feed rate was increased from 1.5 to 3 g/min. The coatings produced at the low powder feed rate are composed of tightly packed deformed particles while the coatings produced at the high powder feed rate contain several voids at the particle-particle interface. Microhardness values of 146 ± 9 and 124 ± 4 $\text{HV}_{300\text{g}}$ were obtained for the coatings produced at low and high feed rates, respectively.

The measured particle velocity distributions, shown in Figure 6.18, demonstrate the effect of powder feed rate on particle velocity. The average particle velocity was reduced from 574 ± 159 to 559 ± 135 m/s as the powder feed rate was increased from 1.5 to 3 g/min. A particle loading effect on the main flow and nozzle clogging may have affected the particle acceleration in the spray gun. As the powder feed rate was increased, the carrier flow became saturated with powder particles, which lowered the momentum transfer between the gas and particles. As a result, the particles were accelerated to velocities lower than the ones obtained in tests conducted at lower powder feed rates. Decreasing the powder feed rate also attenuated the effect of nozzle clogging. Injecting fewer particles (per unit time) in the carrier gas reduces the amount of particles entrained in the slow moving gas of the boundary layer along the nozzle wall. The particle blockage caused by the accumulation of particles would then occur after longer spraying times when lower powder feed rates are used.

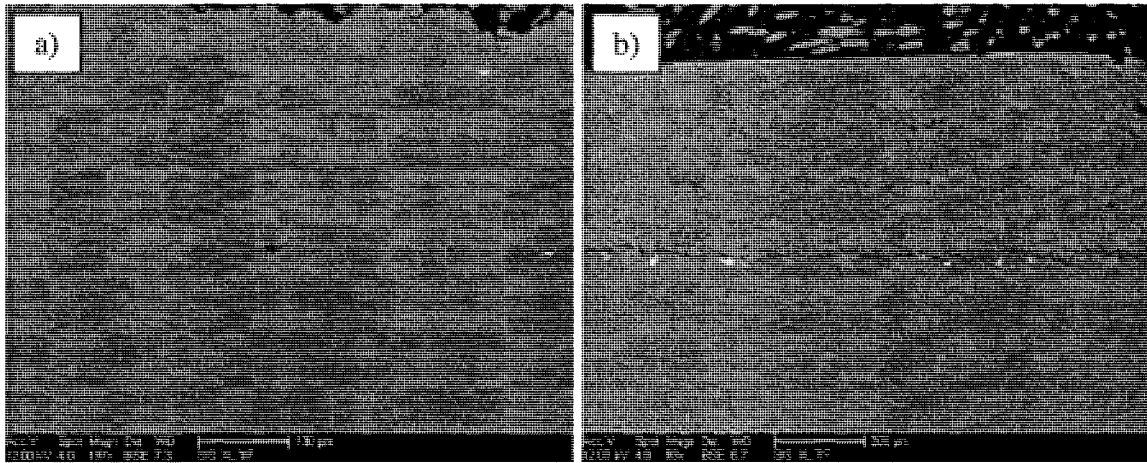


Figure 6.17 SEM images (at different magnifications) of Al-5083 coating produced at powder feed rates of a) 1.5 and b) 3 g/min and at a gas stagnation temperature of 370°C

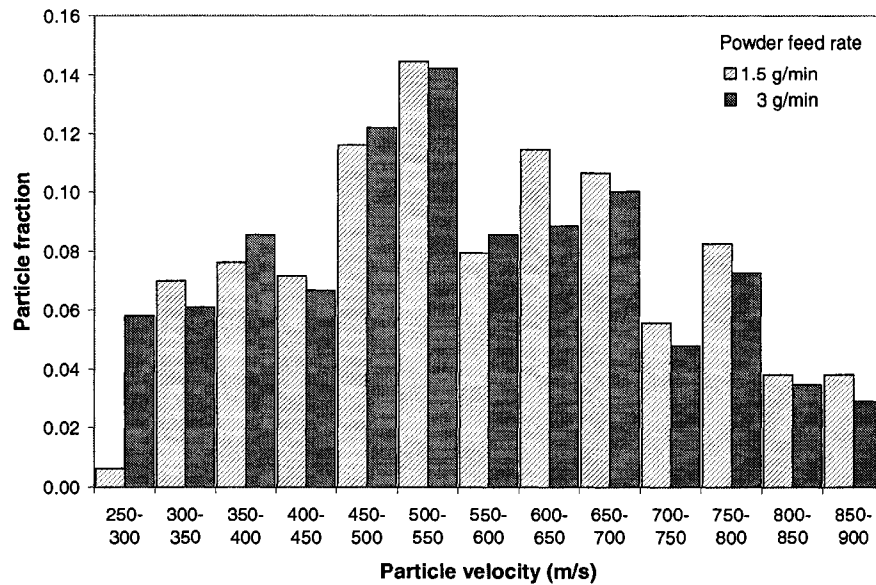


Figure 6.18 Histograms of the Al-5083 particle velocities at powder feed rates of 1.5 and 3 g/min and at a gas stagnation temperature of 370°C

Average bond strengths of 46 ± 7 and 48 ± 4 MPa were obtained for the coatings produced at 1.5 and 3 g/min, respectively. Most of the coating remained attached on the side

on which the bonding agent was applied, as illustrated in Figure 6.19. The values reported then correspond to adhesion strengths. The adhesion strength of the Al-5083 coatings did not vary significantly with the powder feed rate. The SEM images of Figure 6.17 showed that increasing the powder feed rate increases the coating thickness and porosity. The bond strength test results indicate that changing the powder feed rate does not influence the extent of particle plastic deformation at the substrate-coating interface. At both powder feed rates, the particles deformed around the surface irregularities of the substrate similarly.

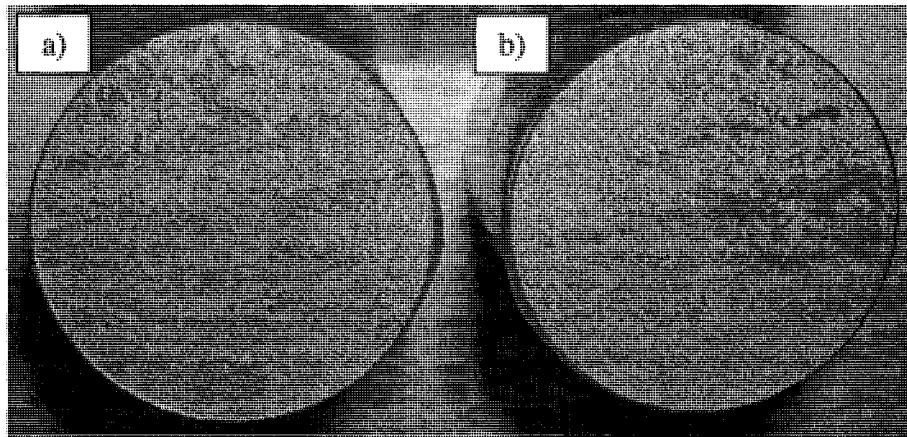


Figure 6.19 Photograph of the bond strength specimens with a) the bonding agent and b) the remainder of the Al-5083 coating after the bond test

6.3.5 Summary

The effects of the gas stagnation temperature and powder feed rate on the characteristics of Al-5083 coatings have been examined. The properties of Al-5083 coatings produced by CGDS are summarized in Table 6.2.

Table 6.2 Properties of Al-5083 coatings

Nozzle exit-to-throat area ratio	Gas stagnation temperature (°C)	Powder feed rate (g/min)	Particle velocity (m/s)	Thickness (μm)	Porosity (%)	Micro-hardness (HV _{500g})	Bond strength (MPa)
13	250	3	521 ± 155	300	1	117 ± 8	-
13	370	3	559 ± 135	400	1	124 ± 4	48 ± 4
13	370	1.5	571 ± 144	250	0.2	146 ± 9	46 ± 7

6.4 Al-12Si Coatings

6.4.1 Powder Description

The Al-12Si powder (Al-111, Praxair Surface Technologies, Indianapolis, IN, USA) was composed of particles ranging from 5 to 45 μm in diameter. As shown in Figure 6.20, these particles have a spherical morphology. The particle size distribution, outlined in Figure 6.21, indicates that the powder has an average diameter of 23 μm.

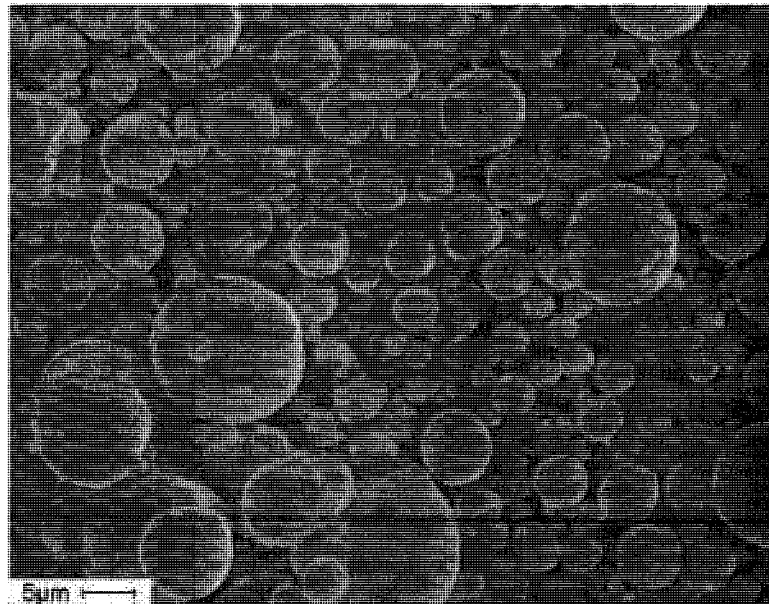


Figure 6.20 Morphology of the as-received Al-12Si powder particles

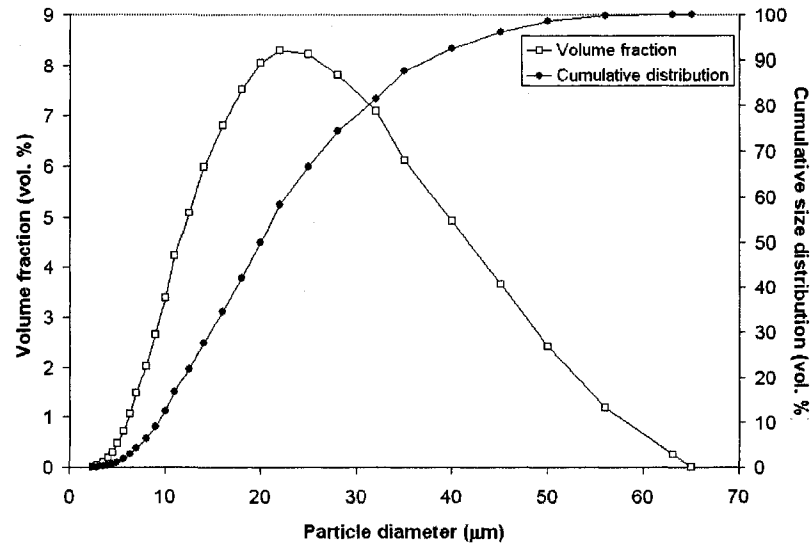


Figure 6.21 Particle size distribution of the as-received Al-12Si powder

6.4.2 Coating Preparation

A fractional factorial investigation was undertaken to study the effects of several spraying parameters from a few experimental runs. Four factors, each with three levels, were chosen to produce Al-12Si coatings. In full factorial testing, each and every combination of parameters with different levels is considered. For a test involving four parameters with each parameter being tested at three levels, the number of tests to be performed is 3^4 , i.e. 81. In a fractional factorial study, only nine test runs are required to study the effects of four parameters at three levels and these runs are presented in Table 6.3.

The effects of stand-off distance, powder feed rate, substrate traverse speed, and substrate surface roughness on the coating hardness, porosity, thickness, and bond strength were examined. The parameters and actual values selected for each test are given in Table 6.4. The substrates with a surface roughness of $0.23 \mu\text{m}$ ($9 \mu\text{in}$) were not grit-blasted.

Surface roughness values of 5.7 and 3.8 μm (226 and 150 μin) were obtained by grit-blasting the substrates with ebony beads³ (20 grit) and glass beads (60 grit), respectively. The nozzle with an area ratio of 13 was chosen and single passes were performed to produce the coatings. The larger nozzle area ratio was preferred since the coatings obtained from the previous nozzle area ratio studies had a lower porosity and more visible plastic deformations. A gas stagnation temperature of 350°C was chosen, since the coatings produced at 50 and 250°C contained a significant number of undeformed particles, as shown in Figure 6.22. These coatings were much more porous than the one produced at 350°C.

Table 6.3 Testing array for the fractional factorial study

Test	Parameter			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 6.4 Parameters and selected test values

Parameter	Level 1	Level 2	Level 3
A. Stand-off Distance (mm)	10	15	20
B. Powder Feed Rate (g/min)	2	4	6
C. Substrate Traverse Speed (mm/s)	2	4	6
D. Substrate Surface Roughness (μm)	0.23	5.7	3.8

³ Also known as copper slag beads

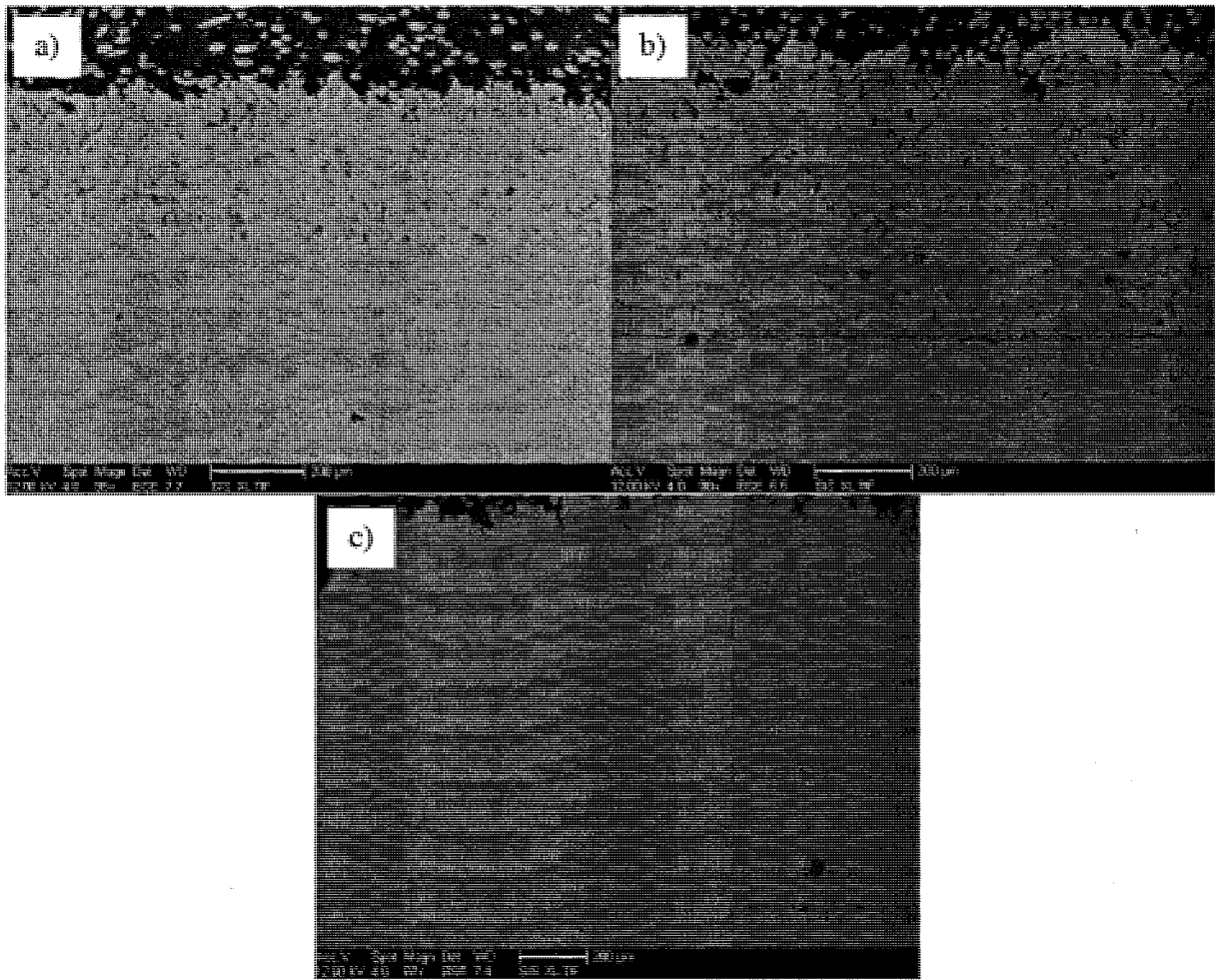


Figure 6.22 SEM images Al-12Si coatings produced at gas stagnation temperatures of a) 50, b) 200 and c) 350°C

The stand-off distance, powder feed rate, substrate traverse speed, the substrate surface preparation were chosen as the variable spraying parameters because it was initially assumed that these parameters did not influence the particle velocity at the exit of the spray gun. However, it was later found that varying the powder feed rate produced a significant particle loading effect. As the powder feed rate was increased, the carrier flow became saturated with powder particles and the particles did not reach the same velocity found in low feed rates. The measured particle velocity distributions, presented in Figure 6.23,

demonstrate that increasing the powder feed rate from 2 to 6 g/min lowered the average particle velocities from 559 ± 132 to 459 ± 162 m/s. The particle velocity then became an additional factor that influenced the coating properties and created dependence between the other spraying parameters.

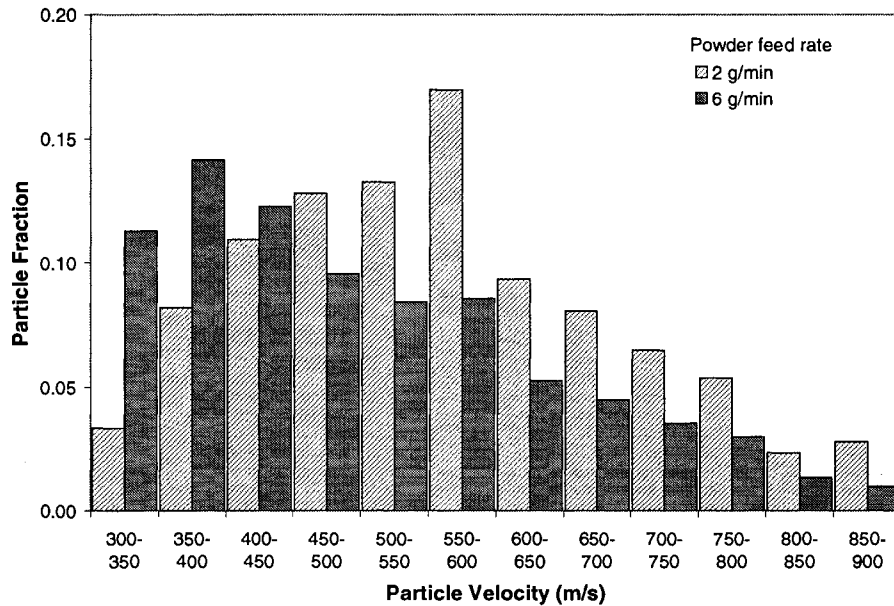


Figure 6.23 Histograms of the Al-12Si particle velocities at powder feed rates of 2 and 6 g/min

The average effects of the spraying parameters were evaluated at each level. For example, the average effect of the stand-off distance (Parameter A) at 10 mm (Level 1) corresponded to the average of the response of the tests where A1 was present (tests 1, 2, and 3 in this case). The parameter that produced the largest changes in the coating properties was identified.

Since several test runs were conducted with each parameter set at different levels, it was possible to generate predictive equations for the coating properties. The correlation between the spraying parameters and coating properties was defined using a multivariable

linear regression model. The relationship of a response variable Y to the spraying parameters A , B , C , and D can be written as:

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D, \quad (6.1)$$

where the β_i coefficients represent the regression factors of the model. For each regression equation, the coefficient of determination, R^2 , the standard error of the estimate, S , and some probabilities, p-values, will be given. R^2 represents the ratio of the variance⁴ of the modeled (Y) values to the variance of the original data values (y), that is:

$$R^2 = \frac{\sum_i (Y_i - \bar{y})^2}{\sum_i (y_i - \bar{y})^2}, \quad (6.2)$$

where $\bar{y}$ and y represent the sample mean and original data value, respectively. A R^2 value close to one suggests that the regression accounts for almost all of the variability with the variables specified in the model [112]. It should also be mentioned that the coefficient of determination does not tell whether the correct regression was used or whether the most appropriate set of independent variables has been chosen. R^2 describes how much variation is being explained by the regression equation. The standard error of the estimate is a measure of the accuracy of the regression line and is found by:

$$S = \sqrt{\frac{(1 - R^2) \sum (y_i - \bar{y})^2}{n - k - 1}}, \quad (6.3)$$

where n and k are the number of measurements and the number of predictors, respectively. The standard error of the estimate may be used to construct prediction intervals for the predicted values ($\pm S$). The p-value is a measure of the appropriateness of rejecting the null

⁴ The variance is the sum of the squared deviation of n measurements from their mean divided by $n-1$.

hypothesis that the regression factors of the model are not related to the response variable, i.e., $\beta_0 = \beta_1 = \beta_2 = \beta_3 = \beta_4 = 0$. A small p-value is evidence against the null hypothesis while a large p-value means little or no evidence against the null hypothesis. The null hypothesis is rejected if the p-value is equal or less than a level of significance, α . The most common used α is 0.05 and this value will be used in this study. A p-value of 0.05 or less signifies that the factors have a significant effect on the response variable at the 5% level.

6.4.3 Coating Microstructures and Properties

The SEM images of the Al-12Si coatings produced under the conditions listed in Table 6.4 are shown in Figure 6.24. The mechanical properties obtained from the fractional factorial parametric study are given in Table 6.5. The average values for the hardness, thickness, porosity, and bond strength of the coatings are 81 HV_{100g}, 734 μm , 1.3%, and 41 MPa, respectively.

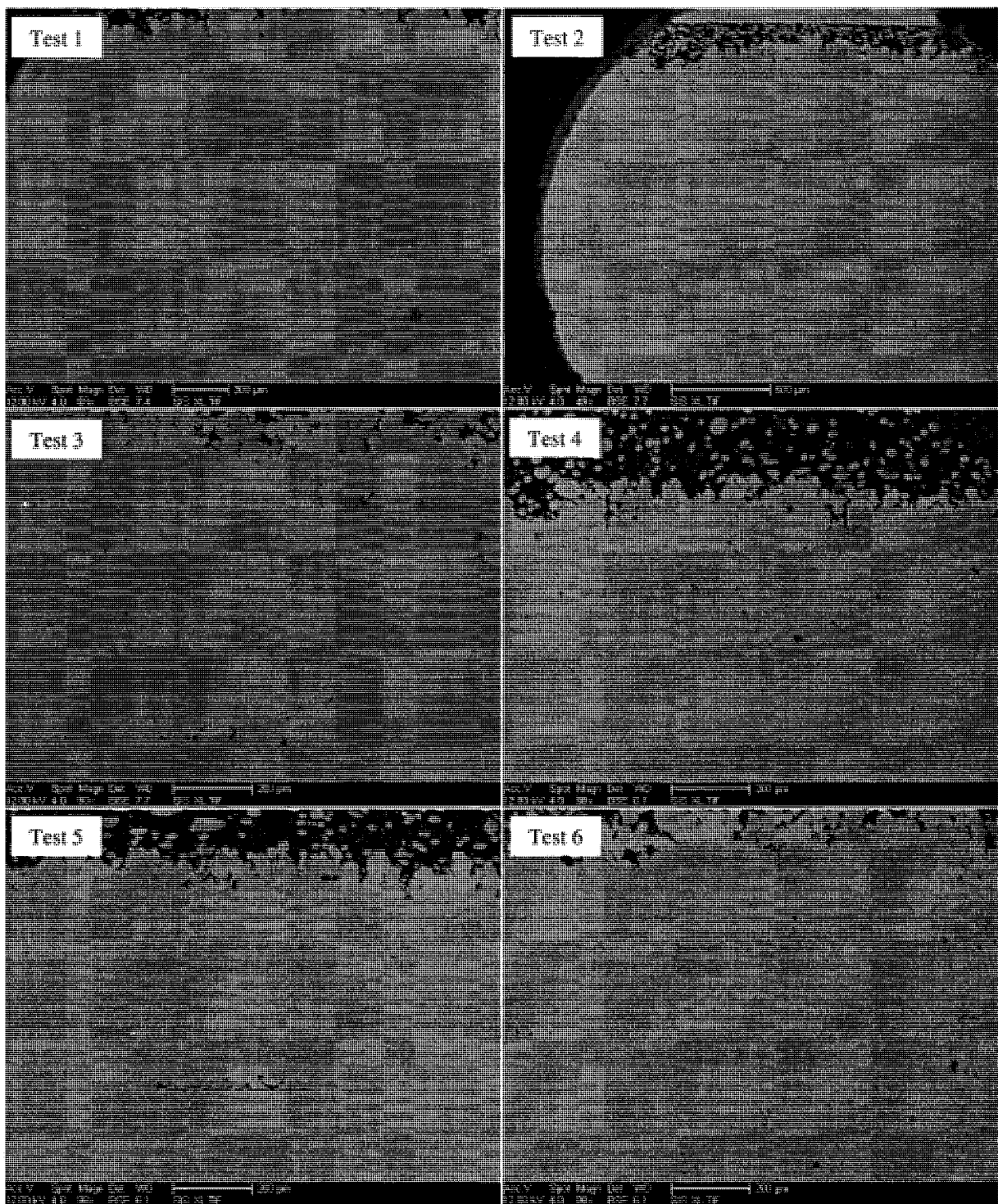


Figure 6.24 SEM images (at different magnifications) of the Al-12Si coatings obtained from the parametric study

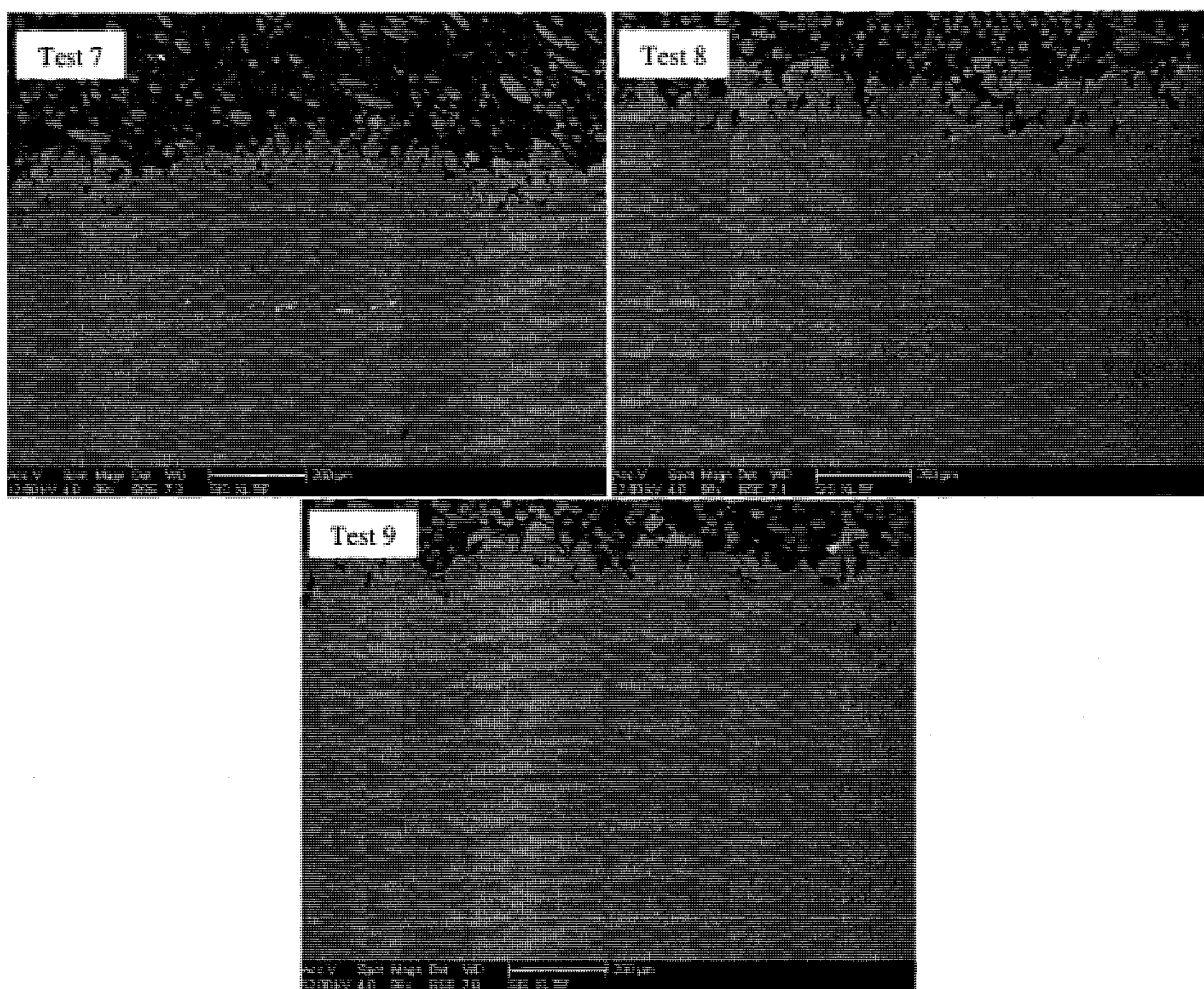


Figure 6.24 (continued) SEM images the Al-12Si coatings obtained from the parametric study

Table 6.5 Mechanical properties of the Al-12Si coatings obtained from the parametric study

Test	Hardness (HV _{100g})	Thickness (μm)	Porosity (%)	Bond Strength (MPa)
1	110	1230	0.05	37
2	112	1090	1	26
3	64	850	2	49
4	82	370	2	68
5	74	590	1	53
6	75	950	0.8	30
7	91	330	3	39
8	76	760	1	35
9	50	440	0.8	33
Average	81	734	1.3	41

6.4.4 Average Effects on Hardness

The average effects of the spraying parameters on the coating hardness are plotted in Figure 6.25. The powder feed rate produced the largest change in the coating hardness and increasing the powder feed rate was found to decrease the coating hardness. As the powder feed rate is increased from 2 to 6 g/min, the particle velocity decreased considerably due to a particle loading effect (see Figure 6.23). At high feed rates, the particles deform partially and hardening effects are not experienced. Increasing the stand-off distance reduces the impact velocity, as demonstrated by the PIV measurements (see Figure 5.6) and the amount of plastic deformation of the particles on impact. The compaction of the previously deposited layers of material by the impinging particles is decreased in coatings produced at high substrate traverse speeds. The hardness should not be affected by the substrate surface roughness. It is reasonable to assume that the substrate surface roughness only has an effect on the first few layers of deposited particles. The next particles would impact on the initial layers and plastically deform to build-up the coating. It is believed the effects of roughness on the coating hardness are due to interactions between the spraying parameters that

influenced the impact particle velocity. For example, the combined effects of the particle loading and velocity drop that occur at high feed rates and at large stand-off distances reduced the particle velocity at impact.

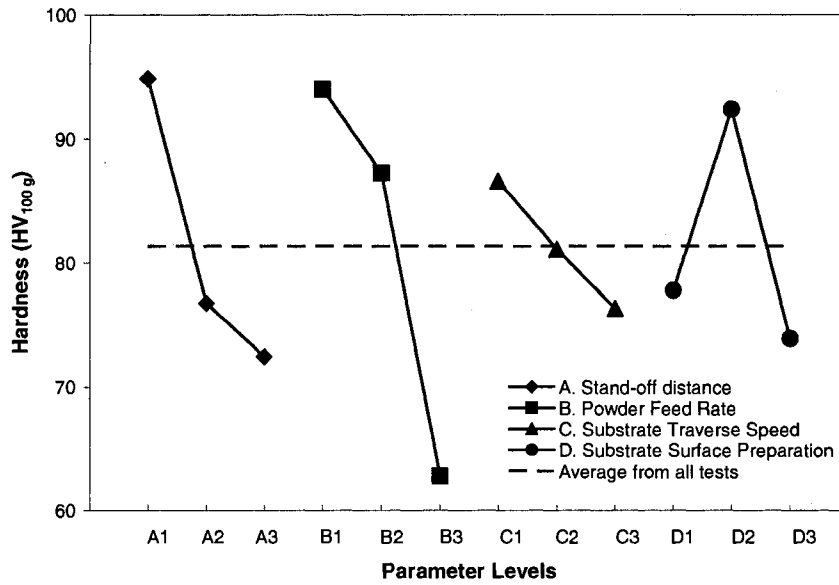


Figure 6.25 Average effects of the spraying parameters on the Al-12Si coating hardness

The hardness of Al-12Si coatings can be correlated with the spraying parameters using the following regression equation:

$$\text{Hardness}(HV) = 149 - 2.24A - 7.80B - 2.57C + 2.18D \quad (6.4)$$

This equation demonstrates that the hardness decreases with stand-off distance (A), powder feed rate (B) the substrate traverse speed (C) but increases with substrate surface roughness (D). An R^2 value of 81% was obtained for the linear regression equation, which indicates that 81% of the variability in the hardness values can be predicted by Equation 6.4. This equation can estimate the coating hardness at a standard error of 12 HV_{100g}. The probability of each coefficient (p-value), given in Table 6.6, indicates that the powder feed rate has the

most significant effect on the hardness, followed by the stand-off. The substrate traverse speed and substrate surface roughness do not correlate well with the hardness. The substrate traverse speed, despite its high p-value, showed the same trend in both the linear regression equation and in the average response curve. The p-value of the substrate surface roughness implies that this factor is not related to the hardness. Figure 6.25 also illustrated that there was not a clear relationship between the hardness and substrate surface roughness.

Table 6.6 P-values for the regression equation for the hardness

Coefficient	p-value
A: Stand-off distance	0.05
B: Powder feed rate	0.04
C: Substrate traverse speed	0.36
D: Substrate surface preparation	0.29

6.4.5 Average Effects on Porosity

Based on the average effects of the spraying parameters on the porosity, shown in Figure 6.26, the substrate traverse speed had the greatest effect on the porosity. Faster substrate traverse speeds reduced the compaction from impinging particles and caused a lack of plastic deformation to fill the voids in the deposited layers of material. A similar effect was produced by augmenting the stand-off distance. As mentioned previously, lower particle impact velocities are obtained at large stand-off distances. The results suggest that the coatings become slightly denser as the powder feed rate is increased. However, the porosities associated with parameters B1, B2 and B3 do not vary significantly, as porosity values of 1.7, 1.0, and 1.2% have been obtained, respectively. In addition, the measured porosity values, found in Table 6.5, do not vary considerably (seven of the nine coatings have a porosity between 0.8 and 2%). The observed change of porosity due to powder feed

rate may be due to errors in the evaluation of the coating porosity and to the combined effects of the stand-off distance and substrate traverse speed. In section 6.3.4, only the powder feed rate was altered and the porosity was found to increase with the powder feed rate as a result of a particle loading effect. The substrate surface preparation should not influence the coating porosity. As it was explained in 6.4.4, the substrate surface roughness is only important for the first few layers of deposited particles. The effect of the surface roughness is attributed to interactions between the spraying parameters that affected the particle velocities and the level of plastic deformation.

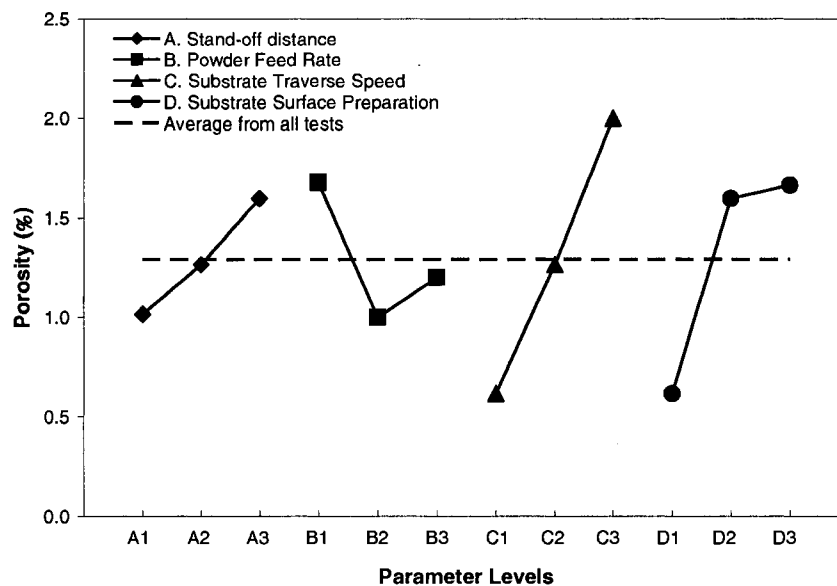


Figure 6.26 Average effects of the spraying parameters on the Al-12Si coating porosity

The relationship between the porosity and the spraying parameters is:

$$Porosity(\%) = -1.11 + 0.0583A - 0.121B + 0.346C + 0.195D \quad (6.5)$$

This equation demonstrates that the porosity increases with stand-off distance (A), substrate traverse speed (C), and substrate surface preparation (D) but decreases with powder feed

rate (B). A R^2 value of 88% and a standard error of 0.43% were obtained for the linear regression equation. According to the p-values in Table 6.7, the substrate traverse speed is strongly related to the porosity, as it was found in Figure 6.26. The powder feed rate has the highest p-value and therefore does not correlate well with the porosity.

Table 6.7 P-values for the regression equation for the porosity

Coefficient	p-value
A: Stand-off distance	0.15
B: Powder feed rate	0.23
C: Substrate traverse speed	0.02
D: Substrate surface preparation	0.04

6.4.6 Average Effects on Thickness

Figure 6.27 illustrates that the stand-off distance produced the largest effect on the coating thickness. The coating thickness decreased as the stand-off distance increased because of particle velocity variations along the jet. The PIV measurements reported in Figures 5.6 and 5.7 demonstrate that the particle axial velocity decreases with distance from the spray gun exit and spreads significantly in the radial direction. Increasing the stand-off distance produced thinner coatings that covered a larger surface area. The results show that the coatings produced at 4 g/min (B2) were thicker than the ones produced at 2 g/min (B1). As it has been reported earlier, the coating thickness increases with powder feed rate. However, if particle loading occurs, the particles are accelerated to slightly lower velocities and undergo partial plastic deformation on impact. The resulting coatings are then more porous and thinner. The coatings produced at 6 g/min (B3) were slightly thinner than the ones at 4 g/min (B2). In these cases, the particle loading effect was more significant and a smaller fraction of the particles was accelerated above the alloy critical velocity. As a result, the deposition efficiency was reduced and fewer particles plastically deformed to build up

the coating. The coating thickness was found to decrease with increasing substrate traverse speed. Increasing the traverse speed reduces the number of particles impacting at one location of the substrate. Figure 6.27 also points out that the coating thickness was the least affected by the substrate surface preparation.

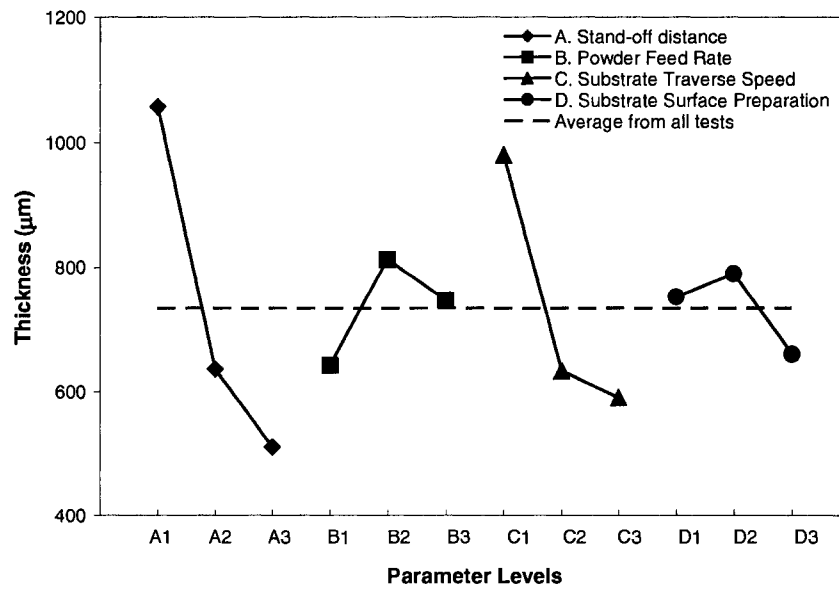


Figure 6.27 Average effects of the spraying parameters on the Al-12Si coating thickness

The following equation shows the correlation of thickness based on the spraying parameters:

$$Thickness(\mu m) = 1833 - 54.7A + 25.8B - 97.5C + 2.47D \quad (6.6)$$

The coating thickness was observed to decrease with stand-off distance (A) and substrate traverse speed (C) while the powder feed rate (B) increases the thickness. The substrate surface preparation (D) did not significantly influence the thickness. Equation 6.6 accounts for 83% of the variability in the data ($R^2 = 83\%$) and has a standard error of 190 μm. The p-values associated with the coefficients are presented in Table 6.8. The stand-off distance and

substrate traverse speed correlate with the coating thickness. The p-value for the powder feed rate indicates that higher order terms could be incorporated to the regression equation to account for the observed nonlinear relationship between the powder feed rate and the thickness. Based on its p-value, the substrate surface preparation has no effect on the thickness and this coefficient could be removed from the regression equation.

Table 6.8 P-values for the regression equation for the thickness

Coefficient	p-value
A: Stand-off distance	0.02
B: Powder feed rate	0.54
C: Substrate traverse speed	0.07
D: Substrate surface preparation	0.93

6.4.7 Average Effects on Bond Strength

The average effects of the parameters on the bond strength, shown in Figure 6.28, reveal that the stand-off distance and substrate surface preparation display no apparent trend. However, the substrate surface preparation produced the largest changes in the coating bond strength. Although the substrates for tests D2 contained the largest roughness at 226 μin , grit contamination may have reduced the number of anchoring sites and influenced the adhesion strength of the coatings. Grit contamination occurs during the grit blasting process when blasting particles become embedded on the substrate surface. Previous studies have reported that there is no true relationship between the bond strength and surface roughness because different blasting media not only change the roughness but also produce different levels of grit contamination and residual stresses on the substrate surface [113, 114]. Using smaller blasting particles reduced the surface roughness as well as the grit contamination, as demonstrated by tests D3 in Figure 6.28. This demonstrated that mechanical interlocking

plays an important role in the adhesion strength of CGDS coatings. The bond strength is seen to increase with the substrate traverse speed. As the traverse speed was increased, the coatings were produced during a shorter spraying time, thus reducing the possibility of nozzle clogging. The nozzle clogging experienced at the lowest traverse speed, affected the particle velocities and their plastic deformation on impact on the substrate. Increasing the powder feed rate also increased nozzle clogging and lowered the bond strength of the coatings on the substrates.

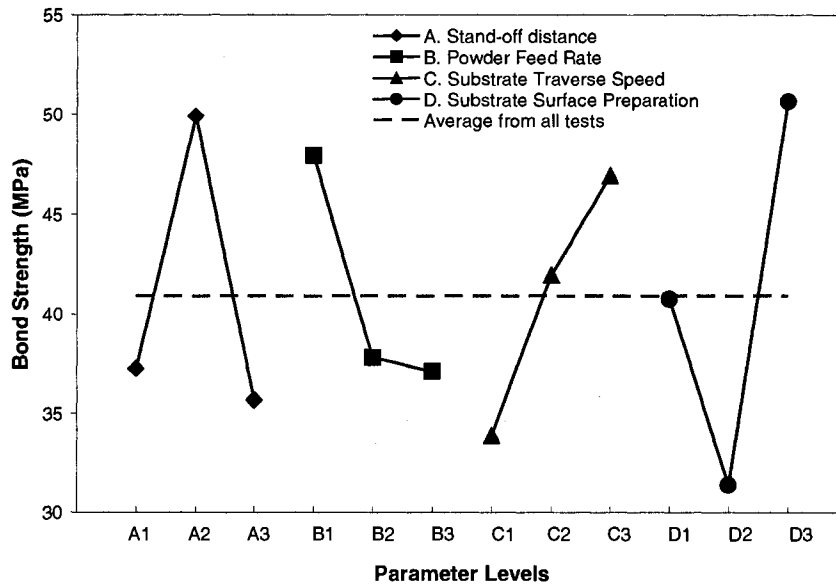


Figure 6.28 Average effects of the spraying parameters on the Al-12Si coating bond strength

The bond strength can be correlated with the spraying parameters using:

$$BondStrength(MPa) = 44.8 - 0.156A - 2.72B + 3.26C - 1.14D \quad (6.7)$$

The coating adhesion strength was found to decrease with increasing stand-off distance (A), powder feed rate (B) and substrate surface roughness (D) while the substrate traverse speed (C) augments the adhesion strength. Equation 6.5 showed a $R^2 = 50\%$ and a standard error of

15 MPa. This poor value of R^2 obtained for the linear regression suggests that higher order terms should be included in the regression equation. The p-values, given in Table 6.9, are all greater than the confidence level of 0.05, which indicates that none of the spraying parameters are statistically related to the bond strength. Grit contamination and nozzle clogging are external factors that influenced the bond strength. The bond strength values predicted by Equation 6.5 correspond to adhesion strengths. During the tests, failures occurred at the substrate-coating interface. Figure 6.29 illustrates that the coating remained attached on the specimen on to which the bonding agent was applied.

Table 6.9 P-values for the regression equation for the bond strength

Coefficient	p-value
A: Stand-off distance	0.90
B: Powder feed rate	0.42
C: Substrate traverse speed	0.34
D: Substrate surface preparation	0.63

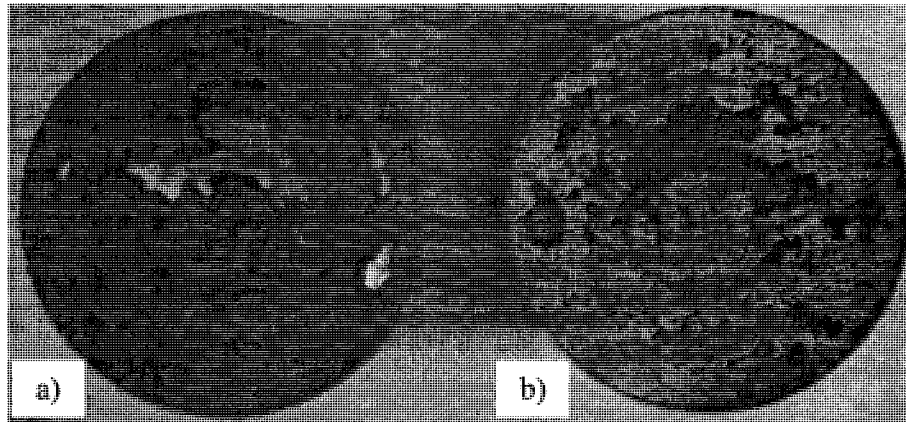


Figure 6.29 Photograph of the bond strength specimens with a) the bonding agent and b) the remainder of the Al-12Si coating after the bond test

6.4.8 Effects of Cryomilling

The conventional Al-12Si feedstock powder was cryomilled for 8 hours in the objective to change the grain size distribution and shape of the particles. Cryomilling is a top-down approach in which the feedstock powder particles are introduced in a high-energy ball mill, grinded, and milled at extremely low temperatures achieved by exposure to liquid nitrogen (see Figure 6.30) [115]. The use of a cryogenic agent reduces the oxygen from the atmosphere, favors the fracturing over welding of ductile particles by lowering the particle temperature, and produces nano-scale oxide and nitride particles that strengthen the aluminum powder. Figure 6.31 illustrates that the powder resulting from the cryomilling process consists of micron-size agglomerations with surfaces rougher than the conventional powder particles (see Figure 6.20). The powder now has an average diameter of 30 μm , as indicated in Figure 6.32. The morphology of the cryomilled powder may lead to higher particle velocities. As a result of their rougher surface, cryomilled particles would experience more drag and be accelerated to higher velocities than the conventional particles.

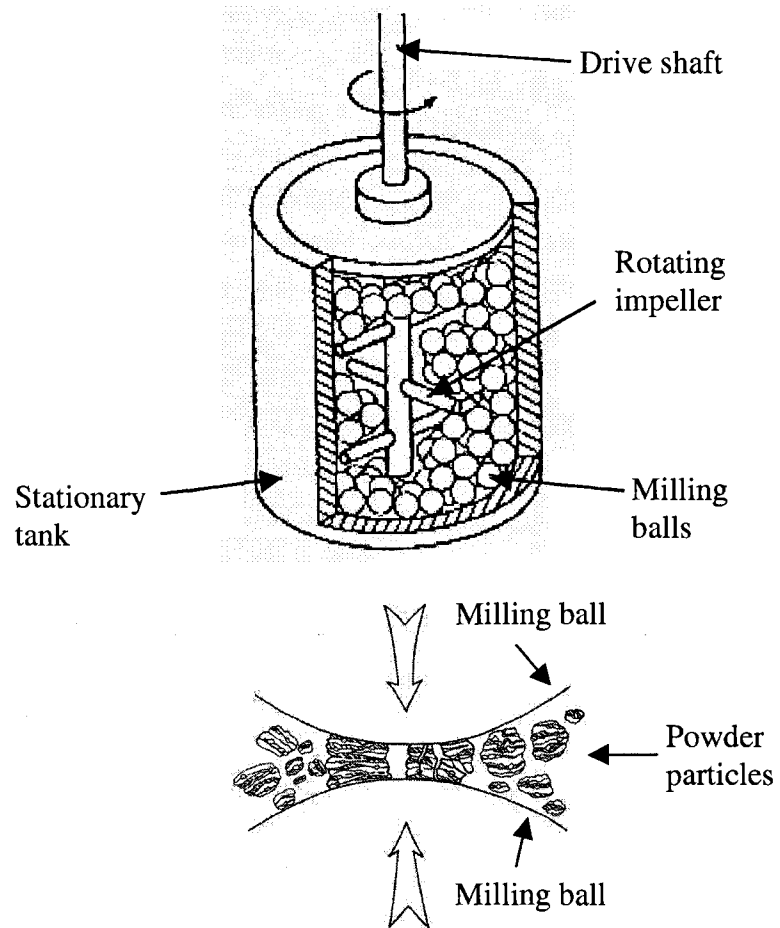


Figure 6.30 High-energy ball mill (top) and ball-powder-ball collision of powder during mechanical milling (bottom) (adapted from [115])

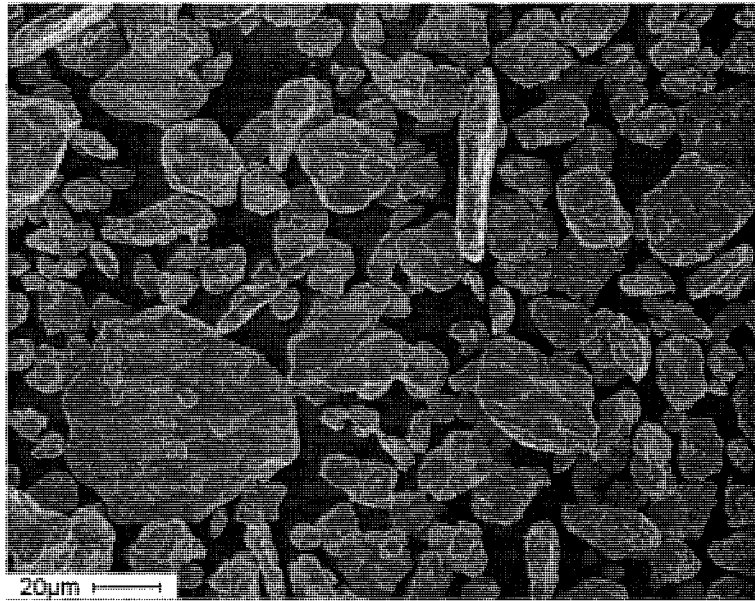


Figure 6.31 Morphology of the cryomilled Al-12Si powder particles

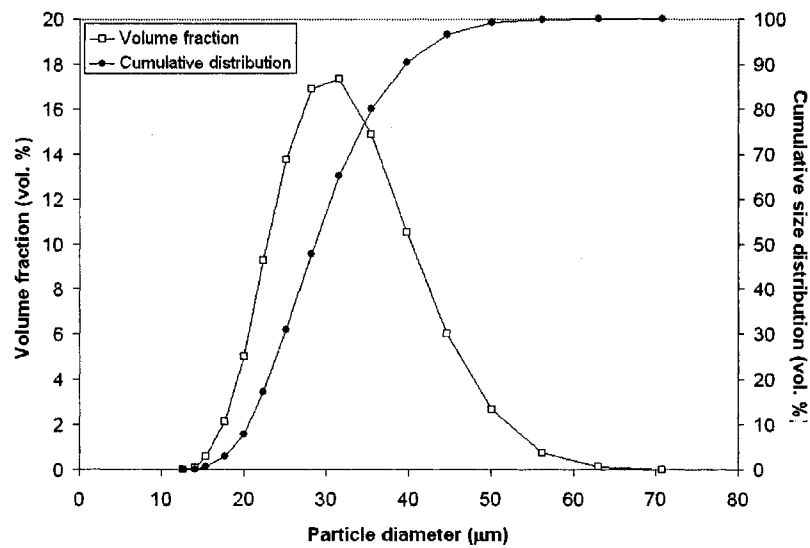


Figure 6.32 Particle size distribution of the cryomilled Al-12Si powder

Cryomilling for 8 hours has been found to considerably reduce the grain size and to produce aluminum alloy powder with a nanocrystalline microstructure, such as Al-5083 [39], Al-2618 [46], and Al-Mg [47] alloys. The XRD patterns of the conventional and

cryomilled Al-12Si powders, shown in Figure 6.33, do not demonstrate that the cryomilling process significantly changed the grain size. A change in the grain size would have been characterized by broadening of the diffraction peaks. A TEM micrograph of the cryomilled powder would provide data on the size of the grains.

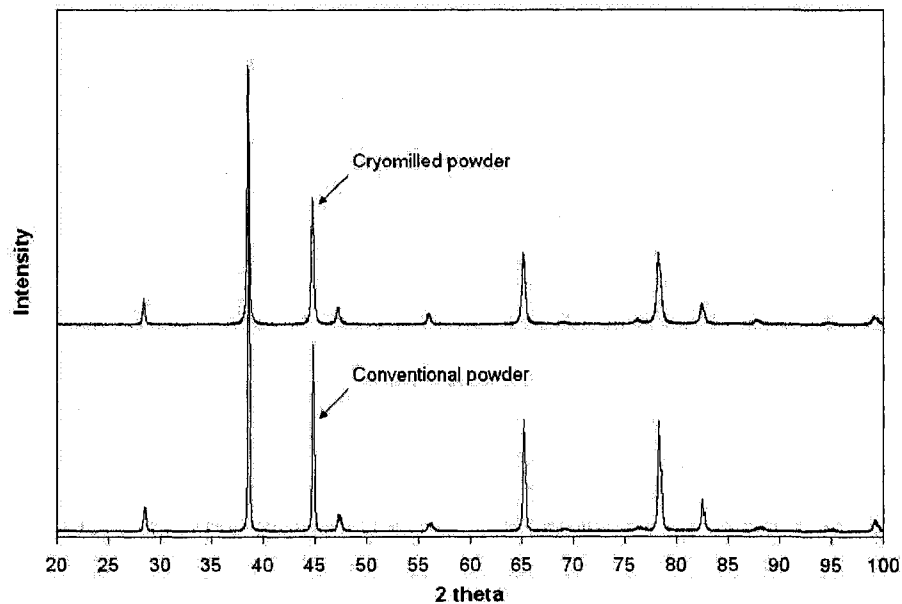


Figure 6.33 XRD of the cryomilled and the conventional Al-12Si powder

SEM images of a coating produced with the cryomilled Al-12Si powder are shown in Figure 6.34. The coatings consist of deformed particles and limited or no porosity (below 0.05%) is present in the coating. This is similar to what was found in the conventional Al-12Si coating (Figure 6.24 – Test 1). An aluminum powder produced by cryomilling is harder than the conventional one due to the grain refinement that occurs during the process [39, 46]. Consequently, cryomilled particles are more difficult to deform and require higher impact velocities than conventional ones to produce dense coatings [116]. In this study, the increase in the particle velocity (due to higher drag coefficients) may have been enough to

compensate for the change in mechanical strength of the powder and generate significant levels of plastic deformation. The coating produced with cryomilled powder was 20% harder than the one produced with the conventional feedstock powder. Microhardness values of 132 ± 7 and 110 ± 6 HV_{300g} were obtained for the coatings produced with cryomilled and conventional powders, respectively. An increase in hardness due to a refinement of the grain size has also been reported [39, 46] and was rationalized on the basis of the Hall-Petch relationship for polycrystalline materials. While the XRD patterns of Figure 6.33 did not show a change in the average grain size of the powder, the powder may have had a mixed grain size distribution. A fine grain size may have been attained in some regions, whereas other regions may have retained their coarse-grained character.

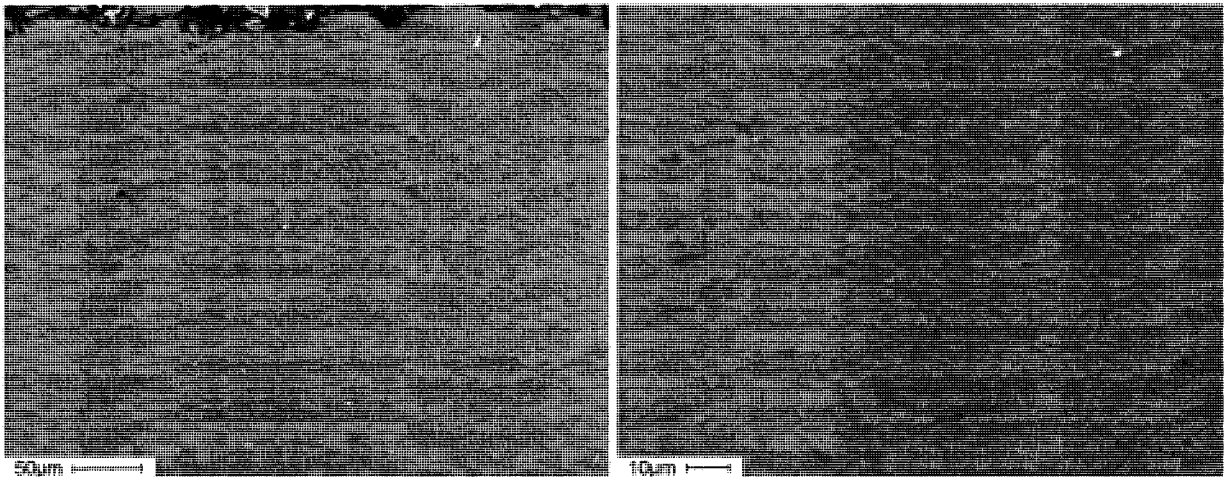


Figure 6.34 SEM images (at different magnifications) of the cross-section of coatings produced with the cryomilled Al-12Si powder

6.5 Al-12Si + SiC Coatings

6.5.1 Composite Powder Preparation

The materials used in this study comprised of the same Al-12Si powder used in Section 6.4 and a reinforcement phase of particulate SiC (Sika, Arendal Smelteverk, Norway). As shown in Figure 6.35, the morphology of the SiC particles is angular with sharp edges as a result of crushing and grinding of SiC lumps that occur during their fabrication. A close examination of the SiC particle in the center of Figure 6.35 reveals a crack, as pointed out by the arrow. It was found that some SiC feedstock particles already contained cracks prior to spraying. Even though the SiC particles are slightly denser than the Al-12Si particles (3.2 g/cm^3 and 2.7 g/cm^3 for the SiC and Al-12Si, respectively), both are expected to reach similar velocities prior to impact on the substrate as irregularly-shaped particles have been shown to experience larger drag coefficient than spherical particles [46, 116]. The reinforcement particles were sieved below 25, 32, and 38 μm to have SiC particles with a size comparable to the Al-12Si particles. The SiC particles below 32 μm were mixed to the matrix alloy powder to create feedstock powder blends containing 20, 30, 40, and 60% volume of SiC. The SiC particles below 25 μm and 38 μm were combined to Al-12Si particles to produce blends with 20% volume of SiC in order to study the effect of reinforcement particle size on the coating formation process and coating properties. A description of the feedstock mixtures used for this study is presented in Table 6.10.



Figure 6.35 Morphology of the SiC particles (the arrow points to a crack in a SiC particle)

Table 6.10 Description of the mixed Al-12Si + SiC feedstock powders

Mixed feedstock powders	SiC size (μm)	SiC (% vol.)
Al-12Si + 20% SiC (< 25)	< 25	20
Al-12Si + 20% SiC (< 32)	< 32	20
Al-12Si + 30% SiC (< 32)	< 32	30
Al-12Si + 40% SiC (< 32)	< 32	40
Al-12Si + 60% SiC (< 32)	< 32	60
Al-12Si + 20% SiC (< 38)	< 38	20

6.5.2 Coating Preparation

SiC-reinforced aluminum alloy coatings were produced using single passes on grit-blasted aluminum substrates with a spray gun having an exit-to-throat area ratio of 13. The stagnation temperature and stand-off distance were 370°C and 10 mm, respectively.

6.5.3 Particle Velocity Measurements

Particle velocity measurements were first undertaken to obtain the in-flight particle velocity distributions of pure and mixed feedstock powders. The particle velocity distributions were compared to determine the effect of SiC particles on the in-flight velocities of the mixed feedstock powder particles. Significant differences between the particles velocities of the pure and mixed feedstock powders might cause variations in the coating properties. The influence of the reinforcement phase within the coatings would then be difficult to dissociate from the one due to the particle velocities. Particle velocity measurements were performed using pure Al-12Si and a mixture of Al-12Si with 30% volume of SiC below 32 μm under the same operating conditions. The particle velocity distributions for these two feedstock powders are shown in Figure 6.36. The velocities range from 300 to 900 m/s and have averages of 559 ± 132 and 581 ± 115 m/s for the pure and the mixed feedstock powders, respectively. Based on these results, it is concluded that adding 30% volume of SiC particles did not produce significant change on the particle velocity. It is rationalized that the slight increase in the average velocity of the blended powders may be attributed to experimental errors. However, it is also possible that the SiC particles are accelerated to higher velocities than the Al-12Si particles which would in turn increase the average measured velocity. The SiC particles are of irregular shape and have a rougher surface which might increase both the drag coefficient and drag forces action on the particles [116]. Since the reinforcement particles did not produce a significant change on the particle velocities, the variations in the coating properties, described in the following sections, will not be the result of a change in the particle velocity distribution but rather due to the presence of SiC particles in the mixed feedstock powders and coatings.

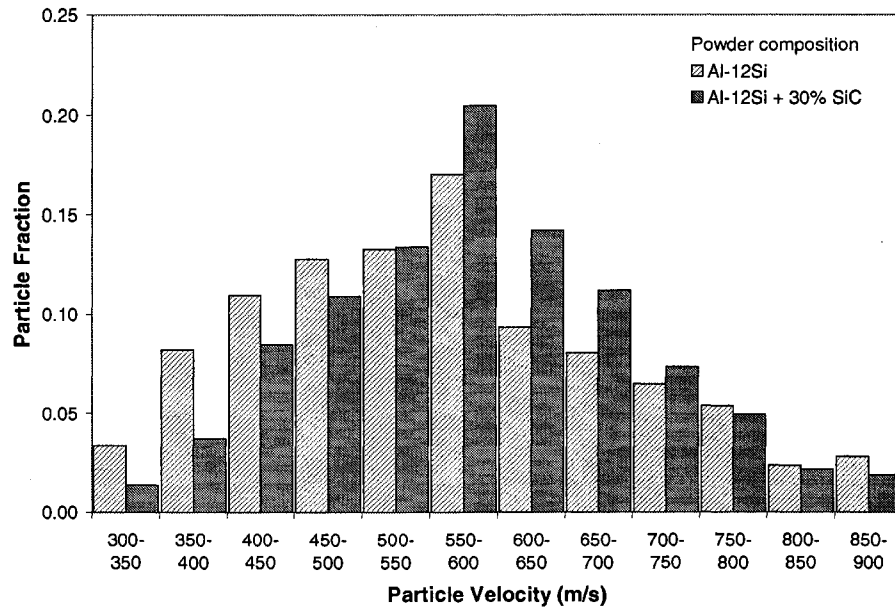


Figure 6.36 Measured particle velocity distributions for the Al-12Si powder and the mixture with 30% volume of SiC particles below 32 μm

6.5.4 Microstructure of the Coatings

SEM images of the cross-sections of CGDS coatings using mixed powders containing 20, 30, 40, and 60% volume of SiC are presented in Figure 6.37. The coatings show a dense and clean microstructure and consist of deformed Al-12Si particles surrounding SiC particles. Porosity levels below 1% were found in all of the composite coatings. The interface between the particles of the matrix is difficult to detect as a result of significant plastic deformation on impact. This suggests that the Al-12Si particles were accelerated beyond their critical velocity. The individual SiC particles, corresponding to the darker spots, are randomly distributed and homogeneously dispersed within the aluminum alloy matrix. Agglomeration of SiC particles, often experienced in casting and powder metallurgy of Al-SiC composites, was not observed in the coatings. The SiC particles

present in the coating maintained their angular morphology and features of the initial feedstock powder (see Figure 6.35). This demonstrates that on impact, the SiC particles did not deform but became confined by the matrix material. A detailed analysis of the SEM images revealed that the average cross-sectional area of the individual SiC particles found in the coatings ranged from 20 to 30 μm^2 while the coating SiC volume content increased from 10 to 20%, respectively. This cross-sectional area of the individual SiC particles indicates that the reinforcement phase mostly consisted of fine particles. The inclusion of mostly small SiC particles in the coatings may be due to differences of the particle impact velocities between the smaller and the larger SiC particles. The momentum transfer between the gas and a particle, or the particle acceleration, is inversely proportional to the particle size (as per Equation 5.1). As a result, higher impact velocities are to be expected for the powders with a small size compared to the particles with a larger size. The small SiC particles would have struck the surface at higher velocities than the larger particles, deformed the aluminum matrix, and lodged themselves in the coatings. The larger SiC particles would not have caused a sufficiently large crater to stick in the coatings and therefore deflected off from the substrate.

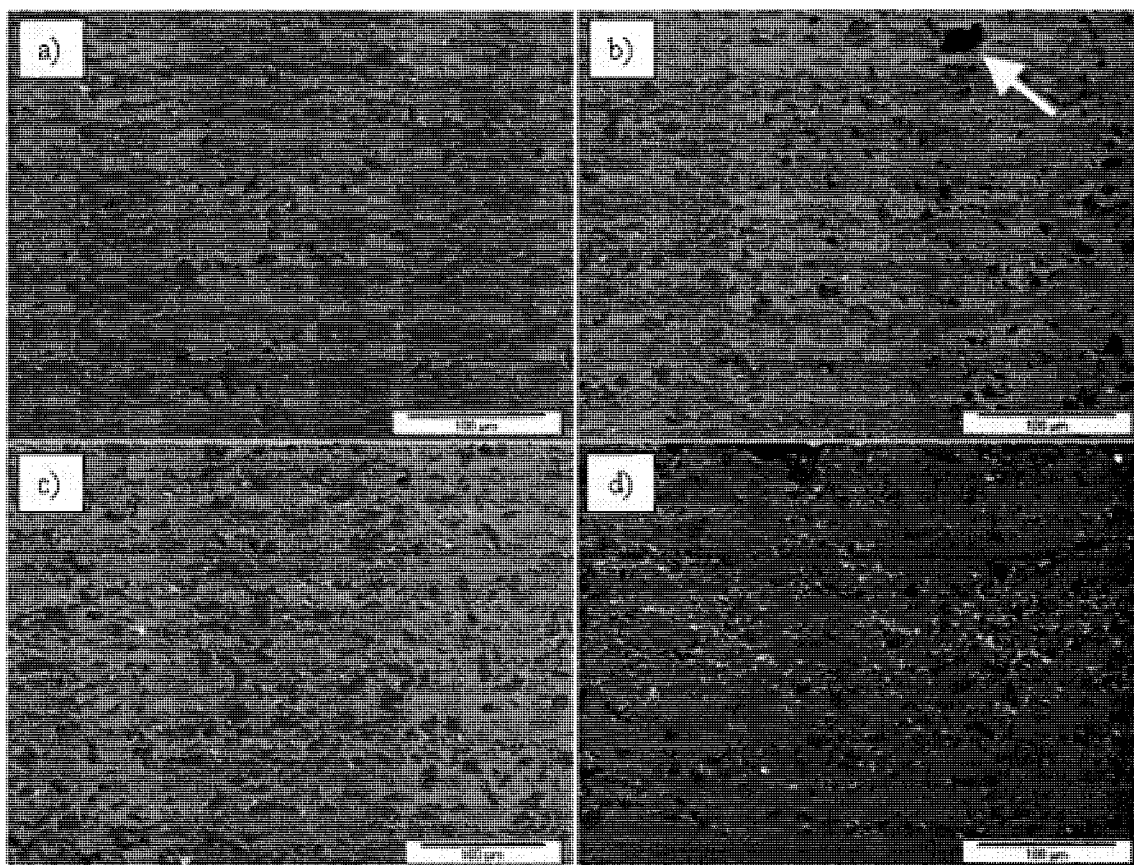


Figure 6.37 SEM images of the cross-sections of composite coatings produced with feedstock powder containing Al-12Si and a) 20, b) 30, c) 40, and d) 60 % vol. of SiC particles below 32 μm . The darker and white spots correspond to SiC particles and spray gun material fragments. The arrow points to a pore resulting from a SiC pullout

The isolated pore, indicated by the arrow, may have been the result of SiC pullout during the polishing process. Pullouts have been observed in other studies on Al-SiC coatings [82, 89]. The examination of Figure 6.37a) at a higher magnification reveals the presence of fractured SiC particles (see Figure 6.38). Different cutting blades were tested and the polishing techniques were varied to determine the effects of the metallographic procedures on these fissured SiC particles of the coatings. It was found that the defects in some of the SiC particles in the coatings did not originate from the sample preparation steps.

The breaking up of these SiC particles most likely occurred during spraying when SiC particles collided with SiC particles of the coating. Such impacts would have extended the existing cracks or induced more defects in the SiC particles. It is expected that particles of Al-12Si striking the SiC would not have caused such fissures. The impacts would have been absorbed by the ductile matrix and have resulted in its plastic deformation around the hard reinforcement particles. Fracturing of reinforcement particles upon impact on the sprayed surface have also been reported during the production of MMC coatings by CGDS [86].

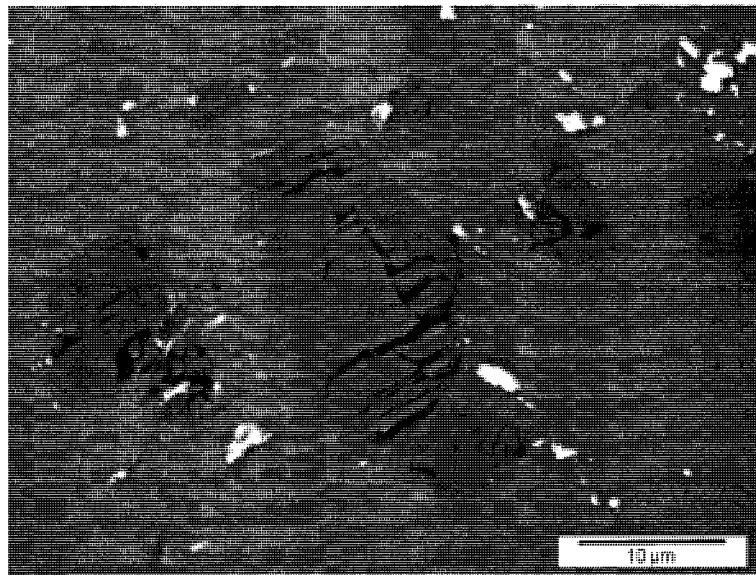


Figure 6.38 SEM image at higher magnification of the central region of Figure 6.37a) showing cracked SiC particles

An electron-dispersive spectroscopy (EDS) analysis revealed that the white regions observed in the coating images were fragments of the spray gun material. This can be attributed to the use of silicon carbide particles, one of the hardest blasting media available, flowing through the nozzle. These particles are likely to erode the walls of the spray gun during the spraying process. The wear debris are entrained and deposited with the mixed feedstock powders. Moreover, increasing the SiC content of the feedstock powder

accentuated the erosion of the wall of the spray gun. The coatings contained from 1 to 4% volume of wear debris as the SiC content in the feedstock powder was varied from 20 to 60% volume, respectively.

Composite coatings with SiC volume fractions varying from 10 to 20% have been produced from mixed feedstock powders with SiC content of 20 to 60% volume respectively, as shown in Figure 6.39. On impact on the sprayed surface, the SiC particles do not deform and a large fraction of the particles bounce off the surface. Some particles may implant themselves in the coating by deforming the matrix material upon impact. This is similar to surface grit contamination that occurs during the grit blasting process. Grit residual content has been found to reach a maximum when the blasting angle is perpendicular to the surface to be cleaned [114, 117] and increases with the blasting pressure [118, 119]. In CGDS, the spray gun generally remains perpendicular to the substrate in order to maximize the deposition efficiency [35] and the operating pressure is well above the ones used in grit blasting. It is also believed that since the constituents of the feedstock powder hit the substrate simultaneously, the Al-12Si particles can deform around the SiC particles and entrap these reinforcements in the coating.

The fraction of SiC retained in the coatings was defined as the ratio of the volume percent of SiC in the coating to the volume percent of SiC in the feedstock powder. This ratio was found to decrease as the SiC volume fraction in the feedstock powders increased, as illustrated in Figure 6.40. For example, in coatings produced with feedstock powders containing 20 and 60% volume of SiC, 50 and 33% of the SiC were preserved, respectively. Increasing the fraction of SiC in the feedstock powder augments the number of impacts of SiC particles on the sprayed surface. Some of these SiC particles will be entrapped in the

coating while others will bounce off the surface. However, fewer particles of Al-12Si can deform around the embedded SiC particles which reduces the proportion of SiC retained in the coating. In order to entrap as much SiC particles as possible, there must be sufficient matrix material to contain reinforcement particles in the coating.

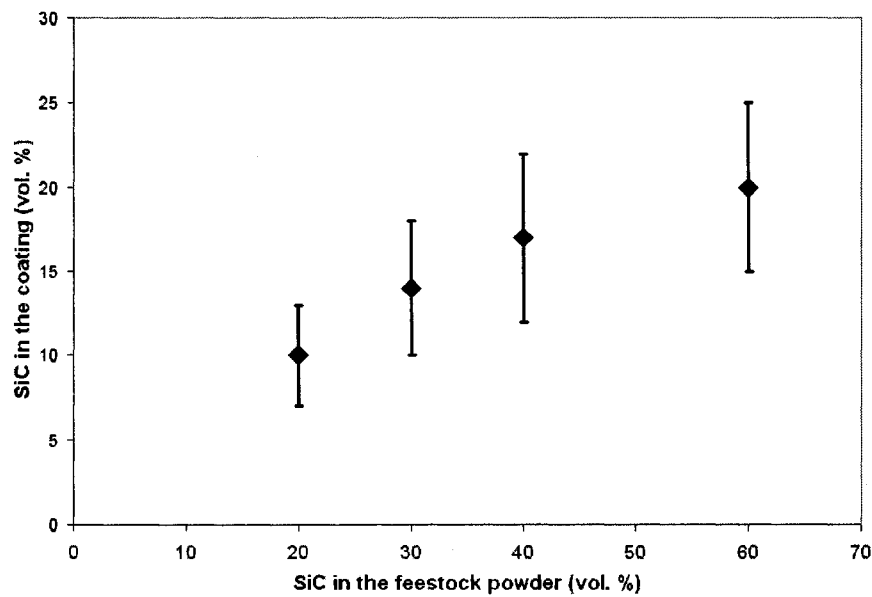


Figure 6.39 Volume fraction of SiC in the coating as a function of the SiC in the feedstock powder

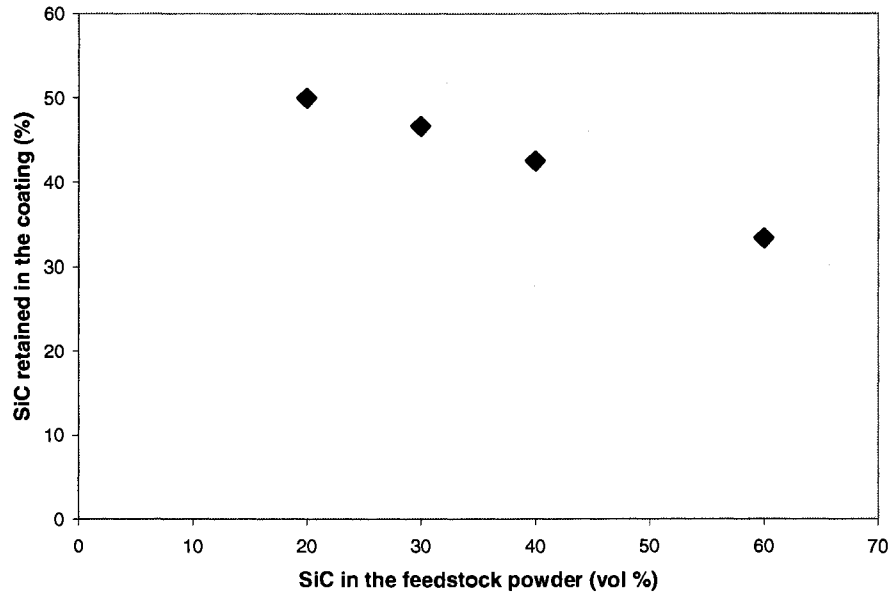


Figure 6.40 Fraction of SiC retained in the coatings as a function of the SiC content in the feedstock powder

SEM images of the coatings produced with feedstock powder containing 20% volume of SiC particles sieved below 25, 32, and 38 μm , are shown in Figure 6.41. Close examination of the images reveal that the size range of the SiC particles in the feedstock powder did not influence the overall microstructure of the coating. In every coating shown, the SiC particles are randomly distributed within the Al-12Si matrix. The coating contained 10% volume of SiC and exhibited porosity levels below 1%. The average cross-sectional area of the individual SiC particles in the coatings produced with SiC particles sieved below 25, 32, and 38 μm were 20, 20, and 40 μm^2 , respectively. Although larger SiC particles were included in the feedstock powder, the reinforcement phase of the coating consisted of fine SiC particles, as it can be observed in Figure 6.41. This is attributed to the high particle velocities associated to the small SiC particles. These particles stuck to the sprayed surface by causing deformation of the matrix material on impact. Because of their lower velocities,

the larger SiC particles did not sufficiently deform the sprayed surface. During the spraying process, these particles deflected off the surface on impact and were not retained in the coating.

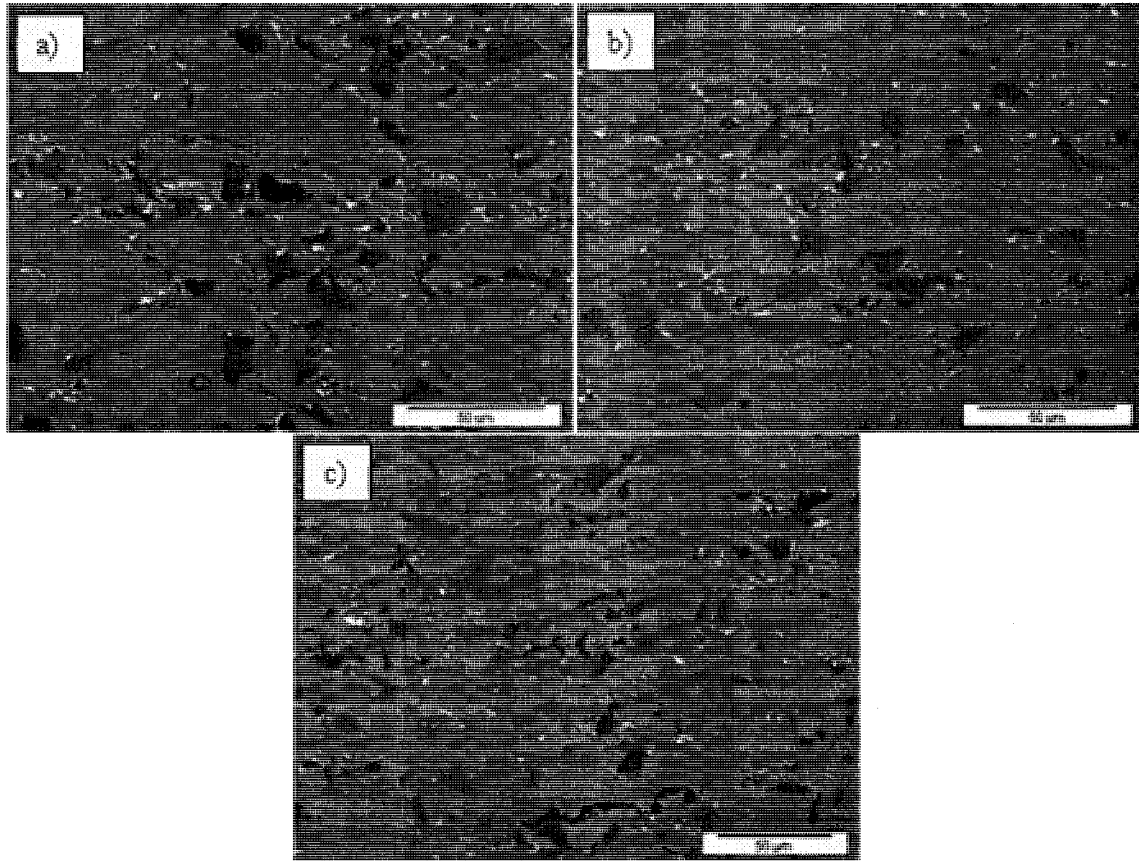


Figure 6.41 SEM images of the cross-sections of composite coatings produced with feedstock powder containing Al-12Si and 20% volume of SiC particles below a) 25, b) 32, and c) 38 μm

The retained fraction of SiC is different than what was reported in another study, where 40% volume of the SiC was retained in the coatings regardless of the SiC content in the feedstock powder [85]. In that study, aluminum particles with a diameter ranging from 51 to 63 μm were used and the particle velocities varied from 400 to 500 m/s. These

differences in the particle size and velocities may have influenced the amount of SiC that could be contained in the coatings.

The loss of SiC particles during the spraying process is unavoidable when blends of aluminum alloy powder and SiC particles are used. In CGDS, the particles must be accelerated above a critical velocity to plastically deform, bond to the substrate, and build up the coating. However, since SiC is brittle, particles of this material did not deform on impact with the substrate. SiC particles become embedded on the sprayed surface and are entrapped by Al-12Si particles that deform around the SiC particles. Reinforcement particles with a fine size distribution could improve the fraction of SiC retained in the coating. The small particles would impact on the sprayed surface at high velocities and become embedded in the coating. Composite powder particles produced by mechanically milling and alloying aluminum and SiC particles may also minimize these losses. As it was described earlier, the mechanical alloying process produces agglomerations of aluminum particles with entrapped fragments of SiC and the resulting composite particles have fine and uniformly distributed reinforcements in the matrix [82, 89, 92]. In plasma spraying, milled powders improve the wettability of SiC by aluminum and augment the fraction of SiC retained in the coatings [89]. However, in CGDS, such composite particles may not undergo the same level of plastic deformation observed in Al-12Si particles. As it will be shown in section 6.6, the reinforcements in the composite powder particles may obstruct and limit the deformation of the matrix, leading to higher porosity levels in the coating.

6.5.5 Bond Strength Measurements

The variation of the bond strength as a function of the SiC content in the feedstock powder is shown in Figure 6.42. Adhesion strength values of 49, 44 and 43 MPa were obtained as the volume fraction of SiC in the coating increased from 0, 10 and 14%, respectively. Examinations of the specimens reveal that the failure occurred at the coating-substrate interface. Most of the coatings remained attached to the specimens on which the bonding agent was applied, as shown in Figure 6.43. An increase of the SiC content in the coating slightly reduced the level of adhesion of the coatings on the substrates. Although the SEM images of the SiC-reinforced coatings revealed substrate-coating interfaces free of defects that could alter the adherence of the coating, the presence of SiC particles at the interface may affect the adhesion strength (see Figure 6.44). These SiC particles at the interface reduced the surface area available for the aluminum matrix to deform around the surface irregularities of the substrate and bond to the latter. As more SiC particles impinge on the substrate, fewer aluminum alloy particles came in contact with the substrate. The number of anchoring sites between the coating and the substrate are then reduced in comparison to coatings reinforced with a lower SiC volume fraction. A thin coating layer of pure Al-12Si could then be sprayed on the surface of the substrate before spraying mixed feedstock powders to reduce the effects of the SiC particles at the substrate-coating interface. The adhesion strength of Al-SiC coatings produced by plasma spraying was found to vary from 68 to 76 MPa due to the formation of a metallurgical bond between the coating and the substrate [82]. In addition, it was reported that a decrease in the metal content at the interface reduces the strength of the bond. The reported bond strength values in this study are below the ones of coatings produced by plasma spraying because of the nature of the

bond. In CGDS, the bonding mechanism is through mechanical anchoring since no bulk particle melting occurs and no metallurgical reactions take place between the sprayed material and the substrate [20].

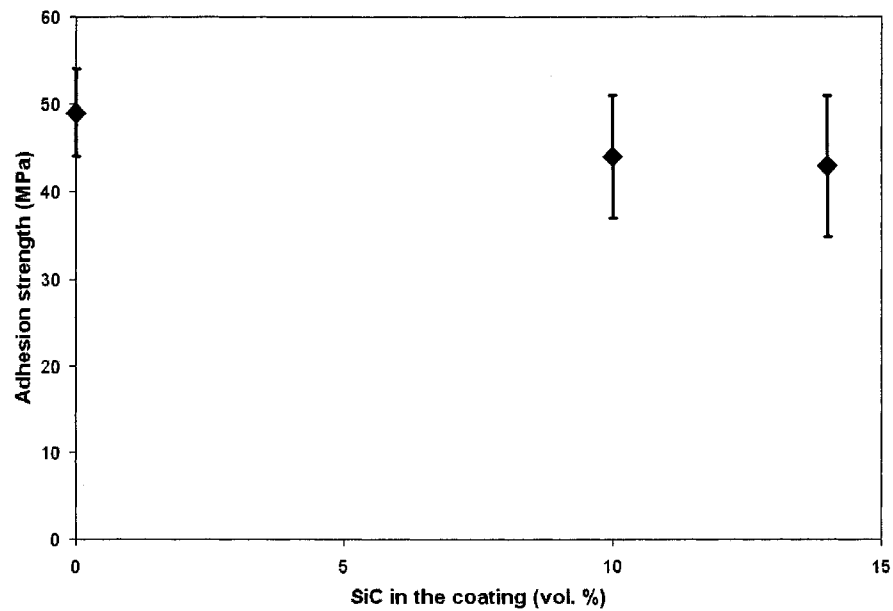


Figure 6.42 Adhesion strength of SiC-reinforced Al-12Si coatings as a function of the SiC content in the coating

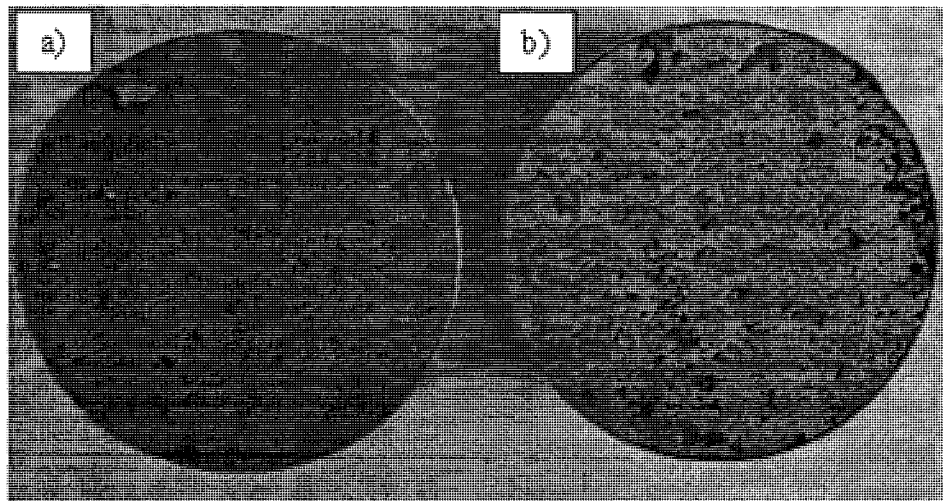


Figure 6.43 Photograph of the bond strength specimens with a) the bonding agent and b) the remainder of the Al-12Si coating with a SiC content of 14% volume after the bond test

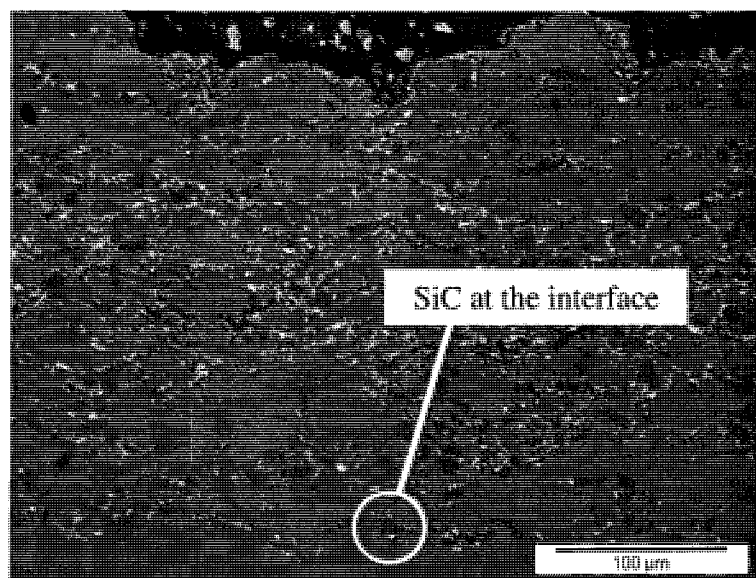


Figure 6.44 SEM image of the substrate-coating interface of a composite coating containing 20% volume of SiC

6.5.6 Hardness Measurements

The SiC particles present in the coatings initiated significant changes in the coating hardness, as illustrated in Figure 6.45. The average hardness of Al-12Si reinforced with SiC particles varied from 145 ± 14 to 205 ± 25 HV_{300g} for coatings containing 10 to 20% volume of SiC. A hardness of 110 ± 6 HV_{300g} was obtained for an Al-12Si coating without SiC reinforcements. Thus, coatings with 10% volume of SiC were found to be 32% harder than pure Al-12Si coatings. The microhardness values of the coatings produced with feedstock powders containing 20% volume of SiC particles below 25, 32, and 38 μm are given in Figure 6.46. The coating hardness values were not altered by the size of the SiC particles in the feedstock powders. As it was shown in Figure 6.41, the reinforcement phase in the coatings consisted of fine SiC particles even though the SiC particle size distribution in the feedstock powders was varied.

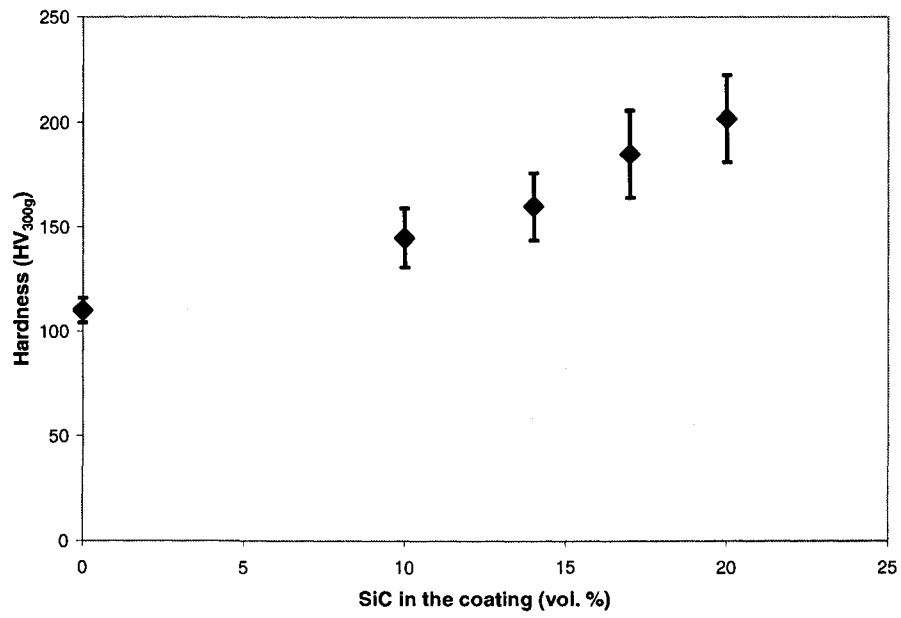


Figure 6.45 Hardness of SiC-reinforced Al-12Si coatings as a function of the SiC content in the coatings

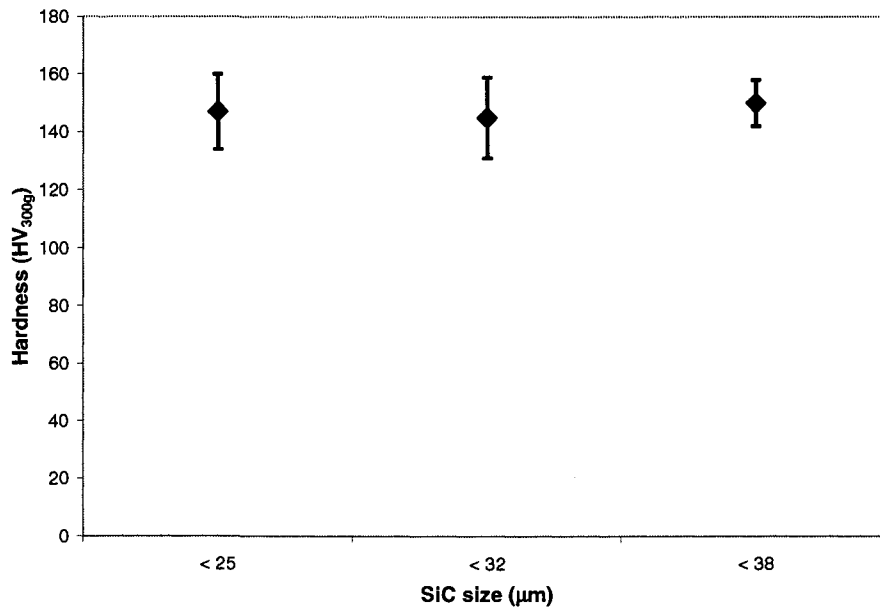


Figure 6.46 Hardness of SiC-reinforced Al-12Si coatings produced with feedstock powder containing 20% volume of SiC particles of different sizes. Each coating contained 10% volume of SiC

6.6 Al-5083/B₄C Coatings

6.6.1 Powder Preparation and Description

This composite powder consisted of nanocrystalline aluminum 5083 alloy matrices reinforced with 10 wt. % of B₄C. The facilities at the University of California at Davis were used to blend the aluminum 5083 alloy and B₄C powders [120]. The Al-5083/B₄C composite powder was produced by cryomilling. Figure 6.47 shows a SEM image of a cryomilled Al-5083/B₄C composite powder. After 8 hours of milling time, grain size measurements performed by transmission electron microscopy (TEM) revealed an average grain size of 28 nm for the aluminum alloy powder [120]. A TEM image of the composite powder is shown in Figure 6.48. The average size of the B₄C particles was determined from optical microscopy analysis and varied from 0.6 to 2 μm . The composite powder particles in Figure 6.49 are of irregular shapes due to particle welding and fracturing during the cryomilling process. From a particle velocity point of view, the morphology of cryomilled particles has been shown to be more suitable for the CGDS technology [116]. Non-spherical particles have larger drag coefficients which lead to higher particle velocities. The particles have a broad particle size distribution ranging between 15 and 150 μm . A wide distribution of particle velocities is expected because of the large particle size distribution of this powder.

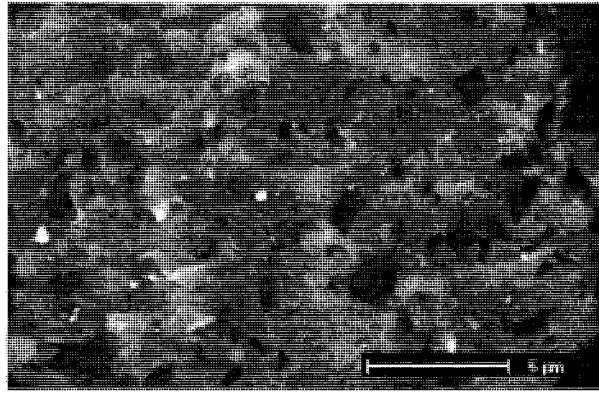


Figure 6.47 SEM image of an Al-5083/ B_4C composite powder. The black fragments represent B_4C particles while the white fragments correspond to Al_2O_3 particles from the alumina grinding media during sample polishing (from [120])

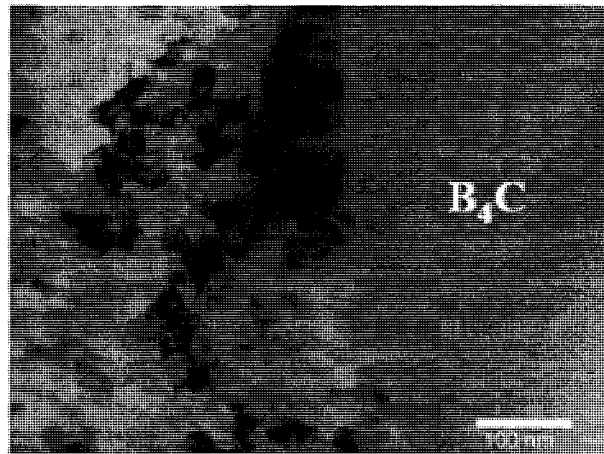


Figure 6.48 TEM image of the Al-5083/ B_4C composite powder cryomilled for 8 hours (from [120])

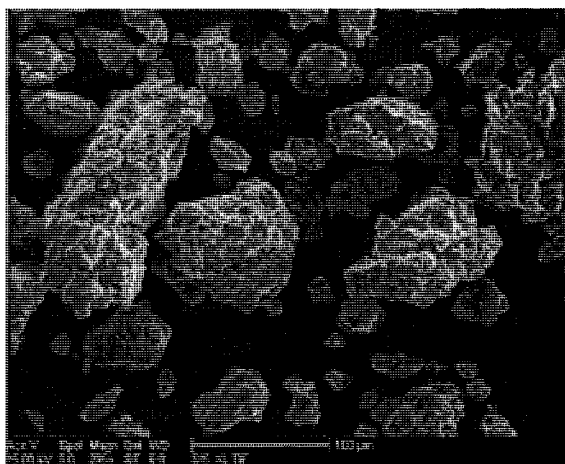


Figure 6.49 Morphology of the Al-5083/B₄C powder particles

6.6.2 Coating Preparation

The effects of the nozzle exit-to-throat area ratio, powder feed rate, and particle size were considered. The substrate traverse speed and stand-off distance were maintained at 2 mm/s and 10 mm, respectively. Coatings were produced at 250 and 350°C in an attempt to evaluate the effects of gas stagnation temperature on the coating formation. The coatings produced at 250°C were too thin to generate meaningful data. Thus, only the results obtained at a gas stagnation temperature of 350°C are presented. A single passage of the substrate in front of the spray gun was used to produce the coatings on the substrates.

6.6.3 Effect of Nozzle Exit-to-Throat Area Ratio

SEM images of Al-5083/B₄C coatings produced with nozzles having exit-to-throat area ratios of 10 and 13 at a powder feed rate of 4 g/min are shown in Figure 6.50. The substrate-coating interfaces revealed pores and defects and the coatings were composed of partly deformed particles surrounded by voids and pores. The interface between the particles is visible and some undeformed particles can be detected in the coatings. Both coatings had

a thickness of 300 μm and the porosity levels were evaluated at 7 and 4% for the Al-5083/B₄C coatings produced with nozzle area ratios of 10 and 13, respectively. As mentioned in section 6.2.2.1, increasing the nozzle exit-to-throat area ratio produces a greater expansion of the gas in the nozzle. The particles are then accelerated to higher velocities due to the increased gas velocity, which enhances their plastic deformation on impact on the substrate and fill the voids in the coatings. The reduced number of voids in the coating produced with the larger nozzle area ratio (Figure 6.50b)) is attributed to an increase of the particle velocity. In addition, the limited particle plastic deformation in the Al-5083/B₄C coatings suggests that the production of dense MMC coatings is dependent on the extent of compaction. Due to the composite structure of the powder, additional impacts from impinging particles may be necessary to deform the aluminum ductile phase and fill the voids surrounding the ceramic phase.

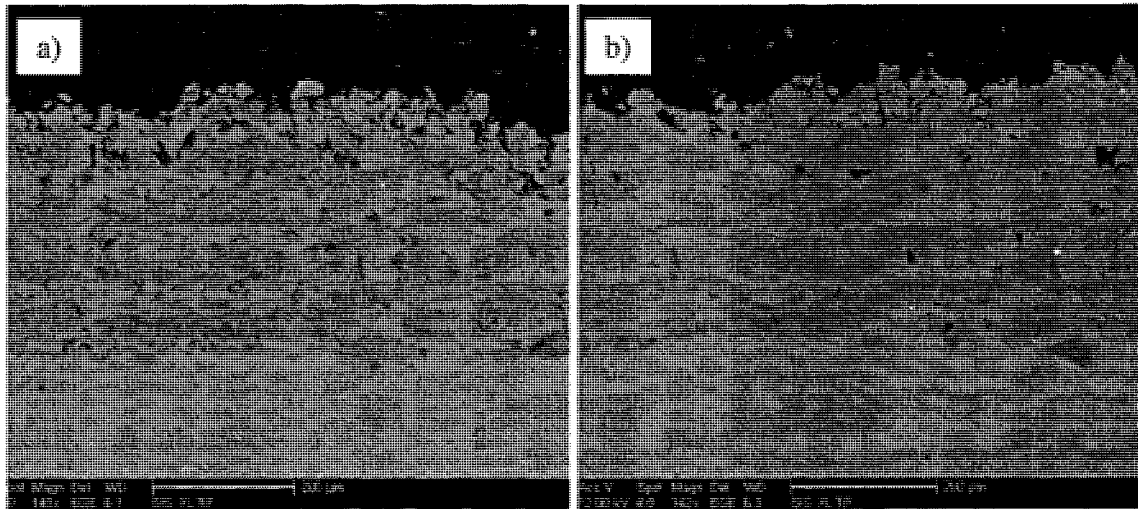


Figure 6.50 SEM images of Al-5083/B₄C coatings for nozzles with an exit-throat ratio of a) 10 and b) 13 and at a powder feed rate of 4 g/min

The composite coatings of Figure 6.50 are significantly different from the coating shown in Figure 6.51, which was produced using nanocrystalline Al-5083 particles without

B₄C reinforcement. Adding B₄C reinforcement to an Al-5083 matrix produced significant changes in the plastic deformation of the composite particles, as suggested by the observed porosity levels. As composite particles impact with the substrate, the B₄C particles entrapped in the aluminum matrix hinder the deformation of the ductile phase. The kinetic energy of the particles is spent on deforming the aluminum ductile phase around the ceramic phase instead of filling the voids between the particles.

Microhardness values of 109 ± 10 and 115 ± 9 HV_{100g} were obtained for the coatings produced with a nozzle area ratio of 10 and 13, respectively. The fine B₄C particles (ranging from 0.6 to 1.8 μm) might have restricted the plastic deformation of the composite particle but they did not influence the coating hardness. The coatings were too porous to show the effects of the ceramic phase on the hardness. A coating hardness value of 261 ± 9 HV_{300g} have been obtained in dense Al-5083 nanocrystalline coatings produced by CGDS [39].

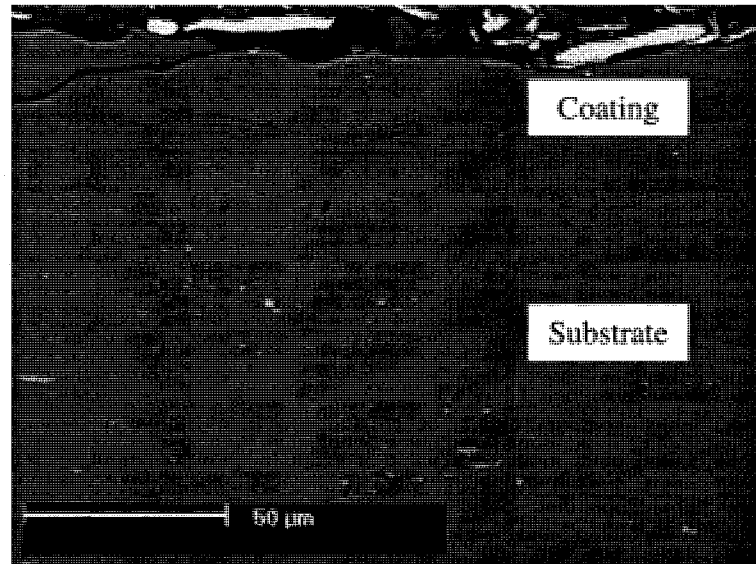


Figure 6.51 Cross-section of a nanocrystalline Al-5083 coating produced by CGDS (from [39])

6.6.4 Effect of Powder Feed Rate

The cross-sectional images in Figure 6.52 depict Al-5083/B₄C coatings produced at powder feed rates of 2 and 4 g/min. The substrate-coating interfaces host some defects such as cracks. The presence of several voids in the coatings implies an insufficient particle plastic deformation. Although the coating thickness increased from 150 to 300 μm by changing the powder feed rate from 2 to 4 g/min, the porosity increased from 2 to 4%. This is the result of a particle loading effect. The histograms of the particle velocity distributions in Figure 6.53 show that the particle velocity decreased from 563 ± 142 to 537 ± 152 m/s when the powder feed rate was increased from 2 to 4 g/min. These particle velocity distributions are slightly broader than the ones obtained with other feedstock powder such as the Al-Co-Ce and Al-5083 particles. As it was shown in Figure 6.49, the Al-5083/B₄C consisted of some large particles. The large particles of the feedstock powder reach lower velocities and expand the range of velocities found in the distribution. The particle velocity was sufficiently high to initiate some plastic deformation of the Al-5083, but not high enough to fill the empty spaces in the coating. Microhardness values of 113 ± 12 and 115 ± 9 HV_{100g} were obtained for the coatings produced at powder feed rates of 2 and 4 g/min, respectively.

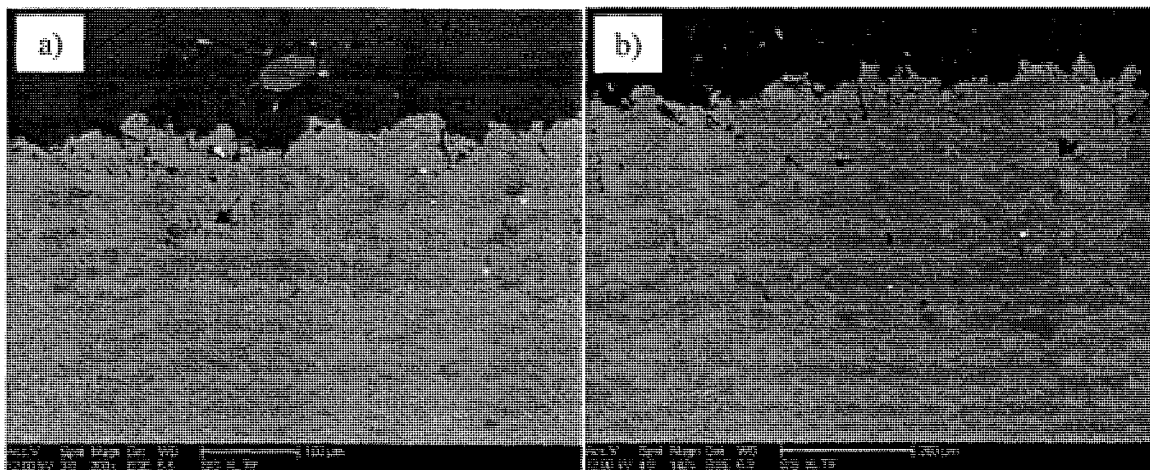


Figure 6.52 SEM images (at different cross-sections) of Al-5083/B₄C coatings produced at a) 2 and b) 4 g/min and at a gas stagnation temperature of 350°C

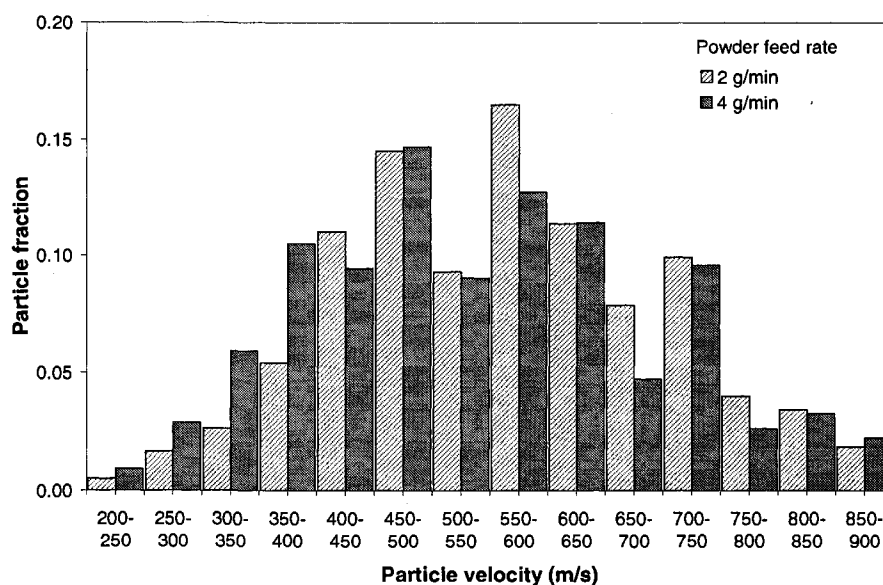


Figure 6.53 Histogram of the Al-5083/B₄C particle velocities at powder feed rates of 2 and 4 g/min and at a gas stagnation temperature of 350°C

The average bond strength values were 39 ± 3 and 33 ± 2 MPa for powder feed rates of 2 and 4 g/min, respectively. As shown in Figure 6.54, most of the coating remained attached on the side on which the bonding agent was applied. The reported values then

correspond to adhesion strength. The Al-5083/B₄C coatings generated the lowest adhesion strengths. This is consistent with the SEM images that showed cracks at the coating-substrate interface. The lack of mechanical bonding between the substrate and the coating may be the result of an insufficient plastic deformation of the particles as they hit the substrate.

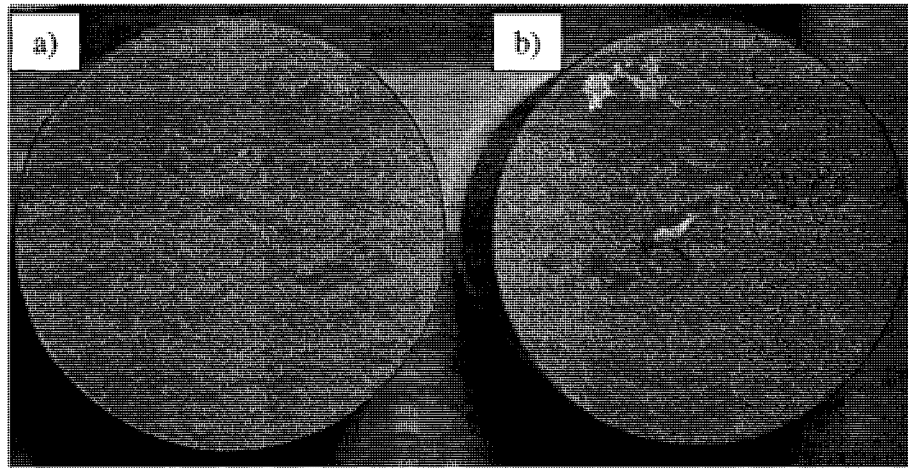


Figure 6.54 Photograph of the bond strength specimens with a) the bonding agent and b) the remainder of the Al-5083/B₄C coating after the bond test

6.6.5 Effect of Particle Size

In an attempt to reduce the porosity to 1%, a level comparable to the other aluminum-based coatings produced in this study, the largest and thus, slowest particles were removed from the bulk feedstock composite powder. A 400-mesh sieve was used to obtain powder particles below 38 μm . The coatings produced with sieved powder, shown in Figure 6.55, were significantly thinner with porosity levels comparable to the coatings obtained from the bulk Al-5083/B₄C feedstock powder. The results indicate that the particles below

38 μm do not deform enough at impact to produce dense and thick coatings. Although the B_4C particles within the aluminum matrix were uniformly distributed, the small particles may contain a larger fraction of hard reinforcement particles than the large particles. Consequently, only a small volume of the aluminum matrix is available for plastic deformation.

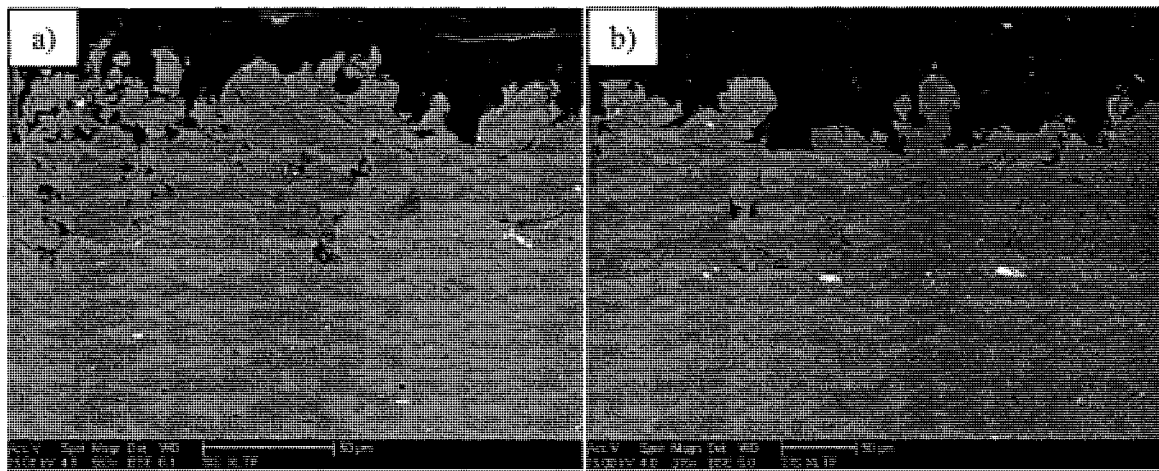


Figure 6.55 SEM images of Al-5083/ B_4C coatings produced with the sieved powder at a) 2 and b) 4 g/min

In order to produce dense nanocrystalline composite coatings by the CGDS process, higher particle velocities may be required. Increasing the gas stagnation temperature would increase the process gas velocity and exert larger drag forces on the particles. Spraying blends of an aluminum feedstock powder with addition of B_4C particles is another alternative. A nanocrystalline aluminum alloy powder could be mixed with different volume fractions of B_4C particles and subsequently sprayed. In this method, the ductile aluminum particles would deform around the hard reinforcement particles and fill the voids in the coating. A slower substrate traverse speed could be used to consolidate dense and thick nanocrystalline composite coatings. The Al-5083/ B_4C deposit depicted in Figure 6.56 was

produced by spraying on a stationary substrate. The continuous impingement of particles initiated some plastic deformation of the partially deformed particles in the coating and lowered the porosity levels.

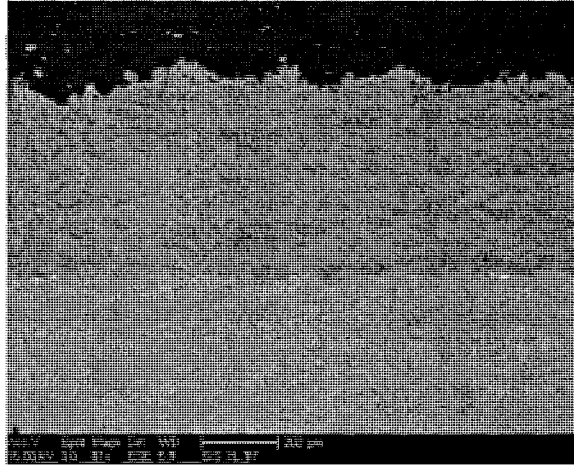


Figure 6.56 SEM image of an Al-5083/B₄C deposit produced on a stationary deposit

6.6.6 Summary

The properties of Al-5083/B₄C coatings obtained in this study are summarized in Table 6.11. The table shows the effects of the nozzle exit-to-throat area ratio and powder feed rate.

Table 6.11 Properties of Al-5083/B₄C coatings

Nozzle exit-to-throat area ratio	Gas stagnation temperature (°C)	Powder feed rate (g/min)	Particle velocity (m/s)	Thickness (μm)	Porosity (%)	Micro-hardness (HV _{100g})	Bond strength (MPa)
10	350	4	-	300	7	109 ± 10	-
13	350	2	563 ± 150	150	2	113 ± 12	39 ± 3
13	350	4	537 ± 152	300	4	115 ± 9	33 ± 2

Chapter 7 – Concluding Remarks

7.1 Conclusions

A research study has been performed to explore and expand the range of applicability of the CGDS process to a wide variety of aluminum alloy coatings. The goals of the work were threefold: to synthesize aluminum-based coatings by CGDS; to evaluate the mechanical properties of these coatings; and to examine the relationships between the particle velocities, microstructures and properties of these coatings.

The first part of this thesis compared the operating characteristics of two different in-flight particle velocity measurement tools: a CSM and a PIV systems. The particle velocities obtained by each system were also presented. It was found that, unlike the CSM measurements, the PIV measurements were highly sensitive to the particle size, particle morphology and powder feed rate due to pixel saturation of the CCD. The results indicated that the CSM was better suited to CGDS because of its ease of implementation and usability.

The second part of this thesis considered the microstructural features and mechanical properties of aluminum-based coatings. Several aluminum alloy coatings were produced from a single pass of the substrate in front of the spray gun and subsequently analyzed. Coatings of Al-Co-Ce, Al-5083 and Al-12Si and metal-matrix composite coatings of Al-12Si + SiC and Al-5083/B₄C were successfully developed. The microstructural analysis examined the micro-hardness, porosity, thickness and defects in the coatings. The bond strength and fatigue strength were evaluated based on standard tests. The properties of several aluminum-based coatings produced by CGDS have been summarized in Appendix C. The following conclusions can be drawn from these interrelated studies:

- The coatings produced with a nozzle having a larger exit-to-throat area ratio have a better microstructure and lower porosity. A larger area ratio allows for a greater expansion of the gas in the nozzle and increases the momentum transfer to the particles. The particles are then accelerated to higher velocities, enhancing their plastic deformation on impact.
- Raising the gas stagnation temperature increases the gas velocity throughout the nozzle, which in turn accelerates the particle to higher velocities. The coatings are thicker because a larger portion of the particle size distribution reaches the critical velocity to plastically deform on impact.
- The effect of powder feed rate on the particle velocities have been found to depend on the size of the feedstock powder. In the case of a fine particle size distribution (such as the one for the Al-Co-Ce powder), increasing the powder feed rate did not affect the particle velocity but produced thicker coatings of the same porosity levels. For powders with a larger size distribution (such as the Al-5083 and the Al-12Si powders), increasing the powder feed rate causes a slight particle loading effect. More particles are entrained in the flow and the particles are accelerated to lower velocities. The resulting coatings are thicker but more porous as the particles undergo partial plastic deformation on impact.
- Increasing the substrate traverse speed reduces the number of particles impinging at one location of the substrate and reduces the compaction of the previously deposited layers of material. Using high substrate traverse speeds produces thinner coatings with a lower hardness and higher porosity. Low substrate traverse speeds improve

the thickness, hardness and density of the coatings but prolong the spraying time and nozzle clogging may be experienced during spraying.

- Grit-blasting produced noticeable effects on the bond strength of coatings. Larger blasting beads increase the surface roughness but may contaminate the surface with grit residuals. Such contamination reduces the number of anchoring sites between the coating and the substrate and lowers the adhesion strength.
- CGDS coatings significantly improved the fatigue performance of the substrates. The compressive stresses induced in the coating during the spraying process delayed crack initiation and propagation.

7.2 Achievements

The results and the conclusions obtained in this study are significant and provide further understanding of the effects of several spraying parameters on the particle velocity and on the coating properties. Part of this research has been presented in conferences [121-123], in conference proceedings [124-126], and in journal publications [127, 128]. The outcome of the analysis of the fatigue behavior of CGDS coating led to a patent application in 2006 [129]. This work has demonstrated that a wide variety of aluminum-based coatings can be produced by CGDS and has documented some of their mechanical properties.

7.3 Recommendations

Based on the results documented in the present research, further studies concerning the properties of aluminum-based coatings produced by CGDS would be valuable. For example:

- Additional measurements should be conducted to obtain the deposition efficiency under the operating conditions used in this study. These measurements could then be used to evaluate the critical velocity of the aluminum alloys for a particular size range.
- Further investigations are required to evaluate the wear properties of conventional and metal-matrix composite coatings. The wear behavior under different operating conditions may be investigated to identify suitable application areas.
- The analysis of the fatigue properties of other aluminum alloy coatings produced by CGDS could be examined. Such studies could be extended to CGDS coatings made of other materials such as nickel, zinc, copper, and steel. The fatigue behavior of amorphous and nanocrystalline coatings produced by CGDS could also be examined.
- A comprehensive study on the effects of grit-blasting on the bond strength would provide practical information on maximizing the bond strength of CGDS coatings.
- Improvements in the nozzle design could be made to avoid the effects of some of the material build-ups on the nozzle walls. Also, different curvilinear nozzles could be tested, with different diverging shapes, lengths and diverging angles.

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Appendix A – Metallographic Specimen Preparation

Procedure

Metallographic specimen preparation can be divided into three distinct steps consisting of sectioning, mounting, grinding and polishing. The equipment and the methods used to prepare the coatings for the microstructural evaluations are described in the following sections.

A.1 Sectioning

The coated substrates of aluminum were sectioned down to smaller samples using an automated precision cut-off machine (Struers Secotom) equipped with a silicon carbide cutting blade. The coated parts were oriented so that the cutting blade kept the coating under compression during cutting to prevent separation from the substrate. Sectioning was conducted at a blade rotational speed of 2200 rpm and at a traverse speed of 0.3 mm/s.

A.2 Mounting

Samples for metallographic inspection were mounted in resin using a Struers LaboPress-3 automatic mounting press. The operating parameters involved in the mounting of the samples are given in Table A.1.

Table A.1 Operating parameters involved in the mounting of samples

Setting	Value
Resin	MultiFast Green hot mounting resin (30 mL)
Temperatures and Times	Heating: 150°C for 7 minutes Cooling: 15°C for 2 minutes
Load	20 kN

A.3 Grinding and Polishing

Grinding and polishing were carried out on an automatic polishing machine (Struers TegraPol-31). Grinding was performed using diamond pads under the conditions in Table A.2. The Piano 220 diamond pad is a resin bonded disk that provides a surface finish comparable to 220-grit silicon carbide papers. Fine grinding and polishing were performed using diamond suspension solutions. A TegraDoser-5 from Struers was used to deliver the liquid abrasive during the fine grinding and polishing steps.

Table A.2 Grinding and polishing parameters used for the metallographic sample preparation

Preparation	Pad	Disc speed (rpm)	Load per specimen (N)	Lubricant	Time (min.)
Grinding	Piano 220	300	30	Water	1:30
Fine Grinding	MD-Largo	150	25	DiaDuo 15 μm^*	3:00
Polishing	MD-Mol	150	25	DiaDuo 6 μm^*	3:00
Polishing	MD-Nap	150	15	DiaDuo 1 μm^*	3:00

* diamond suspension

Appendix B – Radial Particle Velocity Profiles

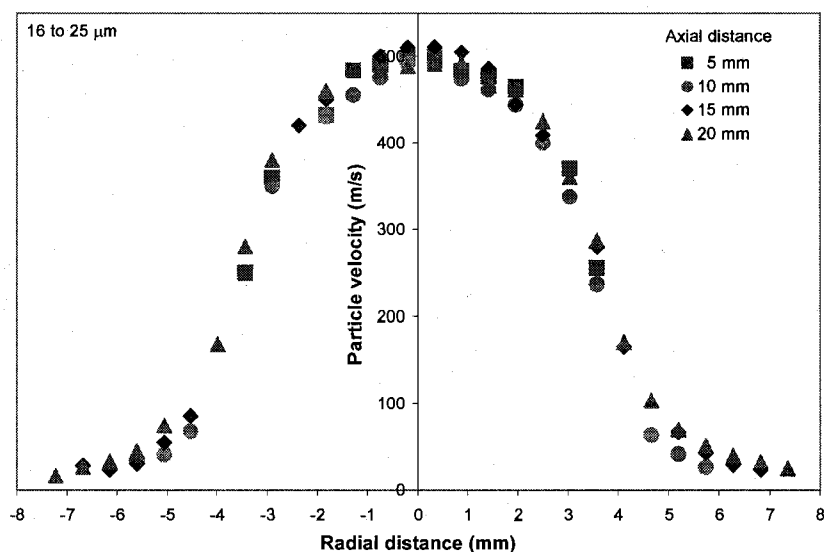


Figure B.1 Radial distribution of the axial particle velocity at several axial distances from the spray gun exit obtained by PIV for the 16 to 25 μm size range

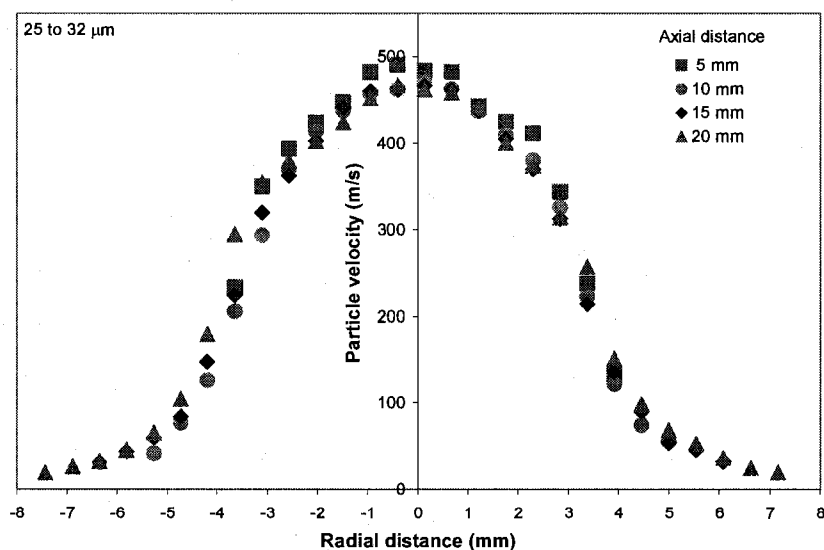


Figure B.2 Radial distribution of the axial particle velocity at several axial distances from the spray gun exit obtained by PIV for the 25 to 32 μm particle size range

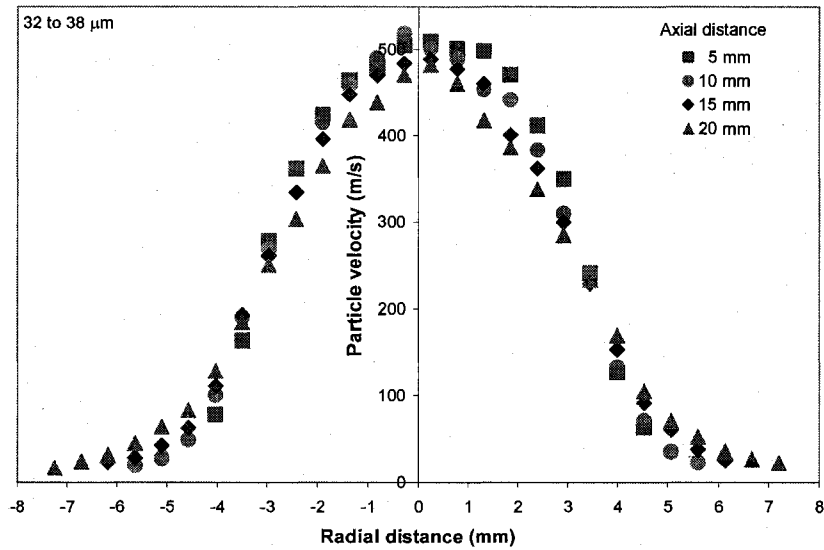


Figure B.3 Radial distribution of the axial particle velocity at several axial distances from the spray gun exit obtained by PIV for the 32 to 38 μm particle size range

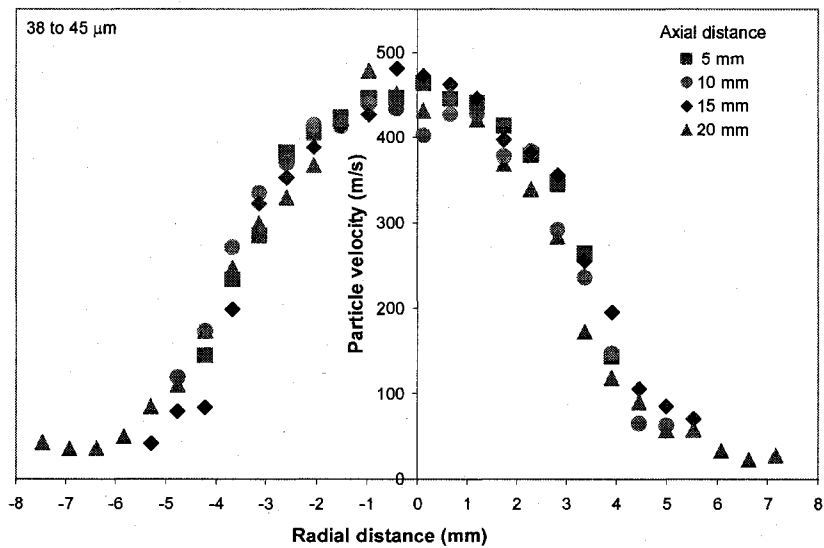


Figure B.4 Radial distribution of the axial particle velocity at several axial distances from the spray gun exit obtained by PIV for the 38 to 45 μm particle size range

Appendix C – Properties of Aluminum-Based Coatings Produced by CGDS

The properties of aluminum-based coatings produced by CGDS are summarized in tabulated form in this appendix. The coatings were produced at a gas stagnation pressure of 1.7 MPa (which corresponded to an operating pressure of 1020 kPa) and from a single pass of the substrate under the spray gun. The substrate traverse speed was 2 mm/s, unless indicated otherwise.

Table C.1 Properties of Al-13Co-26Ce coatings

Nozzle exit-to-throat area ratio	Gas stagnation temperature (°C)	Powder feed rate (g/min)	Particle velocity (m/s)	Thickness (μm)	Porosity (%)	Micro-hardness (HV _{500g})
10	200	6	530 ± 110	200	2	226 ± 12
13	200	6	549 ± 93	200	0.5	229 ± 11
13	370	6	599 ± 103	400	0.5	231 ± 10
13	370	3	605 ± 104	200	0.5	229 ± 13

Table C.2 Bond and fatigue strengths of Al-13Co-26Ce coatings

Nozzle exit-to-throat area ratio	Gas stagnation temperature (°C)	Powder feed rate (g/min)	Bond strength (MPa)	Fatigue strength (number of cycles to failure)		
13	300	4	61 ± 4	11 x 10 ⁶ at 200 MPa	6.6 x 10 ⁵ at 275 MPa	1.6 x 10 ⁵ at 350 MPa

Table C.3 Properties of Al-5083 coatings

Nozzle exit-to-throat area ratio	Gas stagnation temperature (°C)	Powder feed rate (g/min)	Particle velocity (m/s)	Thickness (μm)	Porosity (%)	Micro-hardness (HV _{500g})	Bond strength (MPa)
13	250	3	521 ± 155	300	1	117 ± 8	-
13	370	3	559 ± 135	400	1	124 ± 4	48 ± 4
13	370	1.5	571 ± 144	250	0.2	146 ± 9	46 ± 7

Table C.4 Testing array for the fractional factorial design parametric study to produce Al-12Si coatings

Test	Stand-off distance (mm)	Powder feed rate (g/min)	Substrate traverse speed (mm/s)	Substrate surface roughness (μm)
1	10	2	2	0.23
2	10	4	4	5.7
3	10	6	6	3.8
4	15	2	4	3.8
5	15	4	6	0.23
6	15	6	2	5.7
7	20	2	6	5.7
8	20	4	2	3.8
9	20	6	4	0.23

Nozzle exit-to-throat area ratio: 13

Gas stagnation temperature: 370°C

Table C.5 Properties of Al-12Si coatings

Test	Hardness ($\text{HV}_{100\text{g}}$)	Thickness (μm)	Porosity (%)	Bond Strength (MPa)
1	110	1230	0.05	37
2	112	1090	1	26
3	64	850	2	49
4	82	370	2	68
5	74	590	1	53
6	75	950	0.8	30
7	91	330	3	39
8	76	760	1	35
9	50	440	0.8	33
Average	81	734	1.3	41

Table C.6 Properties of Al-12Si coatings produced from cryomilled powder

Nozzle exit-to-throat area ratio	Gas stagnation temperature (°C)	Powder feed rate (g/min)	Thickness (μm)	Porosity (%)	Micro-hardness ($\text{HV}_{30\text{g}}$)
13	370	2	300	< 0.05	131 $\pm$ 8

Table C.7 Properties of SiC reinforced Al-12Si coatings

SiC in powder (vol. %)	SiC size (μm)	Particle velocity (m/s)	SiC in coating (vol. %)	Porosity (%)	Micro-hardness ($\text{HV}_{100\text{g}}$)	Bond strength (MPa)
0	-	559 ± 132	0	0.5	110 ± 6	49 ± 5
20	< 32	-	10 ± 2	< 1	145 ± 14	-
30	< 32	581 ± 115	14 ± 4	< 1	160 ± 16	43 ± 7
40	< 32	-	17 ± 5	< 1	185 ± 21	-
60	< 32	-	20 ± 7	< 1	202 ± 21	-
20	< 25	-	10 ± 2	< 1	147 ± 13	44 ± 8
20	< 38	-	10 ± 2	< 1	150 ± 8	-

Nozzle exit-to-throat ratio: 13

Gas stagnation temperature: 370°C

Powder feed rate: 2 g/min

Table C.8 Properties of Al-5083/B₄C coatings

Nozzle exit-to-throat area ratio	Gas stagnation temperature ($^\circ\text{C}$)	Powder feed rate (g/min)	Particle velocity (m/s)	Thickness (μm)	Porosity (%)	Micro-hardness ($\text{HV}_{100\text{g}}$)	Bond strength (MPa)
10	350	4	-	300	7	109 ± 10	-
13	350	2	563 ± 150	150	2	113 ± 12	39 ± 3
13	350	4	537 ± 152	300	4	115 ± 9	33 ± 2