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Advancing Cold Spray for Additive Manufacturing: A Study on Particle Morphology, Gas Nature, and Particle Preheating

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Abstract

This investigation aims to understand and improve the deposition quality and rates of cold spray for additive manufacturing in a way that is economically sound and without the detrimental temperature effects seen in traditional metallic additive manufacturing processes. It focuses on materials that are desired by the additive manufacturing community and built upon the current knowledge in cold spray. This thesis is presented as a collection of published, or soon to be published, manuscripts accompanied by an introduction, literature review, and conclusion.

The effect of a non-spherical particle morphology was the first objective investigated. Titanium has been shown repeatedly to require pure helium at very high temperatures and pressures to get dense coatings, however, the unique coral-like morphology resulting from the Armstrong Process was revealed as a key to successful deposition with nitrogen. Using low pressure cold spray, under conditions that would be considered mild, a deposition efficiency of 100% and a porosity of nearly 0% was achieved. This is a promising approach for cold spray as a method for additive manufacturing of titanium parts. The low powder cost and the advantages of additive manufacturing could allow for a substantial cost savings in titanium part production when compared to traditional manufacturing methods. With these cost saving advantages, additive manufacturing of titanium using Armstrong process powder and CS could lead to a paradigm shift of titanium production, allowing titanium to enter markets that under traditional methods would be far too expensive.

Unfortunately, this unique powder morphology was not available in other materials. To address the low deposition efficiency of the other metals of interest, such as aluminum and stainless steel, the concept of mixing the propellant gas was introduced in the second objective. Considering the relative costs of gases, powder, electricity, and labour, the second paper focuses on the concept of optimizing the amount of helium to produce the minimum component cost. It was found that for the specific stainless steel and aluminum alloy powders discussed, costs could be reduced by 44% and 59%, respectively, using the gas mixing system. However, no cost saving was found for the most inexpensive of the powders, pure aluminum.

For gas mixing to be effective, the cost of helium must be offset by the cost of the powders. Therefore, low-cost powders, such as pure aluminum, results in pure nitrogen as the least expensive option. This however doesn't address the low deposition efficiency that is preventing its adoption in cold spray additive manufacturing. The third objective addresses just this, an improvement in deposition efficiency without the introduction of expensive helium. In this study, aluminum particles were preheated using a novel particle preheater that does not clog. This resulted in a deposition efficiency increase of 260% with a minimal increase in electrical costs.

These three objectives, while studied and published separately, all relate to the purpose of this work to improve the process economics without detrimental temperature effects. These findings have been (or will be) published in international peer reviewed journals to add to the collective knowledge.

Preface

A statement regarding the contributions of myself and my co-authors to each of the articles presented in this thesis submission is provided below.

I am the primary author of ***“Cold Spraying of Armstrong Process Titanium Powder for Additive Manufacturing”*** alongside Dr. Ruben Fernández, Dr. Francesco Delloro, and Dr. Bertrand Jodoin. I have contributed directly to this work by planning and executing all work, excluding the finite element modelling. Dr. Ruben Fernández contributed by providing the finite element modelling of the impacts. Dr. Francesco Delloro contributed by providing the image treatment procedure to provide real cross-sectional morphology for the finite element modelling. Dr Bertrand Jodoin, my PhD Thesis Supervisor, guided me through my experimental design and provided insights on my results and discussion. He was also integral in ensuring the quality of the manuscript through his careful review prior to submission. All co-authors of this paper have agreed that I have been the one to produce this work including all the writing, submission, and revision.

I am the primary author of ***“An Economical Approach to Cold Spray Using In-line Nitrogen-Helium Blending”*** alongside Dr. Saeed Rahmati, Dr. Bertrand Jodoin, and Mr. Wally Birtch. I have contributed directly to this article by planning and executing all work found within. Dr. Saeed Rahmati aided throughout the experimental process, acting as the second pair of hands required to operate the gas mixing apparatus and the cold spray system simultaneously. He was also invaluable in helping me process the large number of samples required for characterization. Mr. Wally Birtch aided in the design and manufacturing of the in-line gas mixing apparatus used in this study. Dr Bertrand Jodoin, my PhD Thesis Supervisor, guided me through my experimental design and provided insights on my results and discussion. He was also integral in ensuring the quality of the manuscript through his careful review prior to submission. All co-authors of this paper have agreed that I have been the one to produce this work including all the writing, submission, and revision.

I am the primary author of ***“Independent Control of Particle Temperature and Velocity using a Novel Powder Preheater Design for Low Pressure Cold Spray”*** alongside Dr. Bertrand Jodoin. I have contributed directly to this article by planning and executing all work found within. Dr Bertrand Jodoin, my PhD Thesis Supervisor, guided me through my experimental design and provided insights on my results and discussion. He was also integral in ensuring the quality of the

manuscript through his careful review prior to submission. Dr. Bertrand has agreed that I have been the one to produce this work including all the writing, submission, and revision.

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Table of Contents

Abstract.....	ii
Preface	iv
Table of Contents	vii
List of Tables	ix
List of Figures	x
Abbreviations	xi
1 Introduction	1
1.1 Background	1
1.2 Motivation and Objectives.....	2
1.3 Outline of the Thesis	3
2 Literature Review	5
2.1 Additive Manufacturing	5
2.1.1 Metal Additive Manufacturing.....	6
2.1.2 Additive Manufacturing of Titanium.....	7
2.1.3 Additive Manufacturing of Aluminum and Aluminum Alloys	8
2.1.4 Additive Manufacturing of Stainless Steel	9
2.2 Cold Spray	9
2.2.1 The Fundamentals.....	11
2.2.2 The Critical Velocity.....	13
2.2.3 Influence of the Cold spray Process Parameters	15
2.2.4 Effect of Feedstock Powder	21
2.2.5 Cold Spray of Titanium	29
2.2.6 Cold Spray of Aluminum and Aluminum Alloys	29
2.2.7 Cold Spray of Stainless Steel	30
3 Research Objectives.....	31
3.1 The Effect of Non-Spherical Particle Morphology on the CSAM Process	31
3.2 The Effect of Blended Process Gas Nature on the CSAM Process	33
3.3 The Effect of Independent Particle Preheating on the CSAM Process	34
4 Research Approach and Experimental Design	37

4.1	The Effect of Particle Morphology on the CSAM Process	37
4.1.1	Materials	37
4.1.2	Cold Spray Process	37
4.1.3	Sample Characterization and Particle Velocity Measurement	38
4.1.4	Modeling of Particle Impact Dynamics	39
4.1.5	Post-Processing Heat Treatment	40
4.1.6	Mechanical Testing	40
4.2	The Effect of Process Gas Nature on the CSAM Process	41
4.2.1	Materials	41
4.2.2	Cold Spray Process	42
4.2.3	In-Line Nitrogen-Helium Blending.....	43
4.2.4	Sample Characterization and Particle Velocity Measurement	45
4.2.5	Cost Model.....	46
4.3	The Effect of Independent Particle Preheating on the CSAM Process	48
4.3.1	Materials	48
4.3.2	Cold Spray Process	50
4.3.3	Particle Preheating Trials	50
4.3.4	Equivalent Enthalpy Trials.....	52
4.3.5	Deposition Characterization and Particle Velocity Measurement.....	53
4.3.6	Computational Fluid Dynamics	54
5	Results and Discussion	60
5.1	Research Project 1: The Effect of a Non-Spherical Particle Morphology on the CSAM Process	60
5.2	Research Project 2: Effect of Blended Propellant Gas on the CSAM Process.....	73
5.3	Research Project 3: Effect of Particle Preheating on the CSAM Process	87
6	Conclusions and Future Work.....	114
	References	116

List of Tables

Table 1: CS Parameters during Testing	38
Table 2: Powder Information	42
Table 3: Pertinent CS Parameters	43
Table 4: Flow Rate of Helium for Helium Percentages at Set Deposition Parameters	45
Table 5: Pertinent CS Parameters	50
Table 6: Auxiliary Gas Temperatures Required for Desired Particle Temperatures	52
Table 7: Boundary Conditions for 12 Different Preheating Scenarios	56
Table 8: Boundary Conditions for Particle Preheater Model.....	57

List of Figures

Figure 1: Diagram of SLM process (a) and powder fed DED process (b) (Ref 1).....	6
Figure 2: Schematic of a CS system.....	10
Figure 3: Schematic showing the difference between HPCS (a) and LPCS (b) (Ref 52).	11
Figure 4: (a) A single copper particle after impact with a copper substrate, showing extensive plastic deformation and (b) modeling results of a copper particle impacting a copper substrate showing the progression of deformation with time for two velocities. Modified from (Ref 7).....	12
Figure 5: DE, cohesive strength, and flattening ratio as a function of particle impact velocity quotient (η) for different copper particles sizes (indicated by different dots) under different deposition conditions (Ref 71).....	15
Figure 6: Impact velocity (solid) and exit velocity (dotted) of copper particles of different diameters under set processing conditions (Ref 71).	22
Figure 7: Estimated critical (minimum) diameter required for bonding for different powder materials utilized in CS applications (Ref 6).....	23
Figure 8: An example of how critical velocity and particle impact velocity change with particle size (Ref 6).	25
Figure 9: Effect of particle diameter on particle temperature of copper particles inserted into the high temperature subsonic region of the CS nozzle (Ref 10).	26
Figure 10: Modelling results of chromium carbide-nickel chromium cermet powders with different morphologies. a) Stress field upon impact of dense spherical particles produced with atomization showing redistribution of stresses and low plastic deformation. b) Plastic equivalent strain of an agglomerated and sintered particle showing a high level of plastic deformation (Ref 104).	28
Figure 11: SEM image of coral-shaped titanium powder produced using the Armstrong process.....	32
Figure 12: Dimensions of tensile test specimens (in mm).	41
Figure 13: Process flow diagram showing inline gas mixing.	43
Figure 14: The flow rate (SCFM) of helium required for a volume percentage of helium (throat diameter=2mm, $P_o = 3.4$ MPa and $T_o = 500^\circ\text{C}$).	45
Figure 15: Particle size (diameter) distribution (numerical) of the aluminum powder.	49
Figure 16: SEM overview image of powder (A) and SEM image of powder cross section (B).	49
Figure 17: Schematic of particle preheating system.....	51
Figure 18: Schematic of custom injection system to inject hot gas without preheating the particles for the equivalent enthalpy trials.	53
Figure 19: A 2D representation of the 3D computational domain dimensions for the cold spray nozzle. Red shows inlets and outlets. Blue is the auxiliary gas inlet and is not present for the preheated particle model. Not to scale. All dimensions in mm.	55
Figure 20: A 2D representation of the 3D computational domain dimensions for the powder preheater model. Red shows inlets and outlets. Not to scale. All dimensions in mm.	57

Abbreviations

Abbreviation	Definition
AM	Additive Manufacturing
ASI	Adiabatic Shear Instability
CFD	Computation Fluid Dynamics
CS	Cold Spray
CSAM	Cold Spray Additive Manufacturing
CSM	Cold Spray Meter
CGDS	Cold Gas Dynamic Spray
DE	Deposition Efficiency
DED	Directed Energy Deposition
DRW	Discrete Random Walk
EBM	Electron Beam Melting
EOS	Equation of State
HIP	Hot Isostatic Pressure
HPCS	High Pressure Cold Spray
LPCS	Low Pressure Cold Spray
MN	Numeric Mean
MV	Volumetric Mean
PBF	Powder Bed Fusion
PFR	Powder Feed Rate
PM	Powder Metallurgy
SEM	Scanning Electron Microscope
SLM	Selective Laser Melting
UTS	Ultimate Tensile Strength

1 Introduction

The world of manufacturing is rapidly changing with the growing popularity of 3D printing. The demand for cost-competitive solutions to produce 3D printed metallic components is growing daily. Metals such as titanium, aluminum, and stainless steel have drawn great interest in the community but struggle to find wide stream adoption using the popular printing methods. This thesis explores an alternate process to fill this role and investigates several solutions to advance the viability of that technology.

1.1 Background

Additive manufacturing (AM) is the term adopted for 3D printing of industrial functional components. AM differentiates itself from conventional manufacturing in that it employs the layered addition of material to produce three dimensional parts instead of a bulk process (e.g., casting or forging) or material removal (e.g., machining). There are two main benefits that AM has over conventional methods. The first benefit being free complexity; the creation of high complexity components does not necessarily increase production costs. The second benefit is on demand customizability; each component produced can have different geometry with minimal increase in production time and cost (Ref 1). Current metallic AM technologies, including selective laser (or electron beam) melting and directed energy deposition, are gaining some level of commercial success, however they suffer from detrimental effects that limit their widespread commercial use. These technologies require high temperature processing and have low production rates. The high temperature leads to component distortion, uncontrolled phase transformations, undesirable residual stresses, non-uniform mechanical properties, and excessive chemical contamination (Ref 1–3). The slow production rates increase component cost and lead time substantially.

Cold gas dynamic spraying, or cold spray (CS), is a solid-state thermal spray process traditionally used for coatings, dimensional restoration, and repairs. Over two decades of fundamental studies (Ref 4–12) have established the theoretical principles of the process; which has led to the development of commercial equipment and applications (Ref 13–16). While no longer considered a novel thermal spray process for coatings and repairs (Ref 17–20), it is still in its infancy as an AM process (Ref 21–29). Cold spray additive manufacturing (CSAM) could be used as a direct

process for the production of metallic components, taking advantage of the low temperatures (below melting) and large deposition rates possible with CS systems (up to 500 grams/minute (Ref 30)). This rate is an order of magnitude larger than the current fastest powder based AM technology (83 grams/minute (Ref 31)). The CS process also results in high adhesion to the substrate (Ref 32), which could be used to fabricate extensions on existing parts. Another advantage of the CS process over the powder bed methods is that components are not limited by tray size.

However, the particle velocities required for the production of quality components in CS often demands the use of helium in high quantities (Ref 32–38). Helium's high cost and unstable supply limit its viability for most applications. Using nitrogen at very high temperatures and pressures can also be employed to attain similar particle velocities (Ref 32–38), but these extreme stagnation conditions can lead to degradation of the properties of the previous deposited materials or underlying components, as well as substantially increase CS gun complexity and shorten equipment lifespan. ***The purpose of this investigation is to understand and improve the deposition quality and rates of CSAM in a way that is economically sound and without detrimental temperature effects.*** It is hypothesized that the processing conditions and the feedstock materials can be the keys to improve these metrics and promote the adoption of CS in the AM world.

1.2 Motivation and Objectives

The motivation of this work lays in expanding the potential of CS as an AM technology by addressing the two main drawbacks of conventional powder bed and directed metal deposition AM – high temperature processing and long and expensive build times. CS can employ much lower temperatures and much higher deposition rates compared to these AM technologies. However, the adoption of CSAM is currently limited, as it itself often requires excessively high temperatures and expensive helium to produce high quality components at high deposition rates. ***The motivation of this research will be to improve the deposition rates and deposition quality of CS while minimizing process cost and operating temperatures.***

To achieve the motivation outlined in this discussion, the following three objectives are proposed. Each objective has a primary statement that highlights the proposed broad

contribution of the research to the fundamental science. The secondary statement, in italics, more specifically highlights the engineering and industrialization contribution of the research.

Objectives:

1. Study the effect of a non-spherical particle morphology on the CSAM process.
Investigate and understand the deposition behavior of unique particle morphology for titanium, one of the most desired metals for AM.
2. Study the effect of blended propellant gas on the CSAM process.
Develop and test a gas blending system and create a protocol to improve process economics.
3. Study the effect of particle preheating on the CSAM process.
Develop and test a particle preheating system for low pressure cold spray that can overcome the current engineering roadblocks through independent particle temperature control.

The three objectives outlined are presented in the form of manuscripts, all with the same goal of progressing the science and engineering of CSAM. This investigation alone is not a comprehensive solution to all issues surrounding CS as an AM process, but is part of a bigger framework in understanding CS – as each of these objectives directly fills a gap in our collective knowledge.

1.3 Outline of the Thesis

The presented thesis has been formulated into six chapters. The present chapter (Chapter 1) describes the relevant background information for the proposed study. It also presents the motivation for the investigation and the main objectives of the research.

In Chapter 2, the relevant literature is reviewed, with a strong focus on fundamentally understanding the CS process. A brief explanation of the fluid dynamics of the process is presented and a detailed review of the current theories of adhesion and deformation upon impact is described. This chapter clearly outlines how each of the parameters affects the

deposition process. This chapter also outlines some basics of the traditional AM process, their shortcomings, and highlight the desire for AM.

Chapter 3 describes the main and specific objectives of this investigation. It expands upon the literature to introduce and outline the motivation of the specific objectives and how meeting these objectives should help advance CS for AM.

Chapter 4 provides details of the experimental methodology followed and the research approach taken. For each investigation, the pertinent information such as materials, process equipment and parameters, characterization techniques, and modeling details are presented.

Chapter 5 presents the results and discussion of each experiment. The chapter is structured in the form of three self contained investigations. Each investigation addresses one of the main research objectives and is either published or in the process of being published in a peer reviewed journal.

Finally, Chapter 6 summarizes the main conclusions of each investigation and links them together, highlighting their contributions to the adoption of CSAM. This chapter also provides suggestions of future work to further improve the understanding and promote CSAM.

2 Literature Review

This section summarizes the relevant literature on the subject matter. It provides context of why and how the objectives were chosen, as well as provide a comprehensive knowledge base to understand the approach and significance of each of the investigations.

2.1 Additive Manufacturing

AM is a recent, more formalized, term for what is commonly known as 3D printing or rapid prototyping. The name change itself demonstrates the advancement of the technology - from the production of non-functional prototypes to direct manufacturing of end-use components. The basic principle of the technology is that components are manufactured through the addition of material, typically done by adding layers, with each layer being a thin cross section of the part. There are many benefits to AM, most falling into two main categories.

One benefit seen in AM is free complexity. In conventional manufacturing processes, added complexity requires additional time, equipment, and resources. Therefore, designs must be simplified and streamlined for the manufacturing processes and not necessarily optimized for the application. This restriction does not exist within AM and is one of the key benefits of the technology. This free complexity can be advantageous in many ways, particularly in weight reduction and part consolidation. To truly take advantage of this benefit, considerable thought must be taken at early design stages.

The other main benefit of AM is mass customizability/on-demand production. For traditional manufacturing processes, it is typically required for each piece to be identical and produced in large numbers to be economically feasible. For AM, this requirement is lifted; each component can be customized at no extra manufacturing cost and produced in any quantity. This allows the product to be designed for the needs of the individual consumer, as well as reducing time to market, reducing overhead and storage, and reducing supply chains, transportation costs, etc.

2.1.1 Metal Additive Manufacturing

The recent shift in AM from the prototypes to end-use components was due to the advancement of the technology to be able to produce metal components. This advancement was spurred on by the availability of high energy concentration heat sources (e.g., lasers and electron beams) and the breakthroughs in the production of high purity metallic powders.

The most common type of AM for metals is powder bed fusion (PBF). All PBF processes share a common basic set of characteristics; a high energy thermal source induces fusion between powders that are spread layer by layer. The heat source for metal PBF is typically a laser or electron beam, known as selective laser melting (SLM) (shown in Figure 1(a)) or electron beam melting (EBM), respectively (Ref 1).

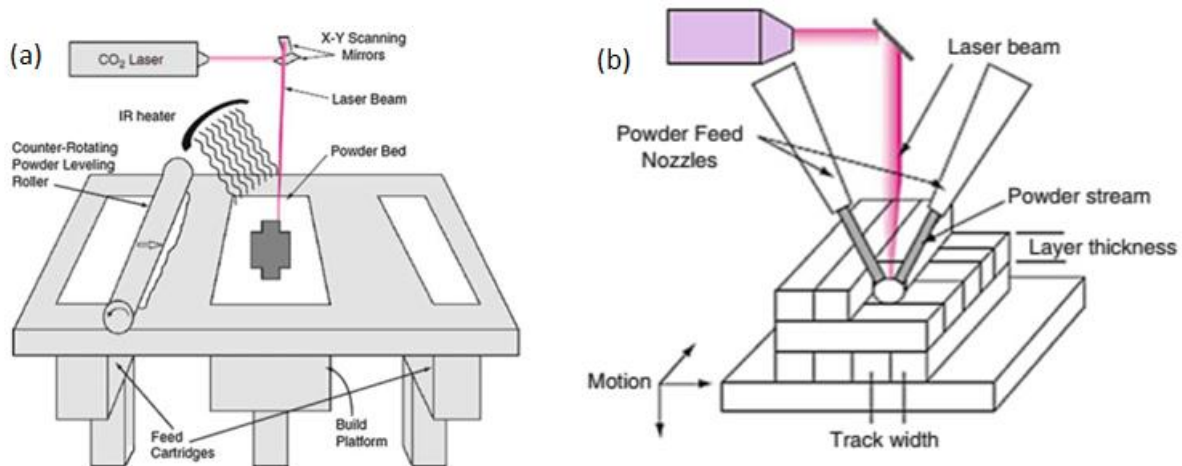


Figure 1: Diagram of SLM process (a) and powder fed DED process (b) (Ref 1).

Another, less common, category of metal AM is directed energy deposition (DED). In this production method, the creation of parts is done by simultaneously feeding and melting feedstock materials. The heat source can be a laser, electron beam, or an electrical arc. These processes have many names, but typically fall into two categories, powder fed (shown in Figure 1(b)) and wire fed. The wire fed DED processes, currently, have the fastest built rates of any of the metal AM technologies outside of CS.

These processes all suffer from the same detrimental effects; they require high temperature processing (melting) and suffer from low deposition rates. The high temperature can lead to component distortion, uncontrolled phase transformations, undesirable residual stresses, non-uniform mechanical properties, and excessive chemical contamination. The low deposition rates can increase component cost and lead time substantially (Ref 1).

2.1.2 Additive Manufacturing of Titanium

Titanium is the 9th most abundant element on earth, has one of the highest specific strengths for a pure metal, maintains good properties at elevated temperatures, and has excellent corrosion resistance. However, the high cost to produce titanium components limits its use to high-end applications where cost is not a primary factor, usually in the aerospace, defense and medical sectors (Ref 39,40). This high cost is the result of two factors: the production of titanium mill product from primary materials requires many costly steps and its reactivity and poor workability make it difficult to cast, forge, and machine (Ref 39).

Typically, titanium is converted from raw primary materials (such as rutile) to titanium sponge through the Kroll Process (Ref 39). It must then be purified through acid leaching and undergo vacuum arc remelting to form an ingot. The latter must then undergo primary fabrication into mill products, casting to a near net shape (Ref 39), or atomized into powder form. Forging is difficult and expensive, requiring many steps and various heat treatments; only rarely is titanium directly forged into finished components. Casting is also possible but challenging due to the materials high reactivity to the atmosphere and to the other refractory materials common in the casting process. Near net shapes can be produced using casting often with a combination of Hot Isotactic Pressing (HIP) and traditional machining, but are limited in scope due to the production costs. As a result of these limitations, components are often produced through machining from large stock, which results in material losses of up to 90% for aerospace parts which accounts for over 60% of the final part costs. Even this traditional machining is difficult as titanium has a tendency for seizing and galling (Ref 40). Due to these cost factors, far less titanium is used in production applications than expected (Ref 39).

AM has recently been used to alleviate some of these cost problems (Ref 1,39,40). It is possible to fabricate intricate parts with good surface finishes with processes such as EBM (Ref 1,41,42)), however, this process is currently limited by a manufacturing rate of 6 grams/minute at the very high end for titanium (modified from (Ref 43,44) using a density of titanium of 4.51g/cm^3 (Ref 39)). This deposition rate leaves much room for improvement. The printed parts also suffer from poor dimensional tolerances and surface finish when compared to machined or cast parts (Ref 45), as well as having a non-uniform grain structure due to uneven melting and heating (Ref 46). The size of these components is also limited to the size of the powder bed and inert environment chamber (Ref 1,41,42).

In most cases, titanium components produced using AM methods require HIP processing (Ref 1,47). By simultaneously applying pressure and temperature to the parts, consolidation of the pores is possible. However, HIP processing significantly affects the final component volume and geometry. This must be considered during the design stages and modeling continues to be a great challenge to accurately predict HIP shrinkage for AM parts. Furthermore, the properties of HIP processed parts are usually found to be coarser than desirable and additional heat treatments are required. Lastly, the majority of these methods currently require the use of expensive, gas atomized, powders. As a result of these downsides, AM of titanium is often limited to small, non-structural components with low quality requirements (Ref 39).

2.1.3 Additive Manufacturing of Aluminum and Aluminum Alloys

Aluminum, and its alloys, offer a high specific strength alternative to titanium at a much lower cost. Aluminum's low density combined with the potential benefits of AM make it an excellent candidate for aerospace applications. However, aluminum faces many challenges when it comes to AM by SLM; often the powder do not flow easily causing issues when spreading a thin layer, the particles reflect up to 91% of the laser energy, the high thermal conductivity results in steep cooling rates and crack formation, strict requirements for the vacuum chamber are necessary due to the oxidative behavior of aluminum, and lastly, the high thermal expansion coefficient results in high levels of residual stress in the parts (Ref 48,49). These challenges substantially reduce the adoption of AM for aluminum and its alloys in the current market.

2.1.4 Additive Manufacturing of Stainless Steel

Steel is the most common engineering material on the planet, accounting for over 80% of all manufactured metal goods (Ref 2). Unlike titanium and aluminum, steel is heavy, so the benefits of topology optimization for weight reduction through AM could be substantial. However, very little production of steel AM parts is being done. Currently, the main draw back of using steel for AM is the cost, as the AM process is expensive when compared to traditional manufacturing. This substantially reduces the potential market for steel AM components. Steels also have their own challenges in AM. Firstly, only stainless steel can be processed due to the rapid oxidation of the powders. Fast cooling rates and high thermal expansion results in residual stresses, pore formation, and anisotropic properties (Ref 2,3). To reduce these flaws, high temperature heat treatment must be performed on the components after manufacturing (Ref 3).

2.2 Cold Spray

CS is not commonly listed as an AM process, however, the concept is very similar to DED processes, but without the disadvantages of excess temperature and slow build rates. CS was originally developed as a metallic coating technology that falls under the broad category of thermal spray. As a thermal spray technology, cold spray is unique in that it relies mostly on the kinetic energy of particles to form coatings instead of thermal energy. In CS, micron sized particles are injected into a high velocity gas stream that is produced through a pressure differential across a converging/diverging nozzle (Ref 4,50,51) (see Figure 2). Drag forces accelerate the particles to high velocities prior to expulsion from the nozzle exit, where they subsequently impact a substrate positioned a short distance away. This high energy impact results in plastic deformation, of both the impacting particles and substrate (or previously deposited particles), which can initiate mechanical and chemical adhesion. The accumulation of these particles results in dense, uniform deposits.

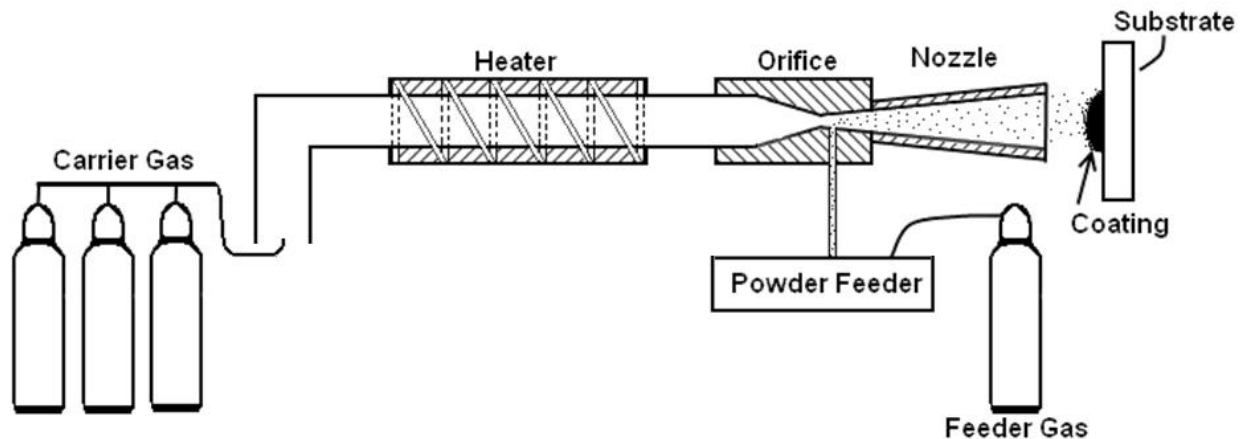


Figure 2: Schematic of a CS system.

The advantage of CS over other thermal spray and AM processes, lays in the name, the process is relatively cold. Other processes operate with temperatures that typically exceed the melting temperatures of the materials involved. These high temperatures result in particle melting; which is desirable in some situations but can lead to degradation of the materials, entrapment of porosity, excessive oxidation, and uncontrolled/undesirable microstructures during cooling. In addition, the excess heat in these processes results in thermal stresses and warping, which limits the thickness of the depositions. In contrast, CS operates below the melting temperature of the materials involved. This ensures that the particles and substrates involved remain solid state and don't suffer from high oxidation, changes in bulk microstructure, or excessive thermal/residual stresses. Additionally, since substantial plastic deformation is a requirement for adhesion, it ensures that deposits have a relatively low porosity level compared to other thermal spray processes. These high purity, low porosity, deposits also are not limited in thickness, which is the key to their potential in CSAM. (Ref 4,5).

In CS, there are two approaches used to inject the particles into the accelerating flow; the most common being upstream (high pressure) injection (HPCS), in which a flow of carrier gas and particles is injected axially in the high pressure/low velocity zone upstream of the nozzle throat. The advantage of this system is that the particles are exposed to the high temperature gas for an extended period of time. The other method of particle insertion is downstream (or low pressure) injection (LPCS) where the carrier gas and particle mixture is injected downstream of the throat

in the high velocity/low pressure section of the nozzle. The advantage of this system is that the particle feeding mechanism is greatly simplified and clogging of the throat area is eliminated, however the particles are only exposed to the gas after expansion, which is at a much lower temperature. The differences can be seen in Figure 3.

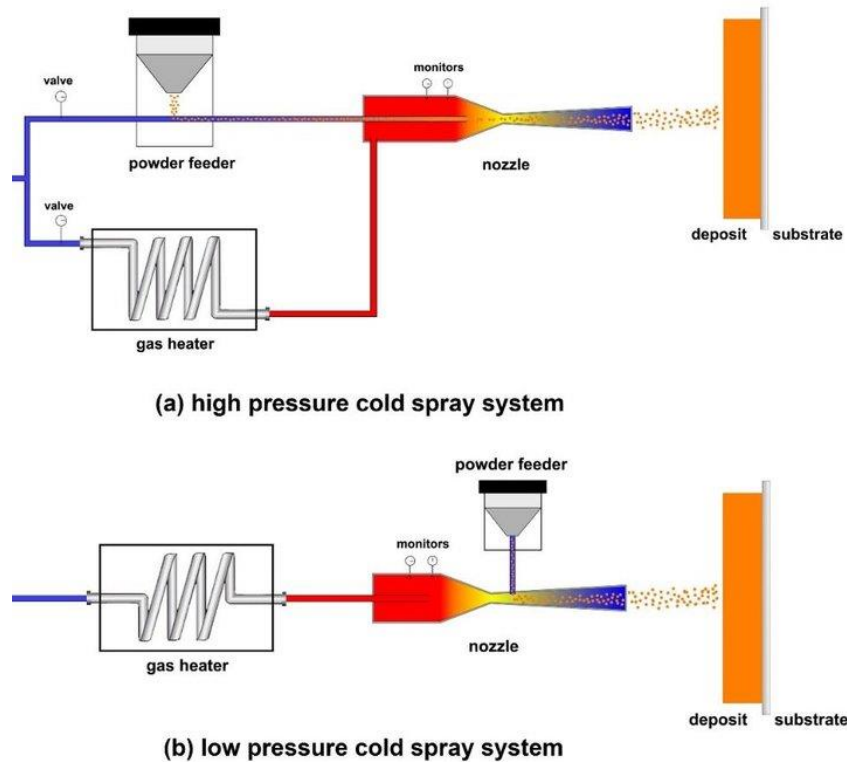


Figure 3: Schematic showing the difference between HPCS (a) and LPCS (b) (Ref 52).

2.2.1 The Fundamentals

In less than a few hundred nanoseconds from initial contact, the high speed particles must completely come to a stop and adhere to the substrate (Ref 53,54). During this short time, the kinetic energy is completely transformed into viscoplastic deformation, stored elastic energy, and thermal energy. The proportion of energy converted to heat increases at high strain rates; with up to 90% under typical cold spray conditions (Ref 55). Due to the short time scales, heat transfer inside the particle is limited, resulting in large increases of local temperature in the zones undergoing deformation. This increase of temperature results in thermal softening, reducing the materials capacity to withstand shear forces. Under the right conditions, localized thermal

softening can outpace strain hardening effects – leading to a state of rapid strain with dropping stress – a phenomenon known as adiabatic shear instability (ASI). These high levels of plastic deformation (shown in Figure 4(a)) are thought to provide the removal of oxide layers and consequently deliver clean metal-to-metal intimate contact zones that are required to achieve metallic bonding. It is currently debated whether ASI is necessary for this intimate contact to occur (Ref 56–58), but using the onset of ASI as a criteria for bonding appears frequently in the literature and often matches empirical data (Ref 6,7,58).

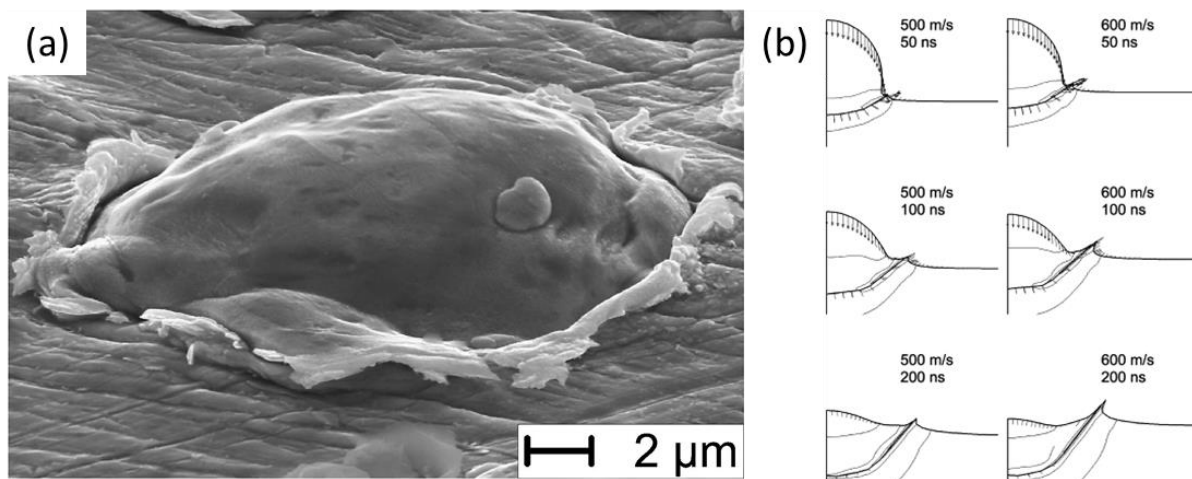


Figure 4: (a) A single copper particle after impact with a copper substrate, showing extensive plastic deformation and (b) modeling results of a copper particle impacting a copper substrate showing the progression of deformation with time for two velocities. Modified from (Ref 7).

When discussing adhesion mechanisms in cold spray, typically metallic bonds are discussed and desired. In a metallic bond, the valence electrons from adjacent atoms are shared in a common cloud. The magnitude of attractive or repulsive forces on two isolated atoms depends on interatomic distances and atomic charge. The contacting of oxide-free surfaces under high pressure developed during impact allows the valence electrons from both materials to cross each other's sphere of influence, resulting in the creation of this metallic bond. The bond is non-directional in nature as the cloud of free electrons shields the positively charged ion core from mutually repulsive electrostatic forces (Ref 59).

While metallic bonds are often present and desired, they are not necessarily the only mechanism for particle deposition. Particles may adhere through mechanical means; known as mechanical interlocking or mechanical bonding. In this case, there is a physical connection between two

materials in contact through the linkage of common surface features. Its presence is known to increase adhesion and in some cases has been shown to be responsible for the majority of the tensile strength of a bond (Ref 60). In addition to the commonly seen mechanical bonding resulting from the substrate surface finish, another type of mechanical bonding is sometimes seen in which the two materials deform so heavily that intermixing of material vortices can occur resulting in high adhesion strength (Ref 61).

2.2.2 The Critical Velocity

Particles that impact at higher velocities are more likely to develop zones of high plastic deformation (demonstrated in Figure 4(b)), which can result in intimate contact of oxide-free surfaces promoting metallic or mechanical bonds. The velocity at which this occurs is the basis for the most fundamental concept in cold spray; the existence of a critical velocity. This is the minimum impact velocity of an individual particle that must be exceeded for adhesion to occur (Ref 50,62–66). This velocity is not necessarily a material constant, although it is often treated as such. This value can be influenced by the material properties of both the particle and the impacted material, the particle's size, the particle's morphology, and the particle/substrate temperature. Hassani-Gangaraj et al. clearly demonstrated this definition of critical velocity in their work using in-situ observations of single impacts (Ref 67). In this study, each individual particle was fully characterized (microstructure, chemical composition, size, velocity, and temperature) and substrate conditions were known. However, to achieve this level of detailed observation, a laser-induced projectile impact test was used. The conditions of the particles in the LIPIT test differs greatly from the particles in a real cold spray gas plume - where differences in particle size, shape, microstructure, chemical composition, and flight history can occur. Therefore, measuring and defining a critical velocity for a specific powder under true cold spray conditions is a challenge. As a practical approach, some authors take the critical velocity as the mean velocity of particles in which 50% of the particles adhere to the substrate (Ref 6,68), while others may take it as the velocity of the largest particles to adhere (Ref 7,69,70). For this work, when discussing critical velocity, the exact definition will be used.

While an analytical solution to determining critical velocity may not be possible at this time, Assadi et al. proposed the following equation to estimate critical velocity by matching a model to experimental results for copper (Ref 71),

$$v_{crit} = k_1 \sqrt{c_p(T_m - T_p) + 16 \frac{\sigma}{\rho_p} \left(\frac{T_m - T_p}{T_m - 293} \right)} \quad (\text{Eq.1})$$

where c_p is constant specific heat of the material, T_m is the melting temperature of the particle, T_p is the impact temperature of the particle, σ is the tensile strength of the particle at 293K, ρ_p is the density of the material, and k_1 is a particle-size-dependent fitting parameter. While this equation is only truly applicable to copper particles in a certain size range, it is thought that all materials fall under a similar equation with different constants. What should be learned from this empirical relation is that as particle impact temperature increases, the critical velocity decreases.

When discussing the quality or the “optimization” of cold spray deposits, the final industrial implementation must be a consideration. The process should be tailored to each application to prioritize desired characteristics. However, in general, the quality of a cold spray deposit can be quantified using characteristics such as porosity, tensile strength, adhesion strength, particle flattening ratio, hardness, etc. (Ref 14,54). In addition to these measurables, one of the most important quantities in the cold spray processes is the deposition efficiency (DE). DE is defined as the percentage of material that is propelled at the substrate that amalgamates into the deposit, similar to the powder capture efficiency in the DED AM process (Ref 1). The DE directly regulates the deposition rate and in turn determines the process economics; such as spray time, gas consumption, electricity costs, maintenance costs, and labour costs. DE also determines the amount of wasted feedstock powder, assuming that the powder is not 100% recyclable. Fortunately, both the coating quality characteristics and the DE are interrelated effects, whereas the conditions imposed to improve one typically improves the other.

However, in contrast to this there have been cases where DE and coating quality indicators are inversely correlated, like in the work of Jenkins et al. (Ref 72), where they demonstrated that purposefully lowering the DE during deposition of aluminum decreased the porosity levels. Examples like this take place at very low DEs and are not common for the CSAM process; however this phenomenon could be explored and exploited to produce high density deposits under conditions typically unsuitable for CS.

While the critical velocity itself may provide information on the minimum requirements for adhesion, depositing under these conditions may not be ideal for AM. It has been known since

the conception of CS that as the particle impact velocity rises, the quality of the deposit and the DE also tend to increase (Ref 38,54,71). It has been shown this is not solely due to increasing particle velocity, but due to increasing particle velocity in relation to critical velocity. Conveniently, Assadi et al. have defined this normalized parameter as the particle impact velocity quotient (η) (Ref 71);

$$\eta = \frac{v_{pi}}{v_{cr}} \quad (\text{Eq.2})$$

where v_{pi} is the particle's impact velocity and v_{cr} is the particle's critical velocity. It has been demonstrated that an increase in the impact velocity quotient increases DE and coating quality characteristics such as flattening ratio and tensile strength (Ref 38,54,71). An example of how this quotient can be useful can be seen in Figure 5. While determining the exact critical velocity for every particle is impossibly difficult, what this demonstrates is that to increase DE and coating quality, one should not only focus on increasing the particle impact velocity but also decreasing critical velocity.

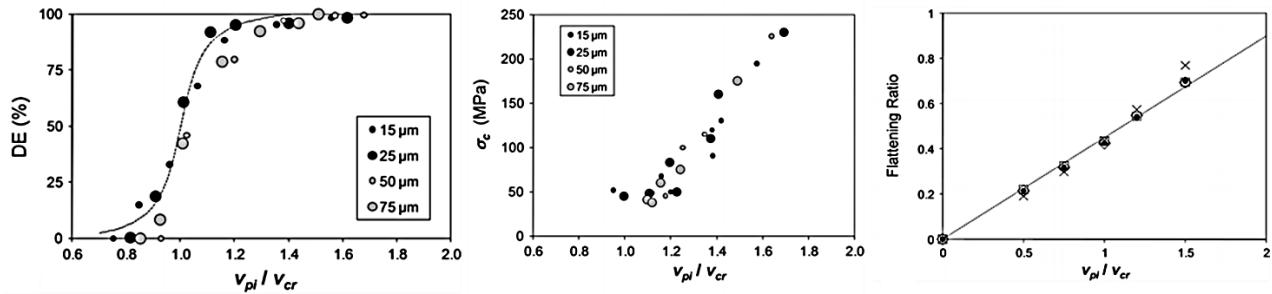


Figure 5: DE, cohesive strength, and flattening ratio as a function of particle impact velocity quotient (η) for different copper particles sizes (indicated by different dots) under different deposition conditions (Ref 71).

The following sections aim to provide a comprehensive understanding on how and why different conditions and parameters influence the cold spray process, the particle impact velocity quotient, and in turn, DE and quality of the final product.

2.2.3 Influence of the Cold spray Process Parameters

The cold spray system, whether a commercial version or in house build, typically has standard set of controllable parameters. The nature of the propellant gas, the stagnation temperature of the gas, the stagnation pressure of the gas, the geometry and material of the nozzle, the velocity

and distance of the substrate in relation to the nozzle exit, and the temperature of the injected particles are all potentially controllable parameters.

2.2.3.1 The Nature of Propellant Gas

To understand how any of the cold spray parameters affect the particle velocity, one must examine the momentum transfer between the accelerated gas and particles. This can be simplified into a 1D drag equation,

$$m \frac{dV_p}{dt} = \frac{1}{2} \rho (V - V_p)^2 C_d A_p \quad (\text{Eq.3})$$

where m is the particle mass, V_p is the particle velocity, t is time, ρ is the propellant gas density, V is the propellant gas velocity, C_d is the drag coefficient, and A_p is the particle cross sectional area. This shows that an increase in the gas velocity should increase the particle velocity, up until the point where the particle is travelling at the same velocity as the gas. For simplicity, the gas velocity at any point is evaluated using the Mach number and the speed of sound at that point,

$$V = M \sqrt{kRT} \quad (\text{Eq.4})$$

where M is the gas local Mach number, R is the specific gas constant, T is the local gas temperature, and k is the gas heat capacity ratio. This relationship demonstrates that the gas velocity, and ultimately the particle velocity, can be greatly influenced by the molecular weight of the propellant gas, as the molecular weight influences both the specific gas constant and the heat capacity ratio. The specific gas constant is a function of the molecular weight of the propellant gas,

$$R = \frac{\bar{R}}{M^*} \quad (\text{Eq.5})$$

where $\bar{R}$ is the universal gas constant and M^* is the molar mass of the gas. The heat capacity ratio is defined as,

$$k = \frac{C_p}{C_v} \quad (\text{Eq.6})$$

where C_p and C_v are the specific heat capacity at constant pressure and volume respectively, which are related to the molecular weight through Eq.7,

$$C_p - C_v = R \quad (\text{Eq.7})$$

Helium, nitrogen, and air are primarily used as CS process gasses. Helium has a substantially lower molecular weight (4.0126 g/mol) when compared to nitrogen (28.013 g/mol) and air (approximately 29 g/mol) (Ref 73). According to the 1D model, the velocity of helium is 2.89 times higher than nitrogen at the same Mach number and local temperature. This higher gas velocity typically results in higher particle velocities when using helium for fixed spray conditions as stated in the original CS patent (Ref 74).

One can deduct from the 1D isentropic approximation that the use of helium will result in higher particle velocities; however, its usage may be prohibitively expensive. It has been demonstrated that the blending of helium and nitrogen result in an increase in particle velocity with an increase in helium concentration (Ref 73,75,76). However, in all the previous gas mixing research, the gas is always premixed in containers at set ratios, thus limiting gas mixing to lab scale spray trials and complex mixing operations.

2.2.3.2 The Stagnation Temperature of the Propellant Gas

The local gas temperature has a significant effect on the gas stream velocity, as seen in Eq.4. The local gas temperature is related to the stagnation temperature through the 1D isentropic relationship,

$$\frac{T_o}{T} = 1 + \frac{(k - 1)}{2} M^2 \quad (\text{Eq.8})$$

where T_o is the gas stagnation temperature. The effect of increasing the gas stagnation temperature has been established by many authors to increase particle velocity (Ref 51,62,68,77–81). In HPCS, this temperature has also been shown to influence particle temperature (Ref 10,82).

2.2.3.3 The Stagnation Pressure of the Propellant Gas

According to the 1D approximation, shown in Eq.4, the gas velocity is completely independent from gas stagnation pressure. However, the particles do not necessarily travel at gas velocity, but are accelerated by the drag force induced by this high velocity gas, which can be estimated through Eq.3.

The cross-sectional area and particle mass will be discussed later and can be considered a constant for this explanation. The drag coefficient varies depending on the instantaneous conditions, but it can be assumed constant for simplicity (Ref 50). As such, the particle velocity is only influenced by the gas density and velocity. The 1D isentropic relationship for the gas density relates it to the local gas Mach number and the gas stagnation density,

$$\frac{\rho_o}{\rho} = \left(1 + \frac{(k-1)}{2} M^2\right)^{\frac{1}{k-1}} \quad (\text{Eq.9})$$

where this stagnation density is given by the ideal gas law,

$$P_o = \rho_o R T_o \quad (\text{Eq.10})$$

For this reason, the increase in gas stagnation pressure will result in an increased drag force and a potentially higher particle velocity. Obviously, the particle velocity will always be limited to the gas velocity (Ref 50).

2.2.3.4 The Nozzle Geometry

The nozzle geometry establishes the local Mach number inside the nozzle at any axial location, which is determined by the nozzle area ratio and is related by the following 1D approximation,

$$\frac{A}{A^*} = \frac{1}{M} \left[\left(\frac{2}{k+1} \right) \left(1 + \frac{(k-1)}{2} M^2 \right) \right]^{k+1/2(k-1)} \quad (\text{Eq.11})$$

where A is the local nozzle area and A^* is the nozzle throat area. From Eq.11, a larger area ratio will increase the local Mach number and therefore the flow velocity. However, it has been stated that there is a limit to the maximum nozzle Mach number (approximately $M=3$) due to complex shockwave/particle interactions (Ref 83).

Nozzle length will also determine the particle residence time in the fast-moving flow. This can result in higher particle velocities for longer nozzles. However, when increasing the nozzle length, the friction between the nozzle wall and gas will increase and new phenomena must be taken into account (Ref 84).

2.2.3.5 Particle Temperature

The temperature of the gas that the particles are exposed to during the process is an important aspect in the CS process – as the particle impact temperature is dependent on it. An increase in

particle impact temperature is known to decrease the critical velocity required for bonding (Ref 6). It has also been shown that an increase in the ratio (η) between impact velocity and critical velocity should improve typically desired quantities in cold spray such as deposition efficiency, flattening ratio, cohesive strength, and adhesion (Ref 71,76). While this notion is generally accepted, some studies have shown that increasing particle temperatures can actually lower adhesion strength – attributed to either increased particle oxidation (Ref 85), decreased crater depth (Ref 86), or decreased tamping effect of non-adhering particles (Ref 87). While this effect of impact temperature on the deposition process and coating quality will vary depending on spray conditions and material combinations, increasing particle impact temperature is generally desirable in cold spray.

In HPCS, the particles are exposed to the high-temperature and high-pressure gas prior to expansion in the nozzle, raising the initial particle temperature. In some cases, the particle injection point is purposely moved farther upstream, prolonging the exposure of the particles to the hot propellant gas (Ref 10). This extended prechamber can result in higher particle impact temperatures, especially for particles with a large thermal mass, which can maintain their temperature through the diverging section of the nozzle (Ref 10). This form of particle preheating is inherent to the HPCS process and is a major reason that HPCS often results in superior deposition characteristics when compared to LPCS with similar particle velocities and spray parameters (Ref 88). However, as this form of particle preheating is inherent to the process, it is difficult to decouple the particle temperature from the spray parameters.

Another approach to particle preheating is to separately heat the particle carrier gas prior to injection. This type of powder preheating has been shown to result in increased deposition quality in both HPCS and LPCS. In HPCS, studies have demonstrated that these results are not just due to the increased particle impact temperature but are partially due to the increase in enthalpy of the propellant gas resulting from the injection of high temperature carrier gas. While most studies do not acknowledge this effect, the influence of this added enthalpy should not be ignored as carrier gas flows can exceed 20% of the overall gas flow (Ref 89). Yin et al. demonstrated that preheating copper particles in this way significantly increased the true stagnation temperature of the propellant gas, when compared to using cold carrier gas (Ref 90). This resulted in an increased particle velocity, which may have contributed to the substantial increases in coating quality seen in their previous study (Ref 91). Yin et al. also demonstrated that

centerline gas velocity in the nozzle is substantially effected by carrier gas flow rate (Ref 92), especially when the carrier gas was unheated.

Particle preheating in LPCS also requires the carrier gas to be preheated. While studies have shown that increasing the temperature of the carrier gas results in increases in deposition efficiency (Ref 71,76), it is attributed purely to the increase in particle temperature, and no studies have addressed the additional enthalpy of the gas injected into the main flow. Like HPCS, this carrier gas has energy, however, in LPCS, it is injected in the low temperature/ high velocity section of the nozzle. This injection cannot affect the stagnation conditions of the propellant gas but may significantly influence the overall gas dynamics of the process downstream of the injection.

2.2.3.6 *The Nozzle Traverse Velocity*

The velocity at which the nozzle travels relative to the substrate is known as the traverse velocity. It has been shown to have no, or minimal, effect on the particle velocity or temperature. However, lower traverse velocities increase the time for heat transfer to occur between the propellant gas and substrate, resulting in possibly higher substrate temperatures (Ref 33,93,94). And higher substrate temperatures have been linked to increased deposition efficiency.

2.2.3.7 *The Standoff Distance*

The distance between the nozzle exit and the substrate is known as the standoff distance (SOD) and must be in a certain range to effectively deposit particles on a substrate. It has been shown that there are three regions when it comes to SOD: Region 1, where the SOD is too small and particle velocities are reduced as a consequence of a strong bow shock; Region 2, where for a medium SOD the particle velocities increase; and Region 3, where a large SOD results in particles decelerating as they are now travelling faster than the gas stream (Ref 62,95). It is therefore recommended to operate in Region 2. However, the distances for these regions will change depending on spray conditions and nozzle geometry, and must be determined experimentally or through modeling. As is expected, the substrate temperature was also shown to decrease with an increase in standoff distance (Ref 91).

2.2.4 Effect of Feedstock Powder

While the effect of the gas/particle interaction is typically the focus of most cold spray research, it has become apparent that the size, shape, microstructure and quality of the feedstock powder have a large influence on the process. Hence, the effect of powder properties needs to be properly explored, understood, and considered in the powder selection process. This section aims to provide a complete reference on the effect of the feedstock particles on deposition quality.

2.2.4.1 Effect of Particle Size

The relationship between the particle size and the CS process is complex; not only does powder size affect the impact conditions (namely particle impact velocity and temperature), but it also directly influences the critical velocity. Most CS studies do not decouple these effects, making the identification of an optimum particle size for cold spray a challenging endeavour.

A simplified force balance approximation of the particle in flight can give insight into how particle size affects its velocity,

$$ma_p = \frac{1}{2}\rho V^2 C_d A_p \quad (\text{Eq.12})$$

where m is the particle mass, a_p is the acceleration of the particle, ρ is the propellant gas density, V is the relative propellant gas velocity, C_d is the drag coefficient and A_p is the particle cross sectional area. The function can be further simplified since both the mass and cross-sectional area of the particle are functions of the diameter,

$$a_p = \frac{3\rho V^2 C_d}{\rho_p d} \quad (\text{Eq.13})$$

where d is the particle diameter and ρ_p is the density of the particle material. From Eq. 13, it becomes clear that for a particle travelling in a gas flow, the acceleration (and ultimately the velocity) of smaller particles should be higher than that of larger ones, with the maximum reachable particle velocity being the gas velocity. However, this simplified approximation may be misleading as the particle velocity upon impact with the substrate may differ from the in-flight velocity. The impingement of the gas jet upon the substrate surface gives rise to the formation of a bow shock. In the region beyond the bow shock, the gas velocity normal to the substrate is

decreased substantially to subsonic speed, its density is largely increased, and its flow path becomes parallel to the substrate surface. These conditions will decelerate the particles in the direction normal to the substrate surface and accelerate them laterally. A full understanding of the interaction between the particles and the region after the bow shock is beyond the scope of this work, but a simplified view is that larger particles will be less affected (reduced deceleration) than smaller particles.

This leads to a complex relationship between impact velocity and particle size. Larger particles will experience less acceleration within the nozzle but their deceleration within the stagnant region behind the bow shock will be reduced and often negligible. Smaller particles acquire a higher velocity at the nozzle exit but may be greatly decelerated in the stagnation zone behind the shock. This relationship has been reported by many authors, but is difficult to generalize since both the acceleration and deceleration of the particles depends greatly on the CS processing conditions such as nozzle design, gas stagnation properties, and standoff distance. However, the impact typically follows a curve similar to Figure 6, where the solid line shows the effect of the deceleration through the bow shock (Ref 71).

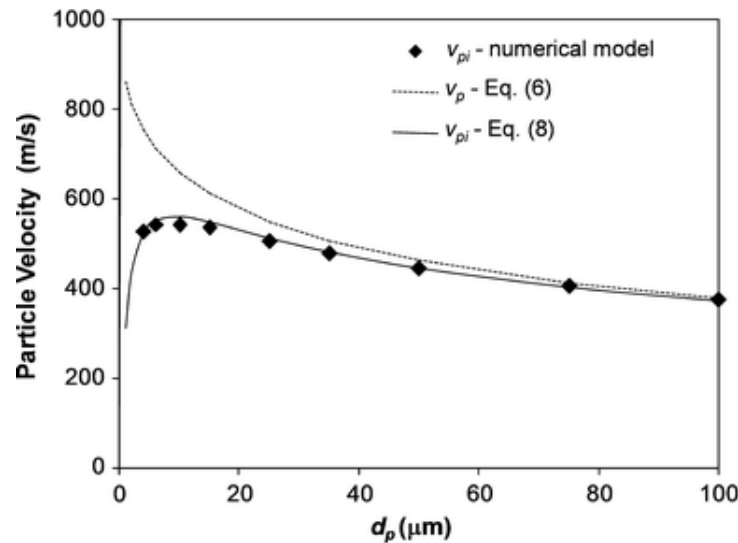


Figure 6: Impact velocity (solid) and exit velocity (dotted) of copper particles of different diameters under set processing conditions (Ref 71).

The trend shown in Figure 6 is crucially important for process optimization in CS. For a material under prescribed spray conditions, there should be a diameter that results in a maximum particle

impact velocity. However, particle size is also known to affect the critical velocity, further complicating the process of choosing an optimal powder size.

It is generally agreed that increasing particle size decreases the critical velocity (Ref 6,58). In the work of Schmidt et al. (Ref 6), the critical velocity is based upon the onset of adiabatic shear instability in the particle (Ref 7), determined through modelling. They propose that for small particle dimensions, occurrence of shear instability (leading to the large deformation required to reach bonding) can be hindered by high cooling rates, which arise due to high temperature gradients within the particle. This leads to the determination of a particle diameter at which adiabatic shear instability will never occur - the minimum critical diameter required for adhesion. Above this diameter, thermal diffusion is hypothesized to be slow and does not prevent localized shear instability to occur at the particle surface, whereas particles smaller than this diameter would not reach adiabatic shear instability. A plot of the estimated minimum diameters for different metals is found in Figure 7.

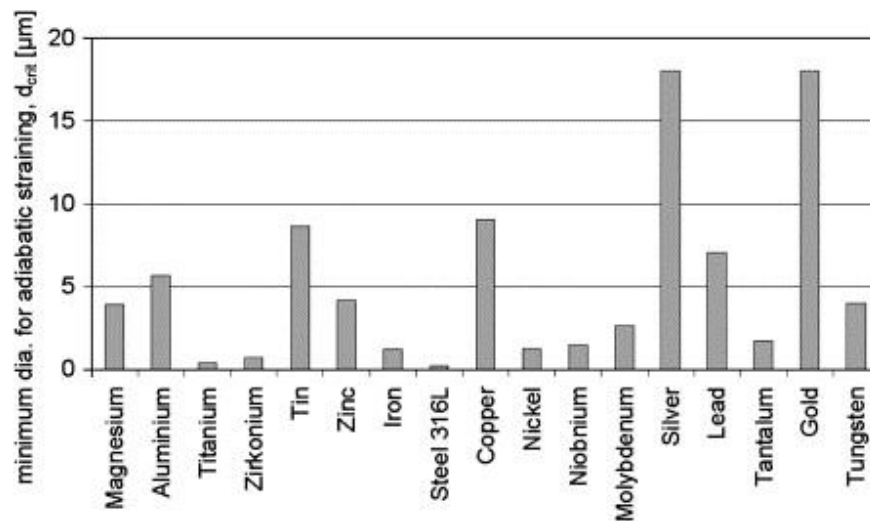


Figure 7: Estimated critical (minimum) diameter required for bonding for different powder materials utilized in CS applications (Ref 6).

From Figure 7, it is observed that the material nature is a significant factor in determining the minimum particle size. For low thermal conductivity materials such as titanium, the minimal particle diameter is much smaller than for a high conductivity material such as copper.

While knowledge of a minimum particle size is helpful, the effect of diameter on the onset of shear instability has also been used to estimate the critical velocity. In their previous definition of critical velocity, the effect of particle size was shown to be k_1 . The effect of particle size on k_1 is given in the equation,

$$k_1 = 0.64 \left(\frac{d_p}{d_p^{ref}} \right)^{-0.18} \quad (\text{Eq.14})$$

where d_p^{ref} is a reference particle diameter, a standard diameter used to experimentally determine the constants in the equation. Eq.1 and Eq.14 indicate that an increase in particle size will decrease the critical velocity. This is attributed to the limited onset of shear instability in smaller particles due to dynamic effects such as; high temperature gradients, higher strain rates and strain-rate hardening, and the higher viscous shear strength in the jetting region (Ref 6).

While the onset of adiabatic shear instability being necessary for adhesion is an ongoing discussion topic (Ref 56–58), this criteria does match the empirical trend. From this criterion alone, one could conclude that using the largest particles possible would ensure the best results due to the lower critical velocity. However, as previously discussed, particle impact velocity is also a function of particle size. Plotting and comparing the particle critical velocity and the particle impact velocity assuming a specific set of spray conditions shows a range of suitable particle diameters, such as in Figure 8. It also suggests that there should be an optimized diameter in which the particle velocity quotient is maximized. However, this diameter cannot be easily determined since it is a function of material properties and spray conditions. As such, it can only be determined using extensive experimentation and modelling efforts.

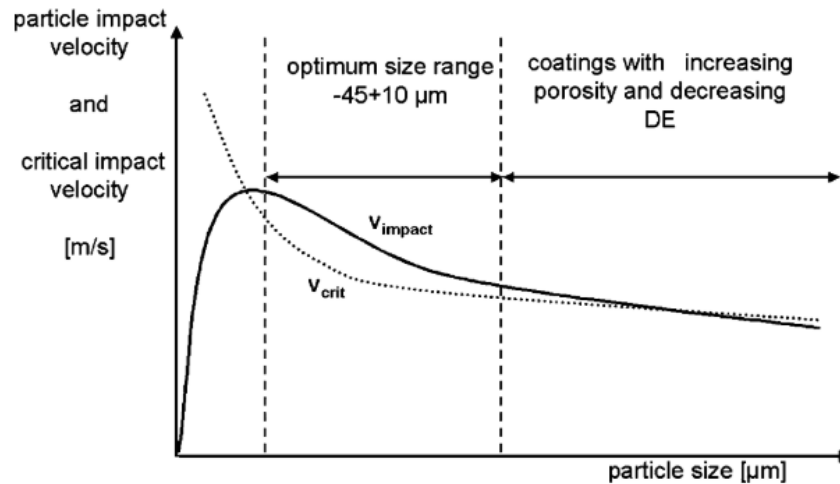


Figure 8: An example of how critical velocity and particle impact velocity change with particle size (Ref 6).

In all the work reported in this section, it has been assumed that the particle impact temperature was the same. However, particle size has a notable effect on particle impact temperature. The low particle temperatures and high particle velocities typical of CS have largely prevented experimental measurement of particle in-flight and impact temperature. Nastic and Jodoin have recorded, for the first time in CS, the temperatures of titanium particles with 150 μm diameter at the exit of the nozzle using a high-speed infrared camera. This new and innovative information was used to validate heat transfer models used in CS to predict particle temperatures (Ref 96). Using these types of models, Schmidt et al. reported that when particles are injected into the high temperature (subsonic) region of the nozzle gas flow, they are heated prior to being cooled down in the supersonic region (Ref 10), as shown in Figure 9. It also lead to the finding that very small particles are heated up quickly in the hot subsonic section but are quickly cooled down in the supersonic section, revealing that larger particles can maintain their temperature over a longer distance (Ref 10,82).

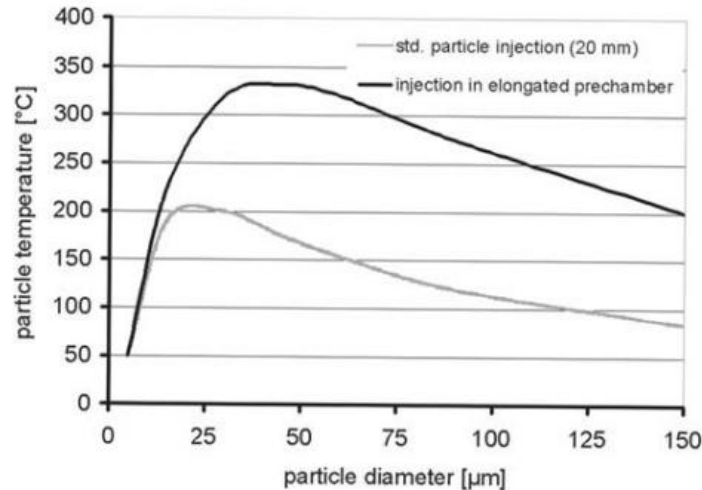


Figure 9: Effect of particle diameter on particle temperature of copper particles inserted into the high temperature subsonic region of the CS nozzle (Ref 10).

However, while larger particles can maintain their temperature longer into the cool section of the flow, Figure 9 shows that particles that are above a certain diameter will have a reduction in temperature. This is due to larger particles requiring more energy to raise temperature during preheating. This effect can be minimized by elongating the prechamber, allowing the particles to be in contact with the hot gas for a longer period of time (Ref 10,82), or through direct particle preheating.

Beyond the immediate effects of particle size discussed in this section, microstructure and oxide contents must also be taken into consideration. Particles of different sizes are not exact scale replicas of themselves – the particle size has a relationship with microstructure and oxide content. This is often overlooked in studies that compare particle sizes but may explain some of the differences proposed in the models for critical velocity. Some studies even go as far as saying that particle size has no effect on critical velocity assuming the material properties and impact temperature could be kept the same (Ref 5,66).

It should be clear that choosing an optimal particle size for CSAM is a challenging task. Particle size directly affects the in-flight velocity, the impact velocity, the impact temperature, and critical velocity. It is difficult to distinguish which effects are most significant, especially when you take into account differences in oxide content and microstructure. The relationship is convoluted and typically extensive experimentation or modelling is necessary to optimize the process.

2.2.4.2 The Effect of Particle Morphology

The effect of the powder morphology on the in-flight particle velocity is consistent across literature; when comparing two particles of equal mass under the same CS conditions, non-spherical particles accelerate to higher velocities than spherical. Comparative studies have demonstrated this for milled (Ref 97), angular (Ref 38), coral like (Ref 98,99), dendritic (Ref 100,101), and water atomized powders (Ref 102). This is easily explained looking at the equation for particle acceleration (Eq. 2); where the drag coefficient and projected area are influential parameters for acceleration and are known to be lower for spherical shapes compared to any of the other powder shapes for the same particle mass (Ref 100,102). If the particle size is large enough to ensure the particle impact velocity is reasonably close to the in-flight velocity (see section 3), then changing the particle shape from spherical to any non-spherical shape should increase the particle impact velocity quotient (η), assuming critical velocity does not change.

Attempts to calculate critical velocity (see Eq.1) often do not consider powder morphology. This is because critical velocity is often considered an inherent material property. Quantifying the effect of different particle shapes on critical velocity adds substantial complexity. There have been numerous studies directly comparing different particle morphologies through experimental and numerical simulations that do demonstrate significant differences in deposition behavior (Ref 38,98,100,101,103). However, these studies do not allow for the decoupling of the sole influence of particle morphology from other effects, such as impact velocity and temperature, microstructure, and chemical composition.

Irregular particles are usually found to travel faster than spherical particles under the same spray conditions; however, this does not always yield a better deposition. Yin et al. showed that during impact, irregular shaped (elongated) particles that do not impact the substrate symmetrically would experience additional torque. While these irregular particles may have the highest value of plastic deformation in the model, this torque was shown to rotate the particle, detaching the bonded areas and deteriorating the coating quality (Ref 103).

This trend of deteriorating quality does not apply to all irregular powders. Luo et al. observed that dendritic nickel powders produced dense depositions while spherical powders would not adhere under the same spray conditions (Ref 100). Similar results were seen by Ko et al. with

copper powders, where the DE of dendritic powders was higher than spherical powders under the same spray conditions (Ref 101). However, this trend was not observed with spongy titanium powder manufactured with the Kroll process. This powder was shown to result in higher porosity depositions when compared to spherical particles (Ref 38). This is hypothesized to be a result of porosity entrapped inside the particles prior to deposition. This closed cell porosity is difficult to eliminate during the CS process since the particle does not collapse easily, unlike the dendritic powders, which have large open porosity.

Fernandez et al. examined the influence of powder morphology for chromium carbide-nickel chromium cermet powders. They found that fully dense spherical particles produced through atomization lead to low plasticity upon impact due to the redistribution of stresses onto the non-ductile ceramic (shown in Figure 10a) (Ref 104). The lack of plasticity resulted in no deposition. Dense particles produced through agglomeration and sintering, did not have the same redistribution of stresses upon impact and therefore experienced high levels of plastic deformation, as seen in Figure 10b. This plasticity resulted in thick and dense deposits (Ref 104). Porous particles, also produced through agglomeration and sintering, were found to build up in a similar manner; however, the pre-existing porosity resulted in internal cracking and peeling of the depositions (Ref 104).

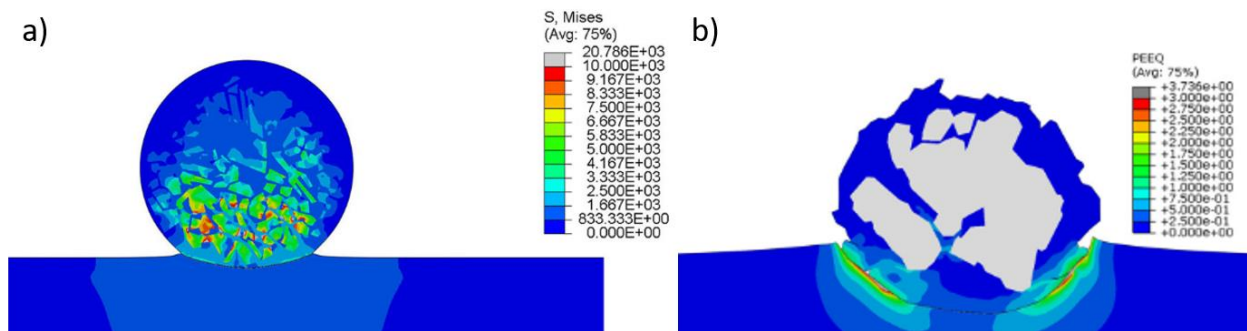


Figure 10: Modelling results of chromium carbide-nickel chromium cermet powders with different morphologies. a) Stress field upon impact of dense spherical particles produced with atomization showing redistribution of stresses and low plastic deformation. b) Plastic equivalent strain of an agglomerated and sintered particle showing a high level of plastic deformation (Ref 104).

2.2.5 Cold Spray of Titanium

CS is of particular interest for highly reactive metals like titanium, as it does not expose the feedstock particles to high temperatures or oxygen (Ref 4,14). In recent years, there has been intensive research into the consolidation of titanium powders using CS (Ref 32,33,35–38,105–107). However, there does not appear to be a clear consensus for the velocity required for titanium particles to adhere (critical velocity) (Ref 6). The early work of Assadi et al. (Ref 7) proposed a critical velocity for titanium slightly below 700 m/s, Schmidt et al. continued this research and proposed a range of critical velocities between approximately 700 m/s to 900m/s for 25 μm spherical particles (Ref 6). Wong et al. showed velocities as low as 602 m/s (Ref 37). What is clear from relevant literature, is that titanium coatings deposited at the lower velocities are highly porous (upwards of 20%) for spherical particles (Ref 33,37). At this level of porosity, the pores are interconnected and no longer offer the desired corrosion protection or mechanical properties (Ref 108).

High porosity levels may be present in titanium even in the cases where high DE and high particle temperatures are observed. The low plastic deformation of titanium particles is believed to result from the high strength and low thermal softening of titanium (Ref 39). As a result of this behavior, it has been found that even with particle preheating only the use of pure helium at extremely high process gas temperatures and pressures (above 800°C and 5 MPa), are used to obtain dense coatings (Ref 38). Although it is possible to deposit titanium using these parameters, several drawbacks can be identified: high working temperatures may result in warping, degradation, and oxidation of the component; and helium can be prohibitively expensive and difficult to source in the quantities required.

2.2.6 Cold Spray of Aluminum and Aluminum Alloys

Aluminum, and its alloys, have been of great interest in the CS community since its inception. As a relatively soft material, deposition is often possible with pure nitrogen as its propellant gas (Ref 69). The aluminum powder is often much less expensive as a raw material than titanium further pushing the use of inexpensive nitrogen over helium. However, under these nitrogen conditions, DE values can be very low for aluminum alloys, being under 5% with typical stagnation conditions

(Ref 109), which are limited by the temperature sensitive nature of the material. This low DE drastically decreases the build rates possible with CSAM, increasing powder and operating costs.

2.2.7 Cold Spray of Stainless Steel

Stainless steels typically require the use of helium as a propellant gas to obtain high density dispositions at DE values that range between 25% and 90% (Ref 102,110,111). High DE with nitrogen has been achieved with some stainless steel alloys, but only using very high stagnation temperatures above 800°C (Ref 112). Lower stagnation temperatures have been used with nitrogen as well (Ref 23), however the DE in these studies is often not reported and is thought to be very low (<5%).

3 Research Objectives

3.1 The Effect of Non-Spherical Particle Morphology on the CSAM Process

Recent advancements in titanium production have introduced a new powder morphology to the market through the Armstrong Process (Ref 113,114). The powder produced through this method has a coral like morphology (Figure 11), which is very different from commonly used powders in CS, such as spherical gas atomized powder, mechanically crushed angular particles, or the titanium sponge morphology created during the Kroll process (Ref 14). It has been shown that the morphology of titanium powder can have an impact on deposition behavior. Wong et al. showed that irregular and sponge titanium morphologies had higher deposition efficiency (DE) when compared to spherical powders (Ref 38). This increase was attributed to a higher particle velocity, as a result of an increase in drag force combined with a lower mass. Wong et al. also observed higher porosity levels in the coatings deposited with the sponge powder created through the Kroll process, attributed to the internal porosity of the feedstock powder (Ref 38). Yin et al. have shown that irregular titanium particles may reduce substrate adhesion as a result of torque acting on the particle during impact with the substrate (Ref 103). However, there have been no studies on the CS of titanium powders produced by the Armstrong process.

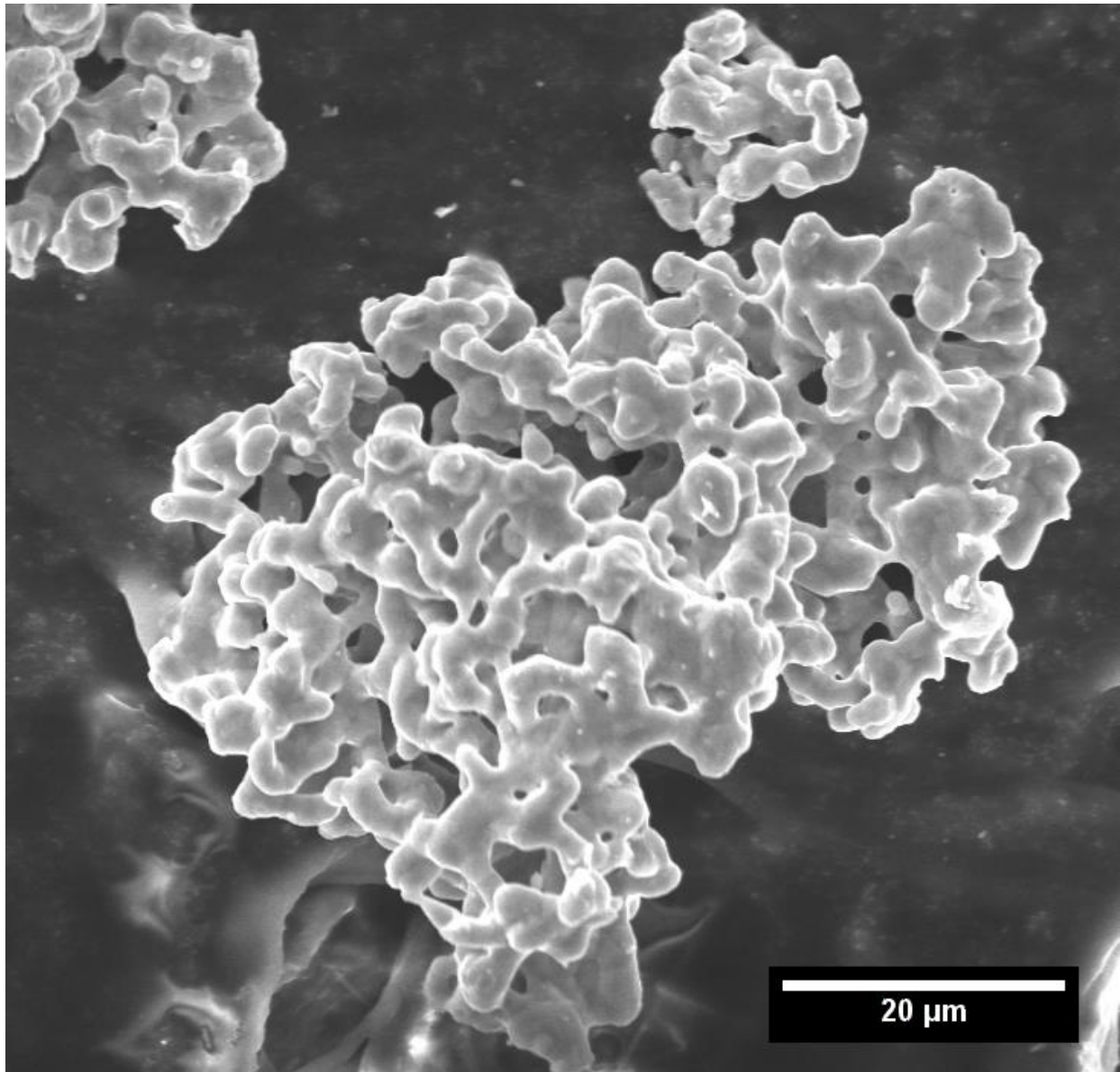


Figure 11: SEM image of coral-shaped titanium powder produced using the Armstrong process.

The powder's unique morphology produces excellent compressibility and compaction behavior when used in traditional powder metallurgy processes, capable of producing compacts with significantly higher green strength and lower porosity than other irregular powders (Ref 113,115). The morphology of the powder should result in a large drag force combined with a lower mass per unit volume when compared to spherical particles. As a result, it is possible that less aggressive CS parameters may be used to reach high deposition efficiency and low porosity deposits.

Furthermore, the powder produced with the Armstrong process is attractive since it can be produced at a significantly lower cost when compared to traditional spherical powder. Normal spherical powder costs upwards of 110 USD/kg to produce, while Armstrong powder, which is produced directly from the reduction of TiCl_4 in a continuous liquid loop, costs only 11-24 USD/kg (Ref 115,116). The combination of the reduced machining costs of AM, the high deposition rates and low operating costs of CS, and low-cost powder from the Armstrong process could significantly reduce the overall cost of producing large, near net shape, titanium components.

This work is a study on the use of unique titanium particle morphology, one produced during production using the Armstrong process (Ref 114), to produce high density deposits with low pressure and low temperature nitrogen as propellant gas. The deposition behavior is examined through deposition efficiency, particle velocity, coating density, and hardness. The understanding of the behavior is further enhanced through particle impact modeling. Lastly, heat treatments will be done to improve the mechanical properties of the AM components.

Unfortunately, this unique powder morphology can currently only be found for titanium powder, as it is a biproduct of the production method. The findings of this study, however, can be extrapolated as general trends and added to the knowledge base in CS as the literature on irregular particles, especially of this shape, is not comprehensive.

3.2 The Effect of Blended Process Gas Nature on the CSAM Process

Since practical limitations of the commercially available equipment may set the maximum gas temperature, pressure, and nozzle geometry in CS, the gas nature itself may be the only parameter available to increase the particle velocity. Helium, nitrogen, and air are primarily used as CS process gasses. Helium has a substantially lower molecular weight (4.0126 g/mol) when compared to nitrogen (28.013 g/mol) and air (approximately 29 g/mol) (Ref 73). According to the 1D model, the velocity of helium is 2.89 times higher than nitrogen at the same Mach number and local temperature. This higher gas velocity typically results in higher particle velocities when using helium for fixed spray conditions as stated in the original CS patent (Ref 74).

One can deduce from the 1D isentropic approximation that the use of helium will result in higher particle velocities; however, its usage may be prohibitively expensive. In recent years helium

recycling systems have been proposed (Ref 33), however, these systems are expensive, bulky, require a carefully controlled and sealed chamber, and do not have 100% capture efficiency. Currently, they have not made a large impact on the commercial CS landscape.

While the effect of helium addition on the gas velocity is clear in the literature (Ref 11,81,95,117,118), the effect of the increased gas velocity on particle velocity, DE, and coating characteristics is much harder to predict. The momentum transfer between the gas and the particle is not only a function of the gas velocity, but of the local gas density and relative local Mach number. The particle impact temperature (a function of gas density, velocity, and temperature and Mach number) and gas impact temperature have also been shown to influence the deposition quality and DE (Ref 10,71,75,94). Because of these complex interactions, experimental work is required to determine the full effect of helium addition.

The purpose of this study is to examine the relationship between helium concentration and coating/deposition characteristics for several commercially available and industrially relevant materials using a novel, in-line, gas-mixing device. The device is designed to improve deposition efficiency through the addition of helium, which is particularly useful for lower pressure and temperature applications with sensitive materials. The relationship between DE and helium content is then used to develop a cost model, which aims to optimize the helium concentration required for the lowest cost coatings. This study omits the use of titanium, as it is known that pure helium at temperatures and pressures above the capacity of this system is required for dense deposits.

3.3 The Effect of Independent Particle Preheating on the CSAM Process

The importance of particle temperature has been clearly outlined in the discussed literature. In HPCS, the particles are exposed to the high-temperature and high-pressure gas prior to expansion in the nozzle, raising the initial particle temperature. Another approach to particle preheating is to separately heat the particle carrier gas prior to injection. This type of powder preheating has been shown to result in increased deposition quality in both HPCS and LPCS. In HPCS, studies have demonstrated that these results are not just due to the increased particle impact temperature but are partially due to the increase in enthalpy of the propellant gas resulting from the injection of high temperature carrier gas. While most studies do not

acknowledge this effect, the influence of this added enthalpy should not be ignored as carrier gas flows can exceed 20% of the overall gas flow (Ref 89).

In HPCS, the true stagnation temperature of the propellant gas is a mixture between the heated propellant gas and the carrier gas. This true stagnation temperature is what the particles are being exposed to prior to expansion, which influences their impact temperature. Attempts to raise or lower particle temperature in HPCS necessarily require the modification of this true stagnation temperature, and therefore will affect the resulting particle velocity and substrate conditions. This relationship can be problematic, as there are many situations in which independent control of the particle temperature could be desirable. For situations in which the substrate is temperature sensitive (such as heat-treated aluminum alloys or carbon-fiber reinforced polymers), a low stagnation temperature must be used, but a higher temperature particle could increase the quality and efficiency of the deposition. Also, in HPCS the stagnation temperature is limited by the melting/clogging of the particle material in nozzle, something that could be avoided with the ability to independently keep the particle temperature low.

Particle preheating in LPCS also requires the carrier gas to be preheated. While studies have shown that increasing the temperature of the carrier gas results in increases in deposition efficiency (Ref 71,76), it is attributed purely to the increase in particle temperature, and no studies have addressed the additional enthalpy of the gas injected into the main flow. Like HPCS, this carrier gas has energy, however, in LPCS, it is injected in the low temperature/ high velocity section of the nozzle. This injection cannot affect the stagnation conditions of the propellant gas but may significantly influence the overall gas dynamics of the process downstream of the injection.

Additionally, an issue that inhibits the widespread preheating of many materials is clogging in the particle preheater itself. Typically, the particles and carrier gas are passed through a high temperature metallic tube, which transfers heat to the gas flow and then to the particles through convection. In most cases, the tube wall temperature is raised through electrical resistance heating, which results in approximate constant heat flux along the length of the tube. This heat transfer mode requires the tube inner wall temperature to be substantially higher than the desired particle temperature, and when the heated particles collide with these high temperature tube walls, weak bonds can be formed - resulting in clogging of the particle preheater. This is

especially true for lower melting temperature particles, such as aluminum, where powder preheating is typically avoided.

This study aims to build an understanding of how the temperature of the carrier gas affects the LPCS process and to demonstrate that particle temperature can be independently controlled. This understanding paves the way for a potential solution to spraying on temperature sensitive materials that prevents the use of elevated spray parameters. Through CFD modelling and experimentation, the particle temperature was decoupled from the temperature of the carrier gas, and the resulting effects on particle temperature, particle velocity, DE, and deposition quality were investigated. To overcome the potential particle heater clogging problem, this study also introduces a novel powder heater design that allows for particles to be taken closer to their melting temperature without encountering with hot metallic walls. This study uses aluminum as the feedstock material, as its low cost make it an unsuitable candidate to use helium, even with mixing, and is not available in the coral-like morphology.

4 Research Approach and Experimental Design

The present chapter explains the research approach proposed to achieve the three objectives previously outlined. For each objective, this chapter details the materials, the experimental setup, the modeling details, and the characterization methods.

4.1 The Effect of Particle Morphology on the CSAM Process

The purpose of this study was to investigate the deposition behavior of the novel coral like titanium powder produced with the Armstrong process.

4.1.1 Materials

The feedstock powder used for this study was commercially pure (grade 2) titanium powder (<325 mesh) from Cristal Metals (Cristal US Inc., Woodridge, IL, USA). It is produced using the Armstrong process. The process produces powder particles with a unique, low bulk density, “coral-like” morphology as seen in Figure 11.

4.1.2 Cold Spray Process

To investigate the effect of process gas pressure and temperature on the deposition behavior of this powder, the parameters in Table 1 were used. The deposition was performed using the commercially available SST Series EP Cold Spray System (Centerline Ltd, Windsor, Canada). This system can provide a maximum gas stagnation temperature of 500°C and a maximum gas pressure of 3.4 MPa. Since densification of this powder in other powder metallurgy processes requires less energy than with spherical powder, it was envisioned that deposition may be possible at lower ranges of parameters than those discussed in the literature (Ref 6,32–38). Therefore, a large range of temperatures and pressures was tested to understand the behavior of this unique powder morphology during the CS consolidation process.

Table 1: CS Parameters during Testing

Parameter	Value
Gas Nature	Nitrogen
Gas Pressure	1.0 – 3.8 MPa
Gas Temperature	100 – 500°C
Powder Feeder Gas Flow Rate	1.7 m ³ /h
Powder Feeder Gas Nature	Nitrogen
Standoff Distance	10 mm

To further understand the deposition behavior of single particles, single impact analysis was completed. This was done by reducing the powder feed rate while holding the other parameters constant in order to see the impact of only one particle at a time on the substrate. For these tests, the substrate was polished commercially pure titanium (grade 2).

4.1.3 Sample Characterization and Particle Velocity Measurement

As received powder, single impact tests, and consolidated powders (thick deposits) microstructures were investigated using a scanning electron microscope (SEM) (EVO-MA10, Zeiss, Germany) and an optical microscope (VHX-2000E, Keyence, Canada). In order to quantify porosity level, cross sections of the deposits were stitched together using the VHX-2000 software at a magnification of 200x. The porosity was then quantified through contrast of the optical images using ImageJ software for three cross sections per deposit. Microhardness testing of the deposits was conducted on the cross-section of polished samples using a Vickers microhardness tester (Struers Duramin-1, Struers Inc., Cleveland, OH, USA) with a 300g load with a dwell time of 15 seconds. To avoid the effect of the stress field, the distance between two indentations was kept greater than three times the length of the indentation. The reported values are the average of a series of 10 indentations for each sample, taken at different areas of the dense center of the deposit. Substrate temperatures were measured using an infrared camera (FLIR E50, FLIR Systems Inc, USA).

Particle velocity measurements were taken using the ColdSprayMeter (CSM) eEVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). This system uses a continuous 2.4 W ($\lambda=810$ nm) laser with a dual slit photomask in order to perform in-flight diagnostic on individual particles. It provides precise velocity of individual particles during flight. In this study, the velocity measurements were

taken at a point 10 mm downstream from the center of the cold spray nozzle exit. Testing was run for several minutes to ensure the collection of a robust set of data to ensure significant results.

4.1.4 Modeling of Particle Impact Dynamics

The aim of the modeling work was to demonstrate that powder morphology can have a capital importance on the densification and bonding seen in the CS consolidation process. This study explores the densification of the coral shaped titanium powder and compares it to the experimental single impact testing. This study also compares the behavior of the coral shaped titanium powder versus the behavior of traditional gas atomized spherical powders through a 2D modeling approach.

Most of the modeling approaches in the field of CS deal with spherical particles (Ref 53,119–124). Few exceptions appeared recently in the literature. A study by Yin et al. (Ref 103) simulated the 2D impact of elliptical-shaped particles. Another dealt with 3D simulation of pseudo-cylindrical particles (Ref 125). For the current work, the modeling used a 2D particle approximation. A specific image treatment procedure was developed, based on a marker driven watershed algorithm, implemented in the open-source SMIL (Simple Morphological Image Library) software. This procedure enables the import of the real cross-sectional morphology of the particles into the finite element software Abaqus/Explicit®. The geometries obtained in this way were meshed using bi-linear quadrilateral elements within Abaqus.

The modeling physics do not differ from most of the modeling efforts presented in the literature (*e.g.* (Ref 126,127) among many others). The “Mie-Gruneisen” equation of state (EOS), describing material state in the high pressure domain and shock wave propagation, was used in the Hugoniot formulation. The widely used Johnson-Cook model (Ref 128) will be selected as an empirically-based representation of the yield stress. The material parameters are readily available in literature for titanium (Ref 119,129) which was decisive for the choice of the Johnson-Cook model. The model involved strain hardening, strain rate hardening and thermal softening.

At the interface between the particle and the substrate, friction was considered. A modified Coulomb model was applied (*i.e.* the limit shear t grows linearly with the contact pressure, until

an upper value is reached). Metallurgical adhesion was not considered as it is not believed to have an important influence on the deformation process during impact. Material properties will be taken from Bae et al. and Giroulx et al. (Ref 119,129).

In order to achieve numerical convergence under intense deformation conditions usually found in cold spray, an adaptive meshing tool (Adaptive Lagrangian Eulerian or ALE) available in the Abaqus software was applied to a domain which corresponded to the particles and the part of the substrate closer to the particle (i.e. the part finely meshed). ALE performed a regularization of the distorted mesh by displacing the nodes at the interior of the selected domain, which resulted in a reduced overall distortion. The solution was then mapped to the new mesh. The whole simulation was divided into several temporal steps, in order to adjust the remeshing parameters during the simulation as often as needed for the benefit of convergence.

4.1.5 Post-Processing Heat Treatment

It is known that in the CS process, the resulting depositions usually contain residual stresses and suffer brittle fracture (Ref 130–132). Performing post deposition heat treatment can reduce porosity and internal defects and improve mechanical properties (Ref 131). These heat treatments can result in recovery, recrystallization and grain growth in the titanium deposits, and were shown to significantly increase the ultimate tensile strength and yield strength of deposits (Ref 131). To enhance the mechanical properties of the deposited components in this study, heat treatments will be performed on selected samples. This will be done under vacuum to prevent oxidation for three different heat treatments based on existing literature; 870°C for 36 hours (Ref 133), 650°C for 8 hours (Ref 134), and 1000°C for 3 hours (Ref 135).

4.1.6 Mechanical Testing

Additional mechanical testing of selected samples was completed after heat treatment to assess the mechanical properties of the fabricated parts. These samples were tested using the standard test method for tension testing of metallic materials (ASTM E8) (Ref 136). The dimensions of the CS fabricated tensile samples can be found in Figure 12.

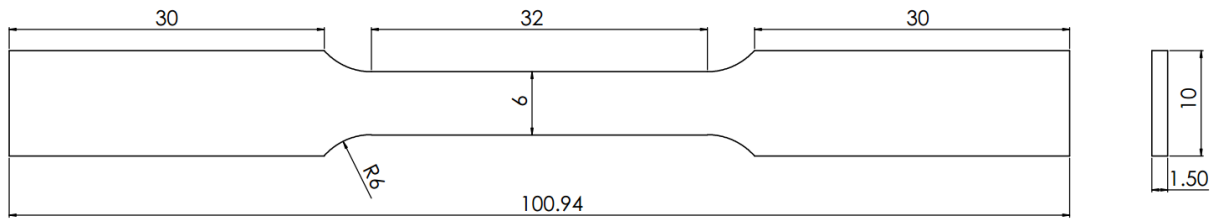


Figure 12: Dimensions of tensile test specimens (in mm).

The tensile test specimens were produced through CSAM. They were deposited on a polished commercially pure titanium (grade 2) substrate with the main traverse direction going along the length of the sample. Since the adhesion to the substrate was weak, they were removed from the substrate mechanically, after which they were heat treated and then final machining was done.

4.2 The Effect of Process Gas Nature on the CSAM Process

The purpose of this study was to examine the relationship between helium concentration and coating/deposition characteristics for several commercially available and industrially relevant materials using a novel, in-line, gas-mixing device.

4.2.1 Materials

Four metallic powders (pure aluminum, aluminum alloy, stainless steel, and CoNiCrAlY) were used to investigate the effects of gas mixing. These powders were chosen because they are commercially relevant and desirable for CSAM. These materials have diverse deposition behaviors, and substantial cost differences. The chemical composition, supplier information, and particle size are found in Table 2.

Table 2: Powder Information

General Name	Chemical Composition	Commercial Name	Supplier			Particle Size
Pure Aluminum	99.5%Al	SST-A5001	Centerline (Windsor) Ltd, Canada			-45 +5 μm
Aluminum Alloy	Al-10%Si-0.3%Mg	TEKMAT™ AlSi10Mg-63/20	Tekna Materials Inc,	Advanced		-63 +2 μm
Stainless Steel	Fe-14.5%Cr-3.5%Cu- 4.5%Ni-0.7%Si- 0.7%Mn-0.3%Nb	15-5PH	Sandvik United Kingdom	Osprey LTD,		90% -10 μm
CoNiCrAlY	Co-32%Ni-21%Cr- 8%Al-0.5%Y	Amdry 9951	Oerlikon Wohlen, Switzerland	Metco AG,		-38 +5.5 μm

All powders were produced through gas atomization, however only the pure aluminum powder exhibited an atypical, non-spherical, morphology. The substrate material used to deposit the pure aluminum and aluminum alloy powders will be as-received 6061-T6511 aluminum alloy cleaned with acetone prior to deposition. The substrate material used to deposit the stainless steel and CoNiCrAlY powders was cold rolled mild steel (AISI 1020) that was prepared with grit blasting, wire brush scrubbing, and acetone cleaning prior to deposition.

4.2.2 Cold Spray Process

In order to investigate the effect of the percentage of helium, the spray parameters were held constant and can be found in Table 3. The maximal temperature and pressure of the system will be used with a typical standoff distance. Traverse velocities will be adjusted between tests to ensure that the deposits did not grow excessively thick during deposition due to changes in deposition efficiency.

Table 3: Pertinent CS Parameters

Parameter	Value
Gas Pressure	3.4 MPa
Gas Temperature	500°C
Standoff Distance	10 mm
Traverse Velocity	5 mms/ to 25 mm/s

4.2.3 In-Line Nitrogen-Helium Blending

In order for the two gasses to be mixed in-line at controllable ratios, both the pressure and flow rates must be regulated carefully. The process flow diagram in Figure 13 represents the set-up that will be used to achieve this.

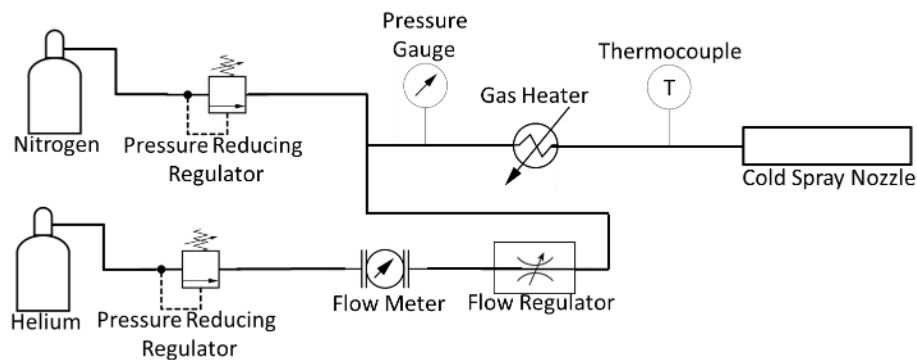


Figure 13: Process flow diagram showing inline gas mixing.

The pressure from the helium storage is first reduced and regulated to a pressure higher than the intended stagnation pressure and suitable for the flow meter. The flow is then regulated using a flow regulator that ensures a constant mass flow (measured in standard cubic feet per minute (SCFM) at the flow meter) regardless of downstream pressures. On the nitrogen side, a pressure regulator then sets the output pressure, which is read by the pressure gauge.

To operate this system, the mass flow rate of helium required for a specific stagnation pressure, temperature, nozzle throat area, and volume percentage of helium must be determined, through calculations. This is done by first finding the overall mass flow rate using,

$$\dot{m} = \frac{A * P_o}{\sqrt{T_o}} \sqrt{\frac{k}{R} \left(\frac{k+1}{2} \right)^{-\frac{k+1}{2(k-1)}}} \quad (\text{Eq.15})$$

where $\dot{m}$ is the mass flow rate, A is the nozzle throat area, P_o is the stagnation pressure measured at the pressure gauge, and T_o is the stagnation temperature measured at the thermocouple. It should be noted here that the k and R values are that of the mixture, calculated.

To calculate the properties for the mixed gas, the molar weight for a helium/nitrogen mixture is found from the following relationship,

$$M^* = x_{He} M_{He} + x_{N_2} M_{N_2} \quad (\text{Eq.16})$$

where x_{He} and x_{N_2} are the molar fractions of helium and nitrogen respectively, and M_{He} and M_{N_2} are the molar masses of helium and nitrogen, respectively.

The ratio of specific heat for the mixture is given by,

$$Cp = Cp_{He} w_{He} + Cp_{N_2} w_{N_2} \quad (\text{Eq.17})$$

where Cp_{He} and Cp_{N_2} are the specific heat for helium and nitrogen, respectively, and w_{He} and w_{N_2} are the mass fraction of helium and nitrogen, respectively. The mass fractions can be found through equations 18 and 19.

$$w_{He} = \frac{x_{He} M_{He}}{M^*} \quad (\text{Eq.18})$$

$$w_{N_2} = \frac{x_{N_2} M_{N_2}}{M^*} \quad (\text{Eq.19})$$

By solving all the aforementioned equations simultaneously, the gas properties can be calculated for any flow mixture and Mach number.

This mass flow rate can be multiplied by the mass fraction of helium (Eqn. 18) and adjusted to SCFM. The flow rate of helium required for different volume percentages of helium, for the parameters outlined in Table 3 is plotted in **Figure 14**.

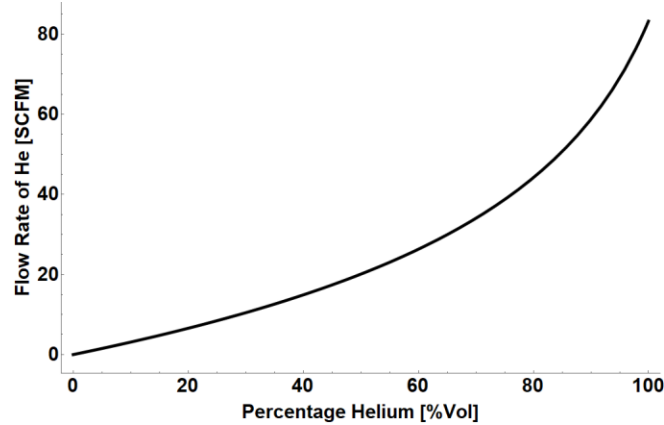


Figure 14: The flow rate (SCFM) of helium required for a volume percentage of helium (throat diameter=2mm, $P_o = 3.4$ MPa and $T_o = 500^\circ\text{C}$).

The SCFM of helium for various helium percentages can be determined and used to set the flow meter. For this study, the helium rates shown in Table 4 were used. For each set of experimental parameters, three separate samples were deposited.

Table 4: Flow Rate of Helium for Helium Percentages at Set Deposition Parameters

Percentage Helium [Vol%]	Helium Flow Rate [SCFM]
0	0
25	8.2
50	19.5
75	37.6
100	80.9

4.2.4 Sample Characterization and Particle Velocity Measurement

The focus of this study is to characterize the effect of gas mixing on the DE of the coatings. DE was measured by weighing the samples before and after deposition and comparing the mass gain with the mass of powder fed. The powder feed rate was measured by running the powder feeder separately from the operation of the CS system for a set amount of time and capturing the powder with a filter bag, which is weighed on a precise scale. While measuring in this method does not account for the different back pressures seen during operation, it is a widely used method in industry and produces consistent results. To ensure that the tests were done with a consistent feed rate, three measurements were taken before deposition and one after ensure consistency. The averaged value of these four tests was the value used in all calculations.

The deposit quality was investigated through microstructural analysis using a SEM (EVO-MA10, Zeiss, Germany) and an optical microscope (VHX-2000E, Keyence, Canada). In order to quantify porosity level, entire cross sections of the deposits were stitched together using the software of the VHX-2000 at a magnification of 300x. The porosity were calculated through contrast analysis of the optical images using ImageJ software for three separate cross sections per deposit (9 images per set of parameters). Microhardness testing of the deposits were conducted on polished samples using a Vickers microhardness tester (Struers Duramin-1, Struers Inc., Cleveland, OH, USA) with a 300g load and a dwell time of 10s. To avoid the effect of the stress field, the distance between two indentations were kept greater than three times the length of the indentation. The reported values are the average of a minimum of 15 indentations for each set of parameters.

Particle velocity measurements were taken using the ColdSprayMeter eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). This system uses a continuous 2.4 W ($\lambda=810$ nm) laser with a dual slit photomask in order to perform in-flight diagnostic on individual particles. It provides the precise velocities of individual particles during flight. In this study, the velocity measurements were taken at a point 10 mm downstream from the center of the cold spray nozzle exit. Testing was run for several minutes to ensure the collection of a robust data set.

4.2.5 Cost Model

The cost model assumes that the coating quality (porosity and hardness) was found to be adequate for the specific application under all deposition conditions. With this assumption, the cost of the deposited powders is calculated if the DE as a function of helium percentage is known. If some conditions do not meet the quality criteria, they can later be eliminated from the optimization. Conditions can then be identified for the least expensive coatings to deposit.

The cost model aims to incorporate all of the significant cost aspects of the process. In order to have a simple comparative value, the dollar cost per unit mass (in gram) of deposit was calculated. This cost per unit mass of coating is found with the following equation,

$$C = PC + GC + LC + EC \quad (\text{Eq.20})$$

where C is the cost per unit mass of coating, PC is the total cost of powder used, GC is the total cost of gas used, LC is labor costs, and EC is the electricity costs.

The powder cost per gram of deposited coating is calculated simply by dividing the cost for one gram of powder (available from the manufacturer) by the DE ,

$$PC = \frac{P}{DE} \quad (\text{Eq.21})$$

where P is the powder (\$/gram) and DE is a function of helium percentage determined experimentally. The cost of gas is dependent on both the length of the spray and the cost of the gas, with the latter varying with the percentage of helium used to produce the coating. The gas costs per second is found with the following equation,

$$GR = w_{He} * \dot{m} * HC + w_3 * \dot{m} * NC \quad (\text{Eq.22})$$

where GR is the gas rate (\$/second), HC is the cost of helium (\$/kg), and NC is the cost of nitrogen (\$/kg).

The time necessary to deposit one gram of coating is found by dividing the mass of the coating (one gram) by DE and the powder feed rate (PFR),

$$t = \frac{1}{DE * PFR} \quad (\text{Eq.23})$$

where t is time (seconds) and PFR is the powder feed rate (grams/second). The total gas cost is then the gas rate multiplied by the time,

$$GC = GR * t \quad (\text{Eq.24})$$

The labor costs is calculated using,

$$LC = LR * t \quad (\text{Eq.25})$$

where LR is the labor rate (\$/second). For electricity costs, the power is estimated through an analysis of the cold spray gas heater itself using the first law of thermodynamics. Assuming an ideal gas, negligible change in kinetic and potential energies, no work, and minimal heat losses to the surroundings, this reduces to,

$$\dot{Q} = \dot{m} C_p (T_o - T_R) \quad (\text{Eq.26})$$

where $\dot{Q}$ is the heat rate (watts) and T_R is the approximate temperature (K) of the gas before heating. The cost of heating then becomes,

$$EC = \dot{Q} * t * ER \quad (\text{Eq.27})$$

where ER is the electricity cost (\$/joule).

The costing Eq. 20-27 are used with the gas mixing and mass flow Eq. 15-19 to determine the actual cost of depositing one gram of powder for any helium percentage, if DE can be estimated as a function of helium content.

4.3 The Effect of Independent Particle Preheating on the CSAM Process

This study aims to build an understanding of how the temperature of the carrier gas affects the LPCS process and to demonstrate that particle temperature can be independently controlled. This understanding paves the way for a potential solution to spraying on temperature sensitive materials that prevents the use of elevated spray parameters. Through CFD modelling and experimentation, the particle temperature was decoupled from the temperature of the carrier gas, and the resulting effects on particle temperature, particle velocity, DE, and deposition quality were investigated. To overcome the potential particle heater clogging problem, this study also introduces a novel powder heater design that allows for particles to be taken closer to their melting temperature without interacting with hot metallic walls.

4.3.1 Materials

To explore the effects of powder preheating through both experimentation and CFD modelling; a powder with a spherical shape, high purity, known properties, tight size distribution, and lack of agglomerates/satellite particles is desired. This allows for more accurate modelling and less variability in experimental results. Spherical pure aluminum powder (Equispheres Inc., Canada) was chosen for this purpose. The particle size distribution analysis (Microtrac S3500, Nikkiso, Japan) can be found in **Figure 15**. The powder has a volume mean (MV) of 49.47 μm and numerical mean (MN) of 44.11 μm . The similar MV and MN values, with the MN values slightly smaller, indicates that the particle distribution of this powder is very narrow. The values used to generate the plot in **Figure 15** are used directly in the CFD modelling to improve accuracy.

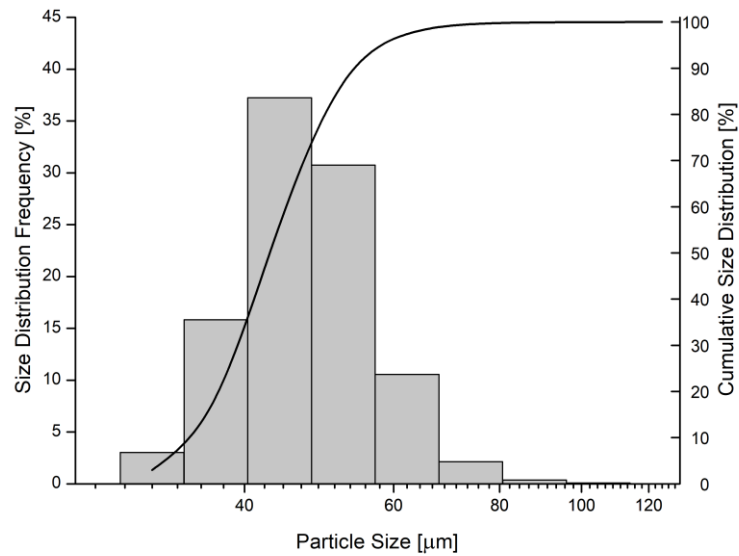


Figure 15: Particle size (diameter) distribution (numerical) of the aluminum powder.

A typical overview of the particles can be seen in **Figure 16**. It can be observed in **Figure 16(A)** that the particles are highly spherical with no agglomeration or satellite particles. The cross section in **Figure 16(B)** shows density of the particles and its regular equiaxed grains. This specific powder has a low DE under typical nitrogen cold spray conditions in LPCS, which should allow a large range of observable effects that could be missed if the baseline case is at a high DE. The particles will be treated as chemically pure aluminum for the model since contamination should not affect the thermal or in-flight characteristics of the particle. The substrates for the study was polished aluminum 6061-T6.

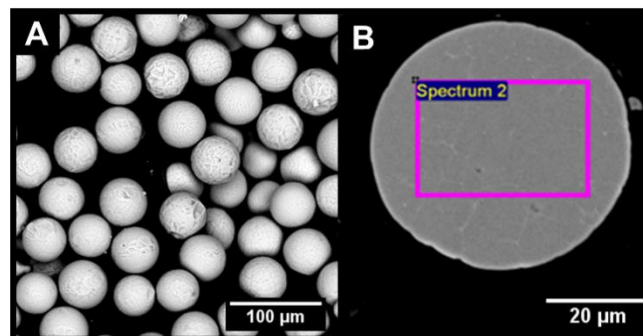


Figure 16: SEM overview image of powder (A) and SEM image of powder cross section (B).

4.3.2 Cold Spray Process

The deposition was performed using the commercially available SST Series EP Cold Spray System (Centerline Ltd, Windsor, Canada). This system can provide a maximum gas stagnation temperature of 500°C and a maximum gas pressure of 3.4 MPa. To prevent issues with nozzle clogging that can occur with aluminum powder, a polymer nozzle with a 2 mm diameter throat was used. Powders were fed using a commercially available rotary powder feeder (Model AT-1200 Rotary Powder Feeder, Thermach Inc, Appleton, WI, USA).

The parameters that will be held constant for all trials can be found in Table 5. For this study, nitrogen gas was used as both the propellant gas at the maximum temperature and pressure of the system with a typical standoff distance.

Table 5: Pertinent CS Parameters

Parameter	Value
Propellant Gas Temperature	500 °C
Propellant Gas Pressure	3.8 MPa
Nominal Powder Feed Rate	6 g/min
Standoff Distance	10 mm
Traverse velocity	20 mm/s
Passes	20

4.3.3 Particle Preheating Trials

In order to prevent clogging of the powder pre-heating apparatus, a novel device was developed for this work. This device consists of two separate flows of gas, one unheated flow carrying the particles and one auxiliary flow which is heated externally with traditional methods. A schematic of the powder preheating system can be found in **Figure 17**. In this design, particles are carried by room temperature gas and mixed with the heated auxiliary gas inside a two-meter-long glass coil; never encountering the hot metal walls of a heater. Glass was chosen as the coil material as it is hard, smooth, has low affinity for adhesion with metallic particles, and could be manufactured through scientific glass blowing techniques. The injection stem, part of the glass coil, was pressed

directly into the injection port of the polymer nozzle, so at no point do the hot particles contact metal. The system was thermally isolated with high temperature refractory ceramic fiber.

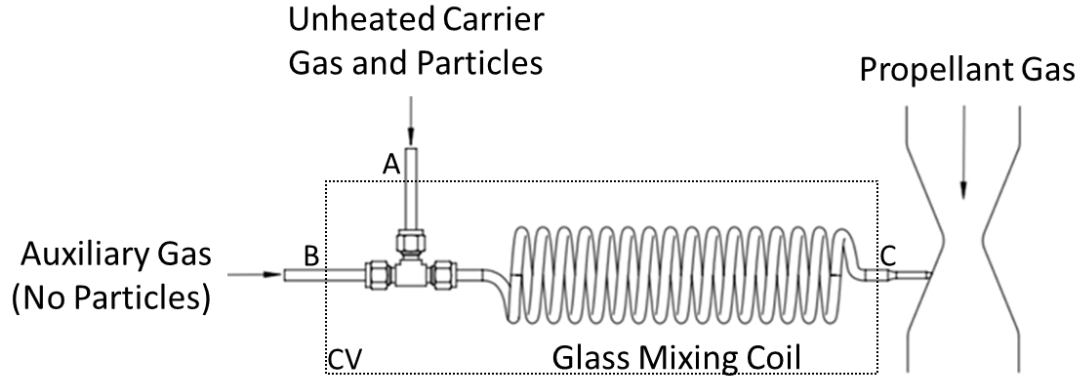


Figure 17: Schematic of particle preheating system.

This configuration allows measuring and controlling the temperatures and flow rates of the two incoming gas flows. Taking the control volume (CV) identified in **Figure 17** and assuming this process is steady state, the system is perfectly insulated, and that thermal equilibrium between the particles and the gas at the exit C has been reached (demonstrated later in the paper), the first law reduces to,

$$\dot{m}_{N_2A}h_{N_2A} + \dot{m}_{N_2B}h_{N_2B} + \dot{m}_P u_{PA} = \dot{m}_{N_2C}h_{N_2C} + \dot{m}_P u_{PC} \quad (\text{Eq.28})$$

where $\dot{m}_{N_2A}$, $\dot{m}_{N_2B}$, and $\dot{m}_{N_2C}$ are the mass flow rates of nitrogen at A, B, and C, respectively, h_{N_2A} , h_{N_2B} , and h_{N_2C} are the specific enthalpies of nitrogen at A, B, and C, respectively, $\dot{m}_P$ is the mass flow rate of particles, and u_{PA} and u_{PC} are the specific internal energies of the particles at A and C, respectively.

Using mass conservation and constant specific heat, Eq. 28 can be rearranged to form a useful equation to determine the temperature of the auxiliary gas required at B for a desired particle preheat temperature at C,

$$T_B = \frac{(\dot{m}_{N_2A} C_{p_{N_2}} + \dot{m}_p C_p) (T_C - T_A)}{\dot{m}_{N_2B} C_{p_{N_2}}} + T_C \quad (\text{Eq.29})$$

where T_A , T_B , and T_C are the temperatures at A, B, and C, respectively, $C_{p_{N_2}}$ is the specific heat of nitrogen at constant pressure, and C_p is the specific heat of the particle material.

To demonstrate the effects of this type of particle preheating and to help validate the model, the particles will be heated to temperatures between 100°C and 500°C, in 100°C increments. The unheated carrier gas will have a mass flow rate of 10 g/min while the mass flow of the auxiliary gas will be five times higher, at 50 g/min Table 6 shows the temperature intervals for the particles in this study and the corresponding auxiliary gas temperature (T_B).

Table 6: Auxiliary Gas Temperatures Required for Desired Particle Temperatures

Desired Particle Temperature (T_C)	Auxiliary Gas Temperature Required (T_B)
Room Temperature	Room Temperature
100°C	126°C
200°C	257°C
300°C	387°C
400°C	518°C
500°C	649°C

4.3.4 Equivalent Enthalpy Trials

In this study, the ratio of carrier gas to propellant gas is approximately 6%. When this carrier gas is heated, it increases the overall enthalpy of the process which may be responsible for a portion of the DE increase experienced in particle preheating. To determine to what extent this added enthalpy is affecting deposition process, an experiment was designed to keep the particle temperature low while adding the equivalent enthalpy from the heated carrier gas. This was done using a custom injection nozzle, shown schematically in **Figure 18**, which allows for the unheated carrier gas and particles to be injected separately from the auxiliary gas.

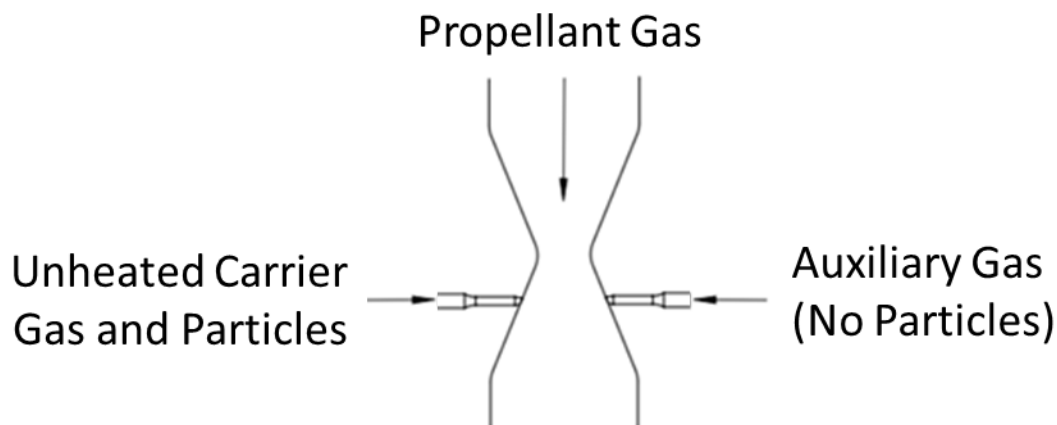


Figure 18: Schematic of custom injection system to inject hot gas without preheating the particles for the equivalent enthalpy trials.

To quantify the effect this added enthalpy has on the process, both modelling and spray trials were conducted using the same flow rates and temperatures employed in the particle preheating trials (Table 6) but with the arrangement shown in **Figure 18**. This will ensure that the exact same amount of energy enters the system, the only difference being that the particles will not be preheated. Any changes in deposition in these trials can be attributed solely to the enthalpy increase of the system and not particle temperature. These trials are referred to as the equivalent enthalpy trials and will reference the corresponding particle preheating temperature to which they have the same enthalpy.

4.3.5 Deposition Characterization and Particle Velocity Measurement

DE was measured by weighing the substrates before and after deposition and comparing the mass gain with the mass of powder fed. Each reported value is an average of 3 samples deposited at each condition. The powder feed rate was measured directly at the powder feeder exit in testing separate from the operation of the CS system, directly before and after spraying.

The deposit quality was investigated through microstructural analysis using a scanning electron microscope (EVO-MA10, Zeiss, Germany) and an optical microscope (VHX-2000E, Keyence, Canada). To quantify porosity level, entire cross sections of each deposit was stitched together using the software of the VHX-2000 at a magnification of 1000x. The porosity was calculated through contrast analysis of the optical images using ImageJ software. Microhardness testing of

the deposits were conducted on polished samples using a Vickers microhardness tester (Struers Duramin-1, Struers Inc., Cleveland, OH, USA) with a 50g load and a dwell time of 10s. To avoid the effect of the stress field, the distance between two indentations was kept greater than three times the length of the indentation. The reported values are the average of a minimum of 15 indentations for each set of parameters (5 per deposit).

Particle velocity measurements were taken using the ColdSprayMeter eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). This system uses a continuous 2.4 W ($\lambda=810$ nm) laser with a dual slit photomask to perform in-flight diagnostic on individual particles. It provides the precise velocities of individual particles during flight. In this study, the velocity measurements were taken at a point 10 mm downstream from the center of the cold spray nozzle exit. Testing was run for several minutes to ensure the collection of a robust data set of over 5000 particle data points.

4.3.6 Computational Fluid Dynamics

The commercially available computation fluid dynamics software, ANSYS Fluent, was used to produce three-dimensional models of the particle preheater, the standard CS nozzle, and the equivalent enthalpy configuration. A discrete phase of particles was also simulated for each of the models.

4.3.6.1 Continuous Phase Modelling of the CS Process

The mass, momentum, and energy equations were solved using a pressure-based solver with a coupled algorithm. To account for compressibility effects, nitrogen was assumed to obey the perfect gas law. Due to the high Reynolds number of the flow, and to solve the Reynolds Averaged Navier–Stokes equations, the k-epsilon model was used, which has been shown to provide accurate flow structure in CS (Ref 137). The flow is assumed to be in a steady-state regime. A 2D representation of the 3D domain is shown in **Figure 19**.

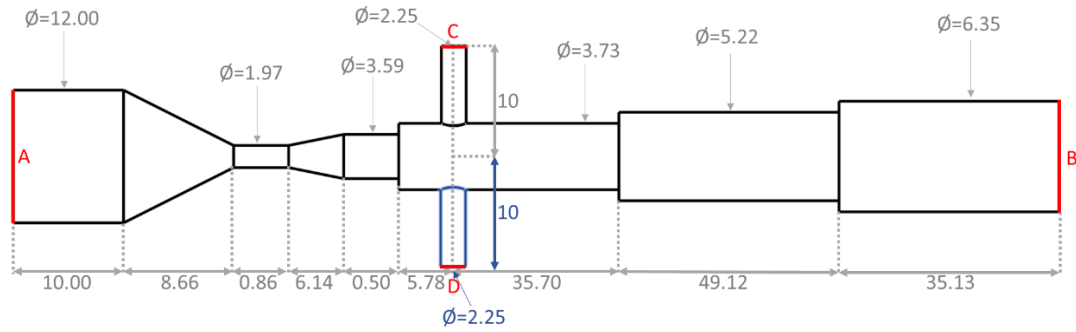


Figure 19: A 2D representation of the 3D computational domain dimensions for the cold spray nozzle. Red shows inlets and outlets. Blue is the auxiliary gas inlet and is not present for the preheated particle model. Not to scale. All dimensions in mm.

All of the surfaces of the domain are taken by default as adiabatic walls, except for the inlets (A, C, and D) and the outlet (B). At the propellant gas inlet (A), the flow was assumed to be uniform and normal to the inlet cross section with a prescribed pressure and temperature. The pressure at the outlet (B) was considered as atmospheric pressure. At the carrier gas inlet (C) and the auxiliary gas inlet (D), the flow was assumed to be uniform and normal to the inlet cross sections with a prescribed mass flow and temperature. Table 7 outlines the boundary conditions used in the model, where each row represents a different trial.

Table 7: Boundary Conditions for 12 Different Preheating Scenarios

Propellant Gas Inlet (A)		Carrier Gas Inlet (C)		Auxiliary Gas Inlet (D)		Outlet (B)
Temperature [°C]	Pressure [MPa]	Temperature [°C]	Mass Flow Rate [g/min]	Temperature [°C]	Mass Flow Rate [g/min]	Pressure [kPa]
500	3.54	15	59.2	NA	NA	101.3
500	3.54	100	59.2	NA	NA	101.3
500	3.54	200	59.2	NA	NA	101.3
500	3.54	300	59.2	NA	NA	101.3
500	3.54	400	59.2	NA	NA	101.3
500	3.54	500	59.2	NA	NA	101.3
500	3.54	15	9.9	15	49.3	101.3
500	3.54	15	9.9	126	49.3	101.3
500	3.54	15	9.9	257	49.3	101.3
500	3.54	15	9.9	388	49.3	101.3
500	3.54	15	9.9	518	49.3	101.3
500	3.54	15	9.9	649	49.3	101.3

The 3D domain was meshed using ANSYS WB meshing tool. Due to the large length scales of the flow, the domain was discretized into an unstructured triangular/tetrahedral mesh. In order to provide higher precision and resolution near the boundaries, inflation was used at the walls with a growth rate of 1.2 and 5 maximum layers. A grid dependency study was performed to determine the appropriate grid size ensuring grid independency. The solutions were iterated until convergence was reached by at least 3 orders of magnitude and then by ensuring that net mass and energy imbalances are below 0.001%.

4.3.6.2 Continuous Phase Modelling of the Particle Preheater

An assumption that was made in this work was that the particles and the gas are injected into the propellant flow at equilibrium conditions, where both gases are fully mixed, and the particles

are at the gas temperature. To confirm that the length of the coil in which the two flows mix was adequate for particles to reach the gas temperature, a 3D model of the powder preheating system was developed. The mixing coil was modeled as a straight tube, as the curvature radius of the coil was 25.4 mm, orders of magnitude larger than the particles and should not affect the results. **Figure 20** is a 2D diagram of the full 3D domain (not to scale). The numerical boundary conditions used for each condition are presented in Table 8, in which each row representing a different trial. The inlet flows are set mass flow rates that match the experiment, and the required temperatures of the hot gas were calculated from Eq. 29. For the pressure at the exit of the preheater, average pressure values were extracted from the solved model of the standard CS process at the point of injection.



Figure 20: A 2D representation of the 3D computational domain dimensions for the powder preheater model. Red shows inlets and outlets. Not to scale. All dimensions in mm.

Table 8: Boundary Conditions for Particle Preheater Model

Desired at Exit	Auxiliary Gas Inlet (A)		Unheated Carrier Gas Inlet (B)		Preheater Exit ©
Temperature [°C]	Temperature [°C]	Mass Flow Rate [g/min]	Temperature [°C]	Mass Flow Rate [g/min]	Pressure [kPa]
15	15	49.3	15	9.85	307
100	117	49.3	15	9.85	320
200	237	49.3	15	9.85	333
300	357	49.3	15	9.85	334
400	477	49.3	15	9.85	354
500	597	49.3	15	9.85	365

The mass, momentum, and energy equations were solved using a pressure based solver with a coupled algorithm. Nitrogen was assumed to obey the perfect gas law and to solve the Reynolds Averaged Navier–Stokes equations, the k-epsilon model was used. The flow was assumed to be in a steady-state regime. The 3D domain was meshed using ANSYS WB meshing tool. Due to the large length scales of the flow, the domain was discretized into an unstructured triangular/tetrahedral mesh. To provide higher precision and resolution near the boundaries, inflation was used at the walls with a growth rate of 1.2 and 5 maximum layers. A grid dependency study was performed to determine the appropriate grid size ensuring grid independency. The solution iterated until convergence was reached by at least 3 orders of magnitude and then by ensuring that net mass and energy imbalances are below 0.001%.

4.3.6.3 Discrete Phase Modelling

For all models, the particles were injected as a discrete phase of inert points in space using a Lagrangian method. In this method, momentum and heat transfer were examined as they pass through each control volume. For the CS model, a high Mach number drag correlation (the Henderson drag correlation), was used. This correlation covers a wide range of particle Mach numbers and Reynolds numbers and has been shown to have accurate results based on experiments in CS (Ref 96,138). For the particle preheater, the default spherical drag law was used as the relative gas velocities were subsonic. In all cases, the particles are assumed to be at a uniform temperature as the Biot number of the particles is well below the threshold of 0.1 required to use the lumped capacitance method. Heat transfer to or from the particle was assumed to be convective and computed using the Ranz and Marshall correlation for forced flow over spherical particles, which has been shown to have good correlation with experimental results (Ref 96). Additional body forces, such as gravity and lift, were not added as they provide little influence on the particle momentum in CS.

Energy transfer was coupled one way from the gas to the particles, ensuring the steady state solution of the continuous phase was unaffected during the discrete phase calculation. For the standard and equivalent enthalpy nozzles, the discrete phase only accounts for approximately 0.65% of the overall mass flow rate in the system, which is considered dilute. While particles in the preheater do account for a larger percentage of the total mass flow, it becomes prohibitively

expensive computationally to account for the effect of the particles on the gas phase while still accounting for the variation in size distribution in the particle stream.

A discrete random walk (DRW) model was applied to simulate the particles' turbulent dispersion. A random eddy lifetime was used with sufficiently large number of tries to ensure that the trajectories include statistical effect of turbulent dispersion. Since the particles are injected radially, some wall/ particle interactions are expected. However, experimental evaluation of the coefficient of restitution for impacts between smooth spherical aluminum particles and the polymer nozzle material could not be found in the literature. Consequently, the impacts were assumed to be perfectly elastic, which Ba et al. have shown to be adequate for the cold spray process (Ref 139).

To accurately model the particle size distribution in this flow, the particles were injected uniformly across the carrier gas inlet surface of the domain with initial temperature and velocity matching that of the gas stream at that point. Injections of nine different particle sizes were chosen, each matching the particle bin sizes shown in **Figure 15**. The resulting averages and distributions were weighted to match the true frequency percentage of particle diameters in the powder.

5 Results and Discussion

This chapter is presented in three sections, each containing a research paper addressing one of the main objectives outlined in Chapter 3. The first two articles are peer reviewed and published in an international journal relevant in the subject of CS, the Journal of Thermal Spray Technology. The third paper is written as a research article and has been submitted to a peer reviewed journal and is awaiting revision at this time.

5.1 Research Project 1: The Effect of a Non-Spherical Particle Morphology on the CSAM Process

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In this work, a method to manufacture low porosity titanium components at high deposition efficiencies is revealed. The components are produced by combining low pressure cold spray using nitrogen as the carrier gas with low-cost titanium powder produced using the Armstrong process. The microstructure and mechanical properties of additive manufactured titanium components are investigated. This peer reviewed paper addresses Objective 1 presented in Section 3.1.



Cold Spraying of Armstrong Process Titanium Powder for Additive Manufacturing

D. MacDonald¹ · R. Fernández¹ · F. Delloro¹ · B. Jodoin¹

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Abstract Titanium parts are ideally suited for aerospace applications due to their unique combination of high specific strength and excellent corrosion resistance. However, titanium as bulk material is expensive and challenging/costly to machine. Production of complex titanium parts through additive manufacturing looks promising, but there are still many barriers to overcome before reaching mainstream commercialization. The cold gas dynamic spraying process offers the potential for additive manufacturing of large titanium parts due to its reduced reactive environment, its simplicity to operate, and the high deposition rates it offers. A few challenges are to be addressed before the additive manufacturing potential of titanium by cold gas dynamic spraying can be reached. In particular, it is known that titanium is easy to deposit by cold gas dynamic spraying, but the deposits produced are usually porous when nitrogen is used as the carrier gas. In this work, a method to manufacture low-porosity titanium components at high deposition efficiencies is revealed. The components are produced by combining low-pressure cold spray using nitrogen as the carrier gas with low-cost titanium powder produced using the Armstrong process. The microstructure and mechanical properties of additive manufactured titanium components are investigated.

Keywords additive manufacturing · Armstrong process · cold spray · powder morphology · titanium

Introduction

Titanium is the ninth most abundant element on earth, has one of the highest specific strengths for a pure metal, maintains good properties at elevated temperatures, and has excellent corrosion resistance. However, the high cost to produce titanium components limits its use to high-end applications where cost is not a primary factor, usually in the aerospace, defense, and medical sectors (Ref 1, 2). This high cost is the result of two factors: The production of titanium mill product from primary materials requires many costly steps, and its reactivity and poor workability make it difficult to cast, forge, and machine (Ref 1).

Typically, titanium is converted from raw primary materials (such as rutile) to titanium sponge through the Kroll process (Ref 1). It must then be purified through acid leaching and undergo vacuum arc remelting to form an ingot. The latter must then undergo primary fabrication into mill products, casting to a near-net shape (Ref 1), or atomized into powder form. Forging is difficult and expensive, requiring many steps and various heat treatments; only rarely is titanium directly forged into finished components. Casting is also possible but challenging due to the materials' high reactivity to the atmosphere and to the other refractory materials common in the casting process. Near-net shapes can be produced using casting often with a combination of hot isotactic pressing (HIP) and traditional machining, but are limited in scope due to the production costs. As a result of these limitations, components are often produced through traditional manufacturing from large stock, which results in material losses of up to 90% for aerospace parts which accounts for over 60% of the final part costs. Even this traditional machining is difficult as titanium has a tendency for seizing and galling (Ref 2).

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Due to these cost factors, far less titanium is used in production applications than expected (Ref 1).

Near-net-shape components using additive manufacturing (AM or 3D printing) and powder metallurgy (PM) methods have recently been used to alleviate some of these cost problems (Ref 1–3). AM of metals can be separated into two broad categories: indirect methods, where a binder is used to bond the metal particles and post-processing is used to remove the binder and consolidate the part, and direct methods, where the final part is created directly without a binder (Ref 4). It is possible to fabricate intricate parts with good surface finishes with processes such as electron beam melting (EBM) (Ref 3–5); however, this process is currently limited by a manufacturing rate of 6 g/min at the very high end for titanium [modified from (Ref 6, 7) using a density of titanium of 4.51 g/cm³ (Ref 1)]. This deposition rate leaves much room for improvement. The printed parts also suffer from poor dimensional tolerances and surface finish when compared to machined or cast parts (Ref 8), as well as having a non-uniform grain structure due to uneven melting and heating (Ref 9). The size of these components is also limited to the size of the powder bed and inert environment chamber (Ref 3–5).

In most cases, titanium components produced using AM or PM methods require HIP processing (Ref 3, 10). By simultaneously applying pressure and temperature to the parts, consolidation of the pores is possible. However, HIP processing significantly affects the final component volume and geometry. This must be considered during the design stages and modeling continues to be a great challenge to accurately predict HIP shrinkage for AM and PM parts. Furthermore, the properties of HIP processed parts are usually found to be coarser than desirable and additional heat treatments are required. Lastly, the majority of these methods currently require the use of expensive, gas-atomized powders. As a result of these downsides, AM of titanium is often limited to small, non-structural components with low-quality requirements (Ref 1).

Cold gas dynamic spraying (CGDS) is a solid-state thermal spray process normally used for coatings and repairs. Over two decades of fundamental studies (Ref 11–19) have elucidated the theoretical principles of the process, which has led to the development of commercial equipment and applications (Ref 20–23). While the CGDS process has become established in recent years, particularly for repairs (Ref 24–27), it is still in its infancy as an AM process (Ref 28–36). CGDS could be used as a direct process for AM of titanium, taking advantage of the large deposition rates possible with CGDS systems [up to 500 g/min (Ref 37)]. This rate is an order of magnitude larger than the current fastest powder-based AM technology [83 g/min (Ref 38)]. CGDS process also results in high adhesion to the substrate (Ref 39), which could be used to

fabricate extensions on existing parts. Another advantage of the CGDS process is component that is not limited by tray size like in other AM processes.

However, according to the literature, helium or extremely high-pressure and high-temperature nitrogen is required to create dense titanium deposits (Ref 39–45). Schmidt et al. (Ref 13) proposed that the critical velocity for titanium is above 700 m/s for adiabatic shear instability to occur. This may limit the possibility of using this process as fabrication tool due to high cost of equipment and operation. The high temperatures required may also lead to degradation of the properties of the original component if the CGDS process is used to produce extensions of existing parts.

Recent advancements in titanium production have introduced new powder morphology to the market through the Armstrong process (Ref 46, 47). The powder produced through this method has a coral-like morphology, which is very different from commonly used powders in the CGDS process, such as spherical gas-atomized powder, mechanically crushed angular particles, or the titanium sponge morphology created during the Kroll process (Ref 21). Furthermore, the powder produced with the Armstrong process is attractive since it can be produced at a significantly lower cost when compared to traditional spherical powder. Normal spherical powder costs upwards of 110 USD/kg to produce, while Armstrong powder, which is produced directly from the reduction of TiCl₄ in a continuous liquid loop, costs only 11–24 USD/kg (Ref 48, 49).

It has been shown that the morphology of titanium powder can have an impact on deposition behavior. Wong et al. showed that irregular and sponge titanium morphologies had higher deposition efficiency (DE) when compared to spherical powders (Ref 45). This increase was attributed to a higher particle velocity, as a result of an increase in drag force combined with a lower mass. Wong et al. (Ref 45) also observed higher porosity levels in the coatings deposited with the sponge powder created through the Kroll process, attributed to the internal porosity of the feedstock powder. Yin et al. (Ref 50) have shown that irregular titanium particles may reduce substrate adhesion as a result of torque acting on the particle during impact with the substrate. However, there have been no studies on the CGDS of titanium powders produced by the Armstrong process.

The powder's unique morphology produces excellent compressibility and compaction behavior when used in traditional PM processes, capable of producing compacts with significantly higher green strength and lower porosity than other irregular powders (Ref 46, 48). The particular morphology of the powder should result in a large drag force combined with a lower mass per unit volume when

compared to spherical particles. As a result, it is possible that less aggressive CGDS parameters may be used to reach high DE and low-porosity deposits.

This work is a preliminary study on the use of unique titanium particle morphology, one produced during production using the Armstrong process (Ref 47), to produce high-density CGDS deposits with low-pressure and low-temperature nitrogen as propellant gas. The deposition behavior is examined through DE, particle velocity, coating density, and hardness. The understanding of the behavior is further enhanced through particle impact modeling. Lastly, CGDS is used to additively manufacture tensile test samples and heat treatments are done to improve the mechanical properties of the AM components. The combination of the reduced machining costs of AM, the high deposition rates and low operating costs of CGDS, and low-cost powder from the Armstrong process could significantly reduce the overall cost of producing large, near-net-shape, titanium components.

Materials and Methods

Feedstock Powder

The feedstock powder used for this study was commercially pure (grade 2) titanium powder (<325 mesh) from Cristal Metals (Cristal US Inc., Woodridge, IL, USA). It is produced using the Armstrong process. The process produces powder particles with unique, low bulk density, “coral-like” morphology as shown in Fig. 1.

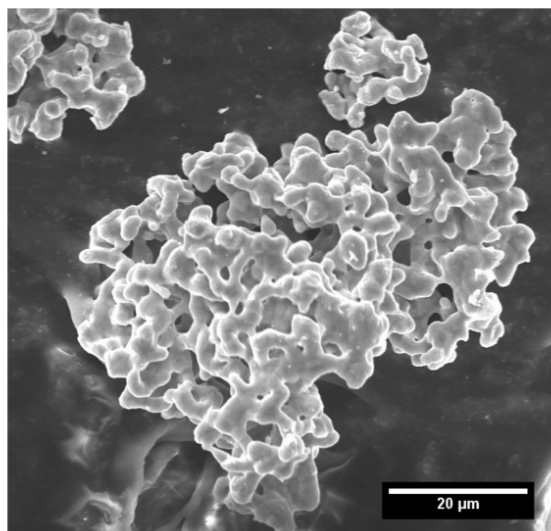


Fig. 1 SEM image of coral-shaped titanium powder produced using the Armstrong process

CGDS Process

The titanium powder was consolidated using the commercially available SST Series EP Cold Spray System (Centerline Ltd, Windsor, Canada). The system has a maximum operating gas temperature of 550 °C and a maximum gas pressure of 3.8 MPa. A stainless steel de Laval nozzle with a 2-mm-diameter throat, a 120-mm-long diverging section, and an exit diameter of 6.6 mm was used. Powder was fed downstream of the orifice at a 45° angle using a commercially available powder feeder from Praxair Surface Technologies (Model 1264, Praxair Surface Technologies, Concord, NH, USA).

In order to investigate the effect of process gas pressure and temperature on the deposition behavior of this powder, the parameters in Table 1 were used. Since densification of this powder in other PM processes requires less energy than with spherical powder, it is envisioned that deposition may be possible at lower ranges of parameters than those discussed in the literature (Ref 13, 39–45). Therefore, a large range of temperatures and pressures were tested in order to understand the behavior of this unique powder morphology during the CGDS consolidation process.

In order to further understand the deposition behavior of single particles, single impact analysis was also completed. This was done by reducing the powder feed rate while holding the other parameters constant in order to see the impact of only one particle at a time on the substrate. For these tests, the substrate was polished commercially pure titanium (grade 2).

Sample Characterization

As-received powder, single impact tests, and consolidated powders (thick deposits) microstructures were investigated using a scanning electron microscope (EVO-MA10, Zeiss, UK) and an optical microscope (VHX-2000E, Keyence, Canada). In order to quantify porosity level, cross sections of the deposits were stitched together using the VHX-2000 software at a magnification of 200×. The porosity was then quantified through contrast of the optical images using ImageJ software for three cross sections per deposit. Microhardness testing of the deposits was conducted on the cross section of polished samples using a Vickers

Table 1 CGDS parameters during testing

Parameter	Value
Gas nature	Nitrogen
Gas pressure	1.0–3.8 MPa
Gas temperature	100–500 °C
Powder feeder gas flow rate	1.7 m ³ /h
Powder feeder gas nature	Nitrogen
Standoff distance	10 mm

microhardness tester (Struers Duramin-1, Struers Inc., Cleveland, OH, USA) with a 300-g load with a dwell time of 15 s. To avoid the effect of the stress field, the distance between two indentations was kept at >3 times the length of the indentation. The reported values are the average of a series of ten indentations for each sample, taken at different areas of the dense center of the deposit. Substrate temperatures were measured using an infrared camera (FLIR E50, FLIR Systems Inc., USA).

Particle Velocity Measurement

Particle velocity measurements were taken using the Cold-SprayMeter (CSM) eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). This system uses a continuous 2.4 W ($\lambda = 810$ nm) laser with a dual-split photomask in order to perform in-flight diagnostic on individual particles. It provides precise velocity of individual particles during flight. In this study, the velocity measurements were taken at a point 10 mm downstream from the center of the cold spray nozzle exit. Testing was run for several minutes to ensure the collection of a robust set of data to ensure significant results.

Modeling of Particle Impact Dynamics

The aim of the modeling work was to demonstrate that powder morphology can have a capital importance on the densification and bonding seen in the CGDS consolidation process. This study shows the densification of the coral-shaped titanium powder and compares it to the experimental single impact testing. This study also compares the behavior of the coral-shaped titanium powder versus the behavior of traditional gas-atomized spherical powders through a 2D modeling approach.

Most of the modeling approaches in the field of CGDS deal with spherical particles (Ref 51–57). Few exceptions appeared recently in the literature. A study (Ref 50) simulated the 2D impact of elliptical particles. Another dealt with 3D simulation of pseudo-cylindrical particles (Ref 58). For the current work, the modeling will use 2D particle approximation. A specific image treatment procedure was developed, based on a marker-driven watershed algorithm, implemented in the open-source Simple Morphological Image Library (SMIL) software. First, thresholding of the image was performed to identify the particle, which was used as a mask for the watershed. The segmented image was then treated with an in-house code in order to extract the external perimeter of the image as a sequence of coordinates. The same procedure was applied to the internal porosity. A piecewise linearization algorithm was then applied to simplify the data and thus reduce the number of points. This procedure enabled to import the real cross-sectional morphology of the particles into the finite

element software Abaqus/Explicit®. The geometries obtained in this way were meshed using bilinear quadrilateral elements within Abaqus.

The modeling physics did not differ from most of the modeling efforts presented in the literature [e.g., (Ref 59, 60) among many others]. The “Mie-Gruneisen” equation of state (EOS), describing material state in the high-pressure domain and shock wave propagation, was used in the Hugoniot formulation,

$$p - p_H = \Gamma \rho (E - E_H)$$

where p is the pressure, ρ the density, E the internal energy, $\Gamma = \Gamma_0 \rho_0 / \rho$, $\eta = 1 - \rho_0 / \rho$, $p_H = \rho_0 c_0^2 \eta / (1 - s\eta)^2$, $E_H = p_H \eta / 2\rho_0$. Subscript zero refers to a standard reference state. The number of independent parameters sums up to three in the EOS: η , s and c_0 . Further details can be found in Antoun et al. (Ref 61).

The widely used Johnson-Cook model (Ref 62) was selected as an empirically based representation of the yield stress. The material parameters were readily available in the literature for titanium (Ref 51, 63) which was decisive for the choice of Johnson-Cook model. The model involved strain hardening, strain rate hardening, and thermal softening. The yield stress is given as:

$$\sigma_{JC} = (A + B\epsilon^n) \left(1 + C \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0} \right) \left[1 - \left(\frac{T - T_0}{T_m - T_0} \right)^m \right]$$

At the interface between the particle and the substrate, friction was considered. A modified Coulomb model was applied (i.e., the limit shear τ grows linearly with the contact pressure, until an upper value, namely $\tau_{\max}$, is reached). Metallurgical adhesion was not considered as it was not believed to have an important influence on the deformation process during impact. All the material parameters are summarized in Table 2.

In order to achieve numerical convergence under intense deformation conditions usually found in cold spray, an adaptive meshing tool (adaptive Lagrangian-Eulerian or ALE) available in the Abaqus software was applied to a domain which corresponded to the particles and the part of the substrate closer to the particle (i.e., the part finely meshed). ALE performed a regularization of the distorted mesh by displacing the nodes at the interior of the selected domain, which resulted in a reduced overall distortion. The solution was then mapped to the new mesh. The whole simulation was divided into several temporal steps, in order to adjust the remeshing parameters during the simulation as often as needed for the benefit of convergence.

Post-processing Heat Treatment

It is known that in the CGDS process, the resulting depositions usually contain residual stresses, and suffer brittle

fracture (Ref 64–66). Performing post-deposition heat treatment can reduce porosity and internal defects and improve mechanical properties (Ref 65). These heat treatments can result in recovery, recrystallization, and grain growth in the titanium deposits and were shown to significantly increase the ultimate tensile strength (UTS) and yield strength of deposits (Ref 65). In order to enhance the mechanical properties of the deposited components in this study, heat treatments were performed on selected samples. This was done under vacuum to prevent oxidation for three different heat treatments based on the existing literature; 870 °C for 36 h (Ref 67), 650 °C for 8 h (Ref 68), and 1000 °C for 3 h (Ref 69).

Mechanical Testing

Additional mechanical testing of selected samples was completed after heat treatment to assess the mechanical properties of the fabricated parts. These samples were tested using the standard test method for tension testing of metallic materials (ASTM E8) (Ref 70). The dimensions of the CGDS fabricated tensile samples are shown in Fig. 2.

Table 2 Material parameters used for model [taken from (Ref 51, 63)]

Symbol	Description	Value
P	Density (g cm^{-3})	8.96
μ	Shear (GPa)	41,400
A	JC (MPa)	90
B	JC (MPa)	292
C	JC	0.025
N	JC	0.31
M	JC	1.09
e_0	JC	1
c_0	EOS (m s^{-1})	3972
S	EOS	1.478
Γ_0	EOS	2
T_m	Melting point (K)	1356
c_v	Heat capacity ($\text{J K}^{-1} \text{kg}^{-1}$)	383
K	Thermal conductivity ($\text{W K}^{-1} \text{m}^{-1}$)	400

JC Johnson-Cooks, EOS equation of state

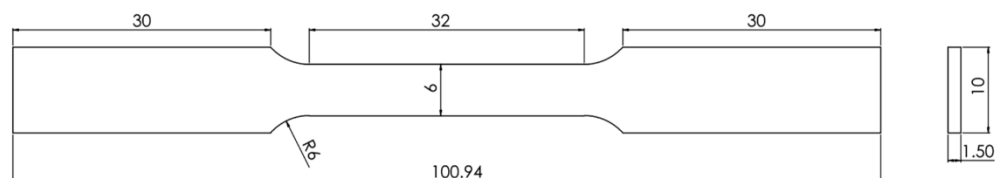


Fig. 2 Dimensions of tensile test specimens (in mm)

Results and Discussion

Deposition Behavior and Sample Characterization

A mapping of the average particle velocities is shown in Fig. 3. This figure shows that as gas pressure and temperature are increased, the average particle velocities also increase. This is what is expected from the literature (Ref 71). What is notable is that all of these velocities are well below the required critical velocity (indicated by a dotted line in Fig. 3) proposed for titanium proposed by Schmidt et al. (Ref 13), which had been confirmed by others in the literature (Ref 40, 45, 72). The low velocities observed in the current work are attributed to the use of nitrogen gas at lower pressures and temperatures than typically used by others. The lower dotted line in Fig. 3 shows the point at which deposition occurred in this study. It appears that critical velocity for this powder is much lower (almost 50%) of that required for the spherical titanium studied by others.

DE was measured by weighing the samples before and after deposition and comparing the mass gain with the mass of powder fed. The powder feed rate was measured directly at the powder feeder exit in testing separate from the operation of the CGDS system. The DE as a function of stagnation temperature for different pressures is shown in Fig. 4. Since the particle velocities were substantially lower than the critical velocities found in the literature, it was expected that DE should also be low. However, the DE was found to reach approximately 90% for the highest particle velocities. Although high DE is expected with titanium, normally much higher velocities than those obtained in this work are required to approach 100% DE (Ref 40, 45, 72).

The density of the deposits as a function of spray process parameters (gas pressure and temperature) is shown in Fig. 5. This figure shows that for all but the lowest parameters, the coatings have high-density levels. It should be noted that these values are averages of the entire cross section of the as-sprayed component, with the majority of the porosity contained in the edges of the deposition, which is a typical characteristic of CGDS titanium (Ref 45, 73).

The results of high DE and low porosity levels suggest that the values reported in the literature for titanium critical

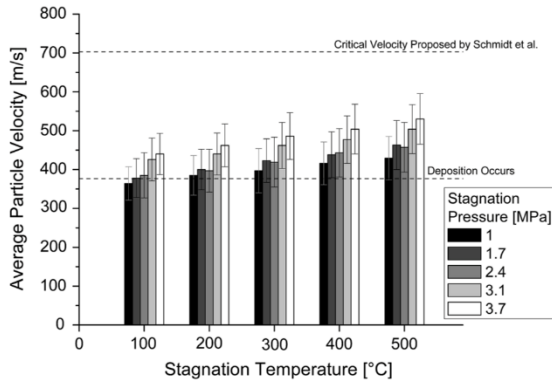


Fig. 3 Average particle velocity for different temperatures and pressures

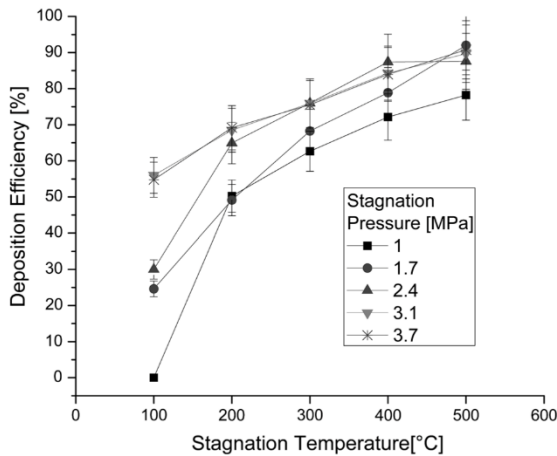


Fig. 4 Deposition efficiency vs gas stagnation temperature for different gas stagnation pressures

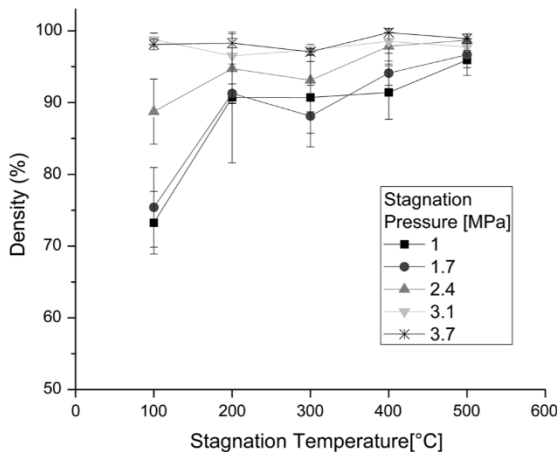


Fig. 5 Coating density vs gas stagnation temperature for different gas stagnation pressures

velocity may not be appropriate for non-traditional powder morphology such as the one used in this work. An example of a dense cross section is shown in Fig. 6(a). This result is unexpected since the particle velocities are well below the velocities required for dense coatings according to the literature. According to Wong et al. (Ref 40), a deposition of spherical particles at over 600 m/s resulted in a coating of approximately 20% porosity and 46% DE. In comparison, the highest velocity average reached in this study was 530 m/s, which reached a DE of 90% and porosity of 1.1%. It is clear from this result that the powder morphology is a critical component of the CGDS process. This densification behavior appears to be similar to high green density that was observed in PM processes using this powder (Ref 48).

Although the coatings were dense, the microhardness only ranged from 55.5 ± 16.0 to 87.2 ± 8.2 HV_{300g}. These values are substantially lower than expected values for bulk commercially pure titanium [145 HV (Ref 1)] and titanium coatings produced through CGDS [>190 HV (Ref 40)]. These results are unforeseen, as in CGDS traditionally dense coatings have a high level of deformation and therefore a high level of cold working which results in higher hardness. The image of the hardness test of as-sprayed component shown in Fig. 6(b) provides some insight into the deposition behavior of this powder. Cracks can be seen propagating from the indentation. These cracks are suspected to be following particle boundaries, demonstrating that there is very little cohesion between particles. This again is unexpected, since in CGDS the particle velocities required to get a dense coating usually results in strong particle to particle cohesion.

Fracture surfaces of the as-deposited component were investigated with SEM and are shown in Fig. 7. The fractographic analysis leads to no signs of the normal fracture mechanisms seen in titanium. The lack of characteristic markings, such as cup and cone dimple rupture, leads to the conclusion that this fracture surface contains little to no metallurgical bonding (Ref 74). These types of fracture surfaces are much closer to those seen in PM at a green state (before sintering) (Ref 75).

Understanding Deposition Through Single Impact Analysis and Modeling of Particle Impacts

In order to enhance the understanding of the deposition behavior of the particles during impact, modeling and single impact testing was done for a single set of deposition parameters. The CGDS spray parameters used to for this model and single impact analysis were 1.7 MPa and 500 °C. These parameters were selected as the DE and density did not appear to increase substantially beyond this point. These CGDS spray parameters resulted in an average particle velocity of 463 m/s. The substrate temperature was

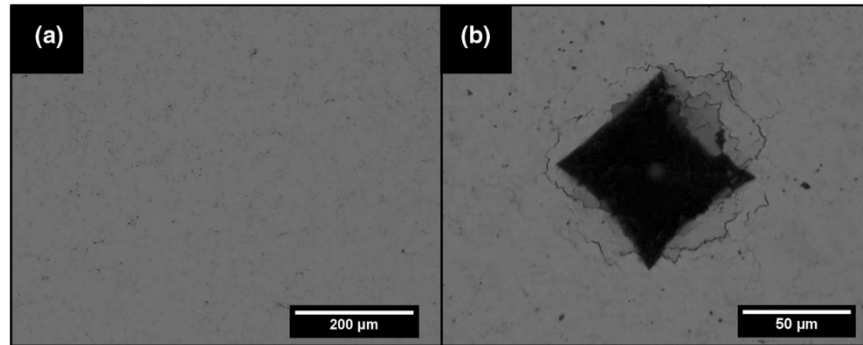


Fig. 6 Optical image showing a near fully dense deposition (a) with cracking around Vickers microhardness indentation (b) (deposited at gas pressure and temperature of 1.7 MPa and 500 °C)

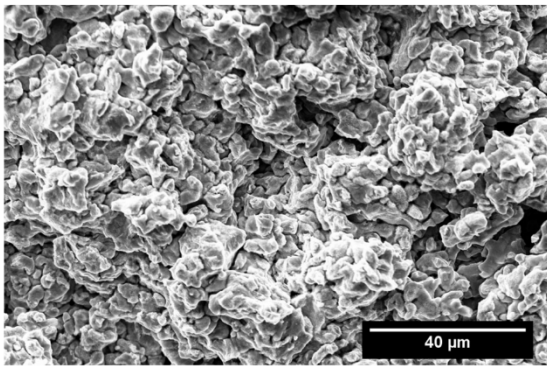


Fig. 7 SEM image of fracture surface of CGDS-deposited titanium powder

found to be 188 °C. This particle velocity and substrate temperature were used as inputs for the model. The particle temperature could not be measured and was assumed to be the same temperature as the substrate at the point of impact.

It is hypothesized that during impact, the unique particle morphology allows the particles to anchor to one another while collapsing and flattening on themselves, resulting in a high DE and dense structure with very little cohesion between the particles. The results of the simulations showing the impact behavior of two particles with real geometries is shown in Fig. 8(a), (b), and (c). This figure acts as a visual aid, showing how, as a result of powder morphology, the particle is able to collapse almost fully during impact. Figure 8(d), (e), and (f), shows SEM images of particles that have not been compacted during impact with the substrate. It is clear from these images that the model accurately predicted the behavior of the coral-shaped particles.

Figure 8 not only shows the method for densification, but sheds light on the how the particles would be able to interlock with each other without creating metallic bonds

between the particles. This interlocking of the particles helps explain why such high DE is achievable at low particle velocities. Spherical particles, which are normally used in CGDS, would require adiabatic shear instability at the impact zone to achieve bonding and form a coating. In this case, this is no longer required for this morphology of powder.

Figure 9 shows the resulting plastic equivalent strain (PEEQ) contours of spherical titanium particles and coral-shaped particles upon impact with the substrate obtained from the model. The spherical particles (Fig. 9a) only have PEEQ in the immediate vicinity of the impact zone. These particles also show no metal jet formation along impact area. This result shows that these spherical particles are unlikely to adhere at these low impact velocities. Figure 9(b) shows areas of much higher peak throughout the particles, but especially at the impact area. This higher PEEQ may be a result of decreased interfacial contact area, which could result in bonding but only on a small fraction of the interface. Zones of deformation can also be seen away from the impact zones of the particles, especially concentrated at thin zones of the particle. This localized plastic deformation results from a torque caused by inertia force of a portion of the particle created during impact. This deformation is responsible for the collapse of the particle and is assumed to be the cause of the resulting easy densification.

It can also be extrapolated that the impact of subsequent particles is responsible for the densification of the remainder of the porosity that is left at the top of the particle. Overall, this deformation results in a much higher flattening ratio for the coral-shaped powder. The flattening ratio, defined by the ratio of the longest length of the particle to the shortest length of the particle, of the center particle in the circular simulation increased by 24%, while the flattening ratio of the center particle in the coral-shaped powder increased by 64%.

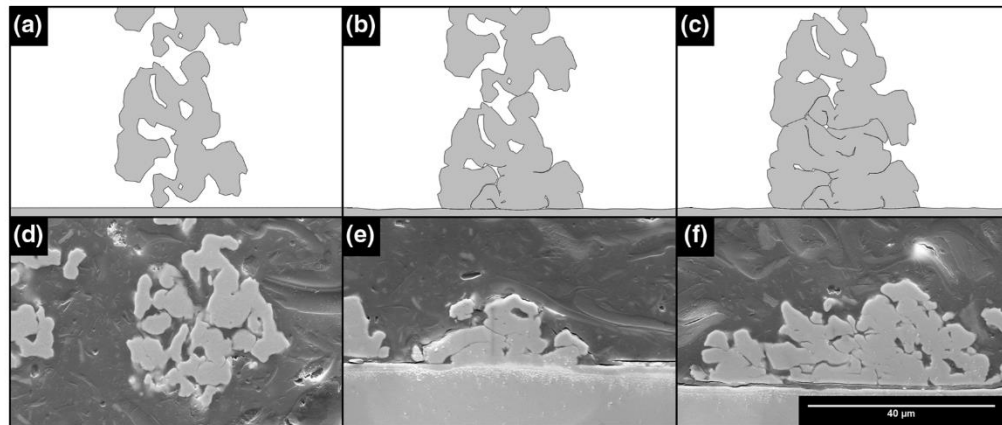
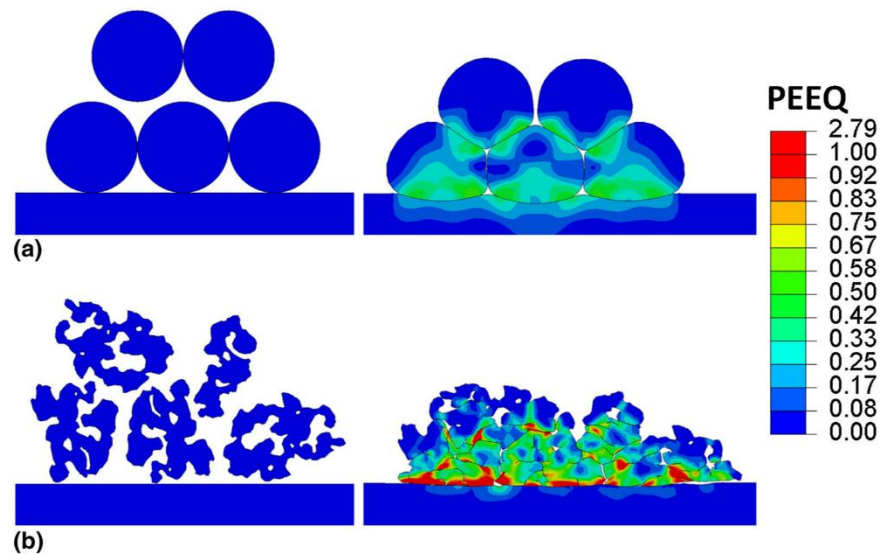


Fig. 8 Modeling and SEM images of densification behavior of coral-like powder showing a particle without impact (a, d), single particle after impact with substrate (b, e), and a multiple particle impact (c, f)

Fig. 9 PEEQ contours of five spherical (a) and five coral-shaped particles (b) before impact (left) and after impact with a velocity of 463 m/s and a temperature of 188 °C (right)



Based on these modeling results, it is sensible to conclude that with the coral-shaped particles, metallurgical adhesion could happen more readily than for the case with spherical particles, with the same impact velocities, due to high localized PEEQ at the impact zones. However, this contact area would be quite small. It was also observed that there was mechanical interlocking between particles. Both of these bonding mechanisms would result in a weak bond, but be favorable to a high DE. The modeling results also demonstrate how this powder is able to reach such high density, even at such low particle velocities through plastic deformation throughout the entire particle, resulting in a high flattening ratio.

Heat Treatment and Resulting Properties

The CGDS parameters used to fabricate the components to be heat-treated are 1.7 MPa and 500 °C. Since the behavior of the deposits appears to be similar to that of green compacts in PM, the low hardness and poor cohesion of the fabricated components can potentially be overcome by growing metallic bonds between particles through heat treatment (Ref 76). These heat treatments were done under vacuum (1×10^{-7} Torr) for the specified times and temperatures listed in “[Post-processing Heat Treatment](#)” section. SEM images of these samples after hardness testing, followed by etching (solution of

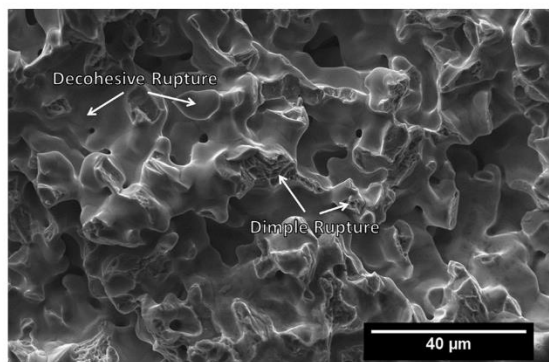


Fig. 10 SEM image of fracture surface of heat-treated tensile specimen

1:1:20 of HF:H₂O₂:deionized water), are shown in Fig. 10, and hardness results are shown in Table 3.

In Fig. 11(a), cracking and delamination between particle boundaries can be seen around the edges of the microhardness indent. Since this sample does not have a heat treatment, it is expected to have the same cracking artifacts seen earlier as well as having a low hardness (Table 3). Figure 11(b) and (d) shows that this cracking around the indents is no longer present. This result shows that cracks can no longer propagate through the particle boundaries, indicating that metallic bonding has occurred between the particles. For the heat treatment C, an increase in hardness is present indicating that the cohesion between the particles has increased; however, cracking at the particle boundaries is still visible indicating that the heat treatment process was not adequate to induce full bonding between the particles (Fig. 11(c)).

It was found that for two of the heat treatments (B and D), the component microhardness was above that for bulk materials. This additional hardness is likely due to increased oxygen content present in the finished component (Ref 1). This small percentage of oxygen was likely present in the original powder as the CGDS process is done in an inert nitrogen environment and the heat treatment occurred in a vacuum ($<10^{-7}$ Torr).

Tensile samples (dimensions found in Fig. 2) were fabricated using CGDS using the using the same spray parameters as the previous heat treatment testing (1.7 MPa

and 500 °C nitrogen). The samples were then separated from the substrate. These samples were heat-treated at 1000 °C for 3 h, as this heat treatment resulted in the highest hardness in the heat treatment testing. After heat treatment, the samples have been machined to final dimensions. Stress relief annealing at 550 °C for 2 h (Ref 1) was done after machining.

Tensile testing of the samples resulted in an UTS of 277 ± 88 MPa. The average value found is above the minimum value listed for UTS in the literature of 240 MPa (Ref 1). However, all three samples underwent brittle fracture with little plastic deformation.

Figure 11(d) shows that the component recrystallized and that the particles were bonded during the heat treatment. Therefore, it would be expected that any residual stress or cold work would be eliminated, and the component should have failed in a similar ductile manner as the bulk material. However, post-fracture analysis showed that the fracture propagated from flaws created during final machining steps at the neck area of the sample. These flaws would have created stress concentrations during tensile testing, resulting crack propagation and sudden, brittle fracture. Therefore, the values for the UTS do not reflect the true strength of the material, but a minimum value for components without stress concentrations.

Fractographic examination of the fracture surfaces using SEM shows a very unique topography. The majority of the fracture area was found to be a smooth surface of irregular shapes without normal fracture patterns such as dimple rupture, cleavage, or fatigue markings. This kind of fracture is referred to as decohesive rupture, which normally exhibits little to no bulk plastic deformation. This type of fracture can occur as a result of a unique microstructure and it is associated with rupture along grain boundaries (Ref 74). In this case, a fracture surface that appears to follow the original particle boundaries is seen. This kind of surface is seen commonly in PM fracture surfaces after sintering (Ref 76).

This fracture surface also shows areas of dimple rupture, showing a failure by a process known as microvoid coalescence (Ref 74). This type of fracture exhibits numerous cuplike depressions, referred to as dimples. This type of mixed fracture mode surface is a result of an inappropriate heat treatment/ sintering, as there is preferential failure along particle boundaries. Continued sintering should

Table 3 Vickers hardness values before and after heat treatment

Designation letter	Temperature (°C)	Time (h)	Hardness (HV _{300g})
A	N/A	N/A	80 ± 12
B	870	36	214 ± 36
C	650	8	164 ± 43
D	1000	3	214 ± 43

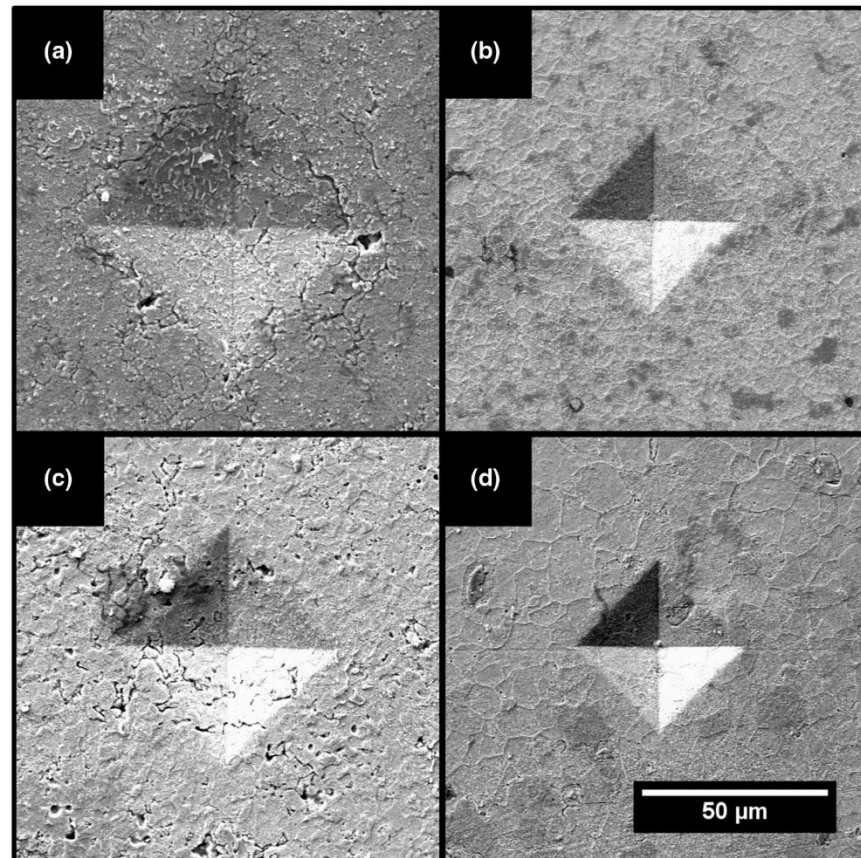


Fig. 11 SEM images of etched samples (a) before heat treatment, (b) after 870 °C for 36 h, (c) 650 °C for 8 h, and (d) 1000 °C for 3 h

increase the number and area fraction of the ductile torn regions (Ref 3, 76).

Conclusion

Fully dense titanium parts were fabricated using CGDS as an AM process. This was accomplished using low-pressure and low-temperature nitrogen as the process gas. The key to this result is attributed to the unique coral-shaped powder morphology that allows the easy densification and deposition through CGDS. Although the properties of these components are not ideal in the as-manufactured state, a short heat treatment of 3 h results in properties comparable to bulk material in terms of hardness and UTS.

This is a promising approach for CGDS as a method for AM of titanium parts. The low powder cost and the advantages of additive manufacturing could allow for a

substantial cost savings in titanium part production when compared to traditional manufacturing methods. CGDS also makes AM of large titanium parts attractive as it addresses some of the drawbacks of the other AM processes such as deposition rates, post-processing and shrinkage, and size limitations. Lastly, the CGDS process cost is kept low due to the ability to use nitrogen and low process parameters—which would not be possible using traditional spherical powders.

With these cost saving advantages, AM of titanium using Armstrong process powder and CGDS could lead to a paradigm shift of titanium production, allowing titanium to enter markets that under traditional methods would be far too expensive.

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5.2 Research Project 2: Effect of Blended Propellant Gas on the CSAM Process

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This work focuses on the development and use of a novel, in-line gas mixing system, designed to provide a blend of nitrogen and helium at any ratio. Deposits produced with different gas ratios are investigated through particle velocity measurements, deposition efficiency, coating porosity, and coating hardness. The experimental results show that helium, even in lower percentages, can have a significant effect on deposition efficiency and coating quality. From the results, a cost model is presented which, when provided experimental values and user costs, can be used to identify the nitrogen-helium ratio that will produce the lowest overall coating cost. This peer reviewed paper addresses Objective 2 presented in Section 3.1.

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PEER REVIEWED

An Economical Approach to Cold Spray Using In-line Nitrogen–Helium Blending

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Abstract The cold gas dynamic spraying process provides an advantageous solution to the deposition, and additive manufacturing, of metals. Namely, it provides a reduced reactive environment, simple operation, and high deposition rates. It is known that the deposition efficiency of the cold spray process can be substantially increased using helium instead of nitrogen as the process gas. However, the use of pure helium can be cost prohibitive and commercially available helium recovery systems constitute a major capital investment and cannot be used with portable systems. This work focuses on the development and use of a novel, in-line gas mixing system, designed to provide a blend of nitrogen and helium at any ratio. Deposits produced with different gas ratios are investigated through particle velocity measurements, deposition efficiency, coating porosity, and coating hardness. The experimental results show that helium, even in lower percentages, can have a significant effect on deposition efficiency and coating quality. From the results, a cost model is presented which, when provided experimental values and user costs, can be used to identify the nitrogen–helium ratio that will produce the lowest overall coating cost.

Keywords cold spray · cost optimization · deposition efficiency · gas blending · gas mixing · helium · nitrogen

Introduction

Cold gas dynamic spraying (CGDS) is a solid-state thermal spray process in which metallic particles are injected into a compressed gas stream that has been accelerated through a converging–diverging (de Laval) nozzle (Ref 1–3). From the infancy of the CGDS process, it has been known that the propellant gas nature has a significant effect on particle velocity. Typically, this increase in particle velocity results in higher deposition efficiency (DE), flattening ratio, and cohesive strengths of coatings (Ref 1, 4–6).

As a result of the complex gas/particle interaction in the CGDS process, numerous modeling investigations and experimental trials have been performed to predict the particle velocities (Ref 7–12). These investigations show that an increase in the gas velocity should increase the particle velocity. For simplicity, the gas velocity at any point is evaluated using the Mach number and the speed of sound at that point,

$$V = M_a \sqrt{kRT} \quad (\text{Eq 1})$$

where M_a is the gas local Mach number, R is the specific gas constant, T is the local gas temperature, and k is the gas heat capacity ratio. The temperature of the gas at any point can be estimated using the 1D isentropic relationship (Ref 11–13),

$$\frac{T_o}{T} = 1 + \frac{(k-1)}{2} M_a^2 \quad (\text{Eq 2})$$

where T_o is the gas stagnation temperature. From Eq 2, it can be seen that for the same nozzle geometry (setting the local

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gas Mach number) and gas nature, an increase in stagnation temperature will result in a higher local temperature, which in turn will result in a higher local gas velocity (and therefore particle velocity). This relationship has been established by many authors (Ref 3, 7, 14–19). However, many practical limitations exist in how high this temperature can be. Nozzle clogging (Ref 20–22), substrate overheating (Ref 14, 23), and limits of commercially available equipment (Ref 24) are all factors that set the upper limit for a particular spray. An increase in the gas stagnation pressure should result in increased drag force experienced by the particle and a potentially higher particle velocity as well. Typically, this pressure is also limited [max of 6.89 MPa (Ref 25)] in the commercial available systems for practical reasons (such as gas consumption and gas heater capacity). It should also be noted that the particle velocity is limited to the gas velocity, regardless of the pressure (Ref 13).

The nozzle geometry is also an important factor for particle velocity as it determines the local Mach number, the acceleration time, and the heat transfer the particles will experience. Nozzle parameters such as inlet, throat, and exit diameters as well as convergent and divergent sections lengths have been shown to have an effect on particle velocity (Ref 12, 24, 26). However, gas dynamic principles limit the maximum Mach number at the nozzle exit (Ref 27), material constraints such as the need for high-temperature-resistant polymers (Ref 22), and practical fabrication and machining limitations restrict the extent to which the velocity can be improved through nozzle design. Because of these limitations, very few nozzles designs are commercially available for each system.

Since these practical limitations may set the maximum gas temperature, pressure, and nozzle geometry, the gas nature itself may be the only parameter available to increase the particle velocity. This effect of the nature of the gas is seen in Eq 1 through the specific gas constant and the heat capacity ratio. The specific gas constant is a function of the molecular weight of the propellant gas,

$$R = \frac{\bar{R}}{M^*} \quad (\text{Eq 3})$$

where $\bar{R}$ is the universal gas constant and M^* is the molar mass of the gas. The heat capacity ratio is,

$$k = \frac{C_p}{C_v} \quad (\text{Eq 4})$$

where C_p and C_v are the heat capacity at constant pressure and volume, respectively, which are related to the molecular weight through Eq 5.

$$C_p - C_v = R \quad (\text{Eq 5})$$

Helium, nitrogen, and air are primarily used as CGDS process gasses. Helium has a substantially lower molecular

weight (4.0126 g/mol) when compared to nitrogen (28.013 g/mol) and air (approximately 29 g/mol) (Ref 5). According to the 1D model, the velocity of helium is 2.89 times higher than nitrogen at the same Mach number and local temperature. This higher gas velocity typically results in higher particle velocities when using helium for fixed spray conditions as stated in the original CGDS patent (Ref 3).

One can deduce from the 1D isentropic approximation that the use of helium will result in higher particle velocities; however, its usage may be prohibitively expensive. While in recent years helium recycling systems have been shown to keep the costs competitive with nitrogen (Ref 28), these systems are expensive and cannot be used in combination with portable CGDS systems typically used for in-field repairs. It has also been demonstrated that the blending of helium and nitrogen result in an increase in particle velocity with an increase in helium concentration (Ref 5, 12, 25). However, in all the previous gas mixing research, the gas is always premixed in containers at set ratios, thus limiting gas mixing to laboratory scale spray trials and complex mixing operations.

To calculate the velocities for the mixed gas, the molar weight for a helium/nitrogen mixture is found from the following relationship,

$$M^* = x_{\text{He}}M_{\text{He}} + x_{\text{N}_2}M_{\text{N}_2} \quad (\text{Eq 6})$$

where x_{He} and x_{N_2} are the molar fractions of helium and nitrogen, respectively, and M_{He} and M_{N_2} are the molar masses of helium and nitrogen, respectively (Ref 25).

The ratio of specific heat for the mixture is given by,

$$C_p = C_{p_{\text{He}}}w_{\text{He}} + C_{p_{\text{N}_2}}w_{\text{N}_2} \quad (\text{Eq 7})$$

where $C_{p_{\text{He}}}$ and $C_{p_{\text{N}_2}}$ are the specific heat for helium and nitrogen, respectively, and w_{He} and w_{N_2} are the mass fraction of helium and nitrogen, respectively (Ref 25). The mass fractions can be found through Eq 8 and 9.

$$w_{\text{He}} = \frac{x_{\text{He}}M_{\text{He}}}{M^*} \quad (\text{Eq 8})$$

$$w_{\text{N}_2} = \frac{x_{\text{N}_2}M_{\text{N}_2}}{M^*} \quad (\text{Eq 9})$$

By solving all the aforementioned equations simultaneously, the gas velocity is calculated for any flow mixture and Mach number. As an example, the choked velocity at a nozzle throat (Eq 1 with $M_a = 1$), for a CGDS process operating at stagnation temperature and pressure of 500 °C and 3.4 MPa, respectively, is plotted in Fig. 1 as a function of the volume percentage of helium used in the gas mixture.

The effect of helium addition on the gas velocity is clear from Fig. 1 and is in agreement with the literature (Ref 7–11). However, the effect of the increased gas velocity on

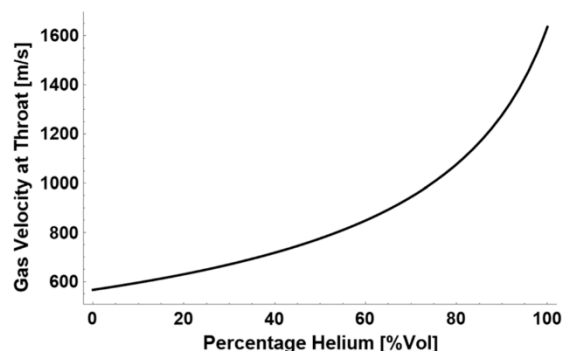


Fig. 1 Gas velocity at nozzle throat ($M_a = 1$) as a function of volume percentage of helium in process gas mixture

particle velocity, DE, and coating characteristics is much harder to predict. The momentum transfer between the gas and the particle is not only a function of the gas velocity, but of the local gas density and relative local Mach number. The particle impact temperature (a function of gas density, velocity, and temperature and Mach number) and gas impact temperature have also been shown to influence the deposition quality and DE (Ref 4, 6, 23, 25). Because of these complex interactions, experimental work is required to determine the full effect of helium addition.

The purpose of this study is to examine the relationship between helium concentration and coating/deposition characteristics for several commercially available and industrially relevant materials using a novel, in-line, gas mixing device. The device is designed to improve deposition efficiency through the addition of helium, which is particularly useful for lower pressure and temperature application on sensitive substrates or with portable systems. The relationship between DE and helium content is then used to develop a cost model, which aims to optimize the helium concentration required for the lowest cost coatings.

Materials and Methods

Materials

Four metallic powders (pure aluminum, aluminum alloy, stainless steel, and CoNiCrAlY) were used to investigate the effects of gas mixing. These powders were chosen because they are commercially relevant, have diverse deposition behaviors, and substantial cost differences. The chemical composition, supplier information, and particle size are found in Table 1.

Images showing the morphology and size of the powders are presented in Fig. 2. All powders were produced

Table 1 Powder information

General name	Chemical composition	Commercial name	Supplier	Particle size
Pure aluminum	99.5%Al	SST-A5001	Centerline (Windsor) Ltd, Canada	– 45 + 5 μm
Aluminum alloy	Al-10%Si-0.3%Mg	TEKMAT TM AISI10 Mg-63/20	Tekna Advanced Materials Inc, Canada	– 63 + 2 μm
Stainless steel	Fe-14.5%Cr-3.5%Cu-4.5%Ni-0.7%Si-0.7%Mn-0.3%Nb	15-5PH	Sandvik Osprey LTD, United Kingdom	90% – 10 μm
CoNiCrAlY	Co-32%Ni-21%Cr-8%Al-0.5%Y	Andry 9951	Oerlikon Metco AG, Wohlen, Switzerland	– 38 + 5.5 μm

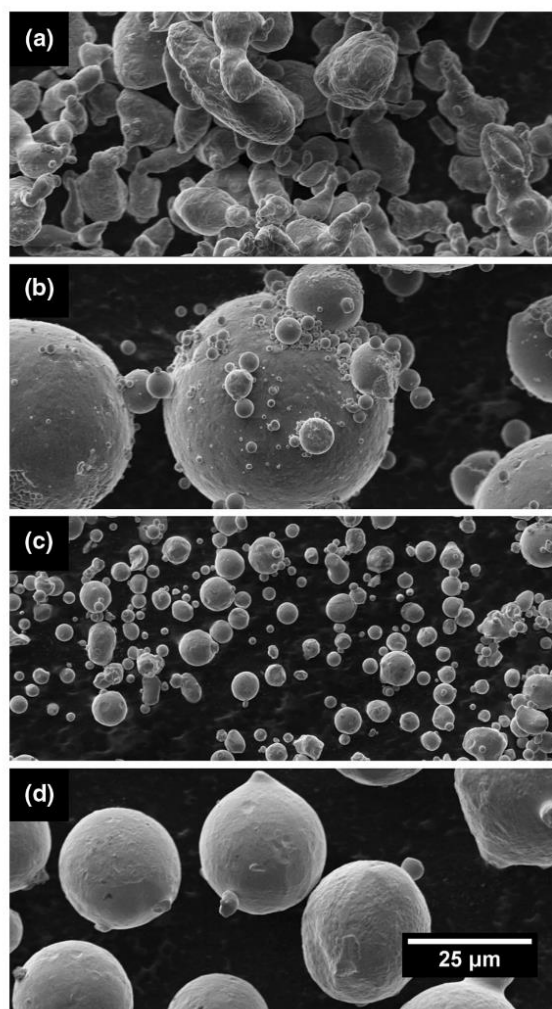


Fig. 2 Images of the pure aluminum (a), aluminum alloy (b), stainless steel (c), and CoNiCrAlY (d) powders at the same magnification (1000 $\times$)

though gas atomization; however, only the pure aluminum powder exhibited an atypical, non-spherical, morphology. It can also be seen in Fig. 2 that the particle sizes vary drastically between each powder, with the largest powder being the aluminum alloy (Fig. 2a) and smallest being the stainless steel (Fig. 2b). The aluminum alloy powder (Fig. 2b) also shows a large size distribution within the powder. The sprayability of this powder could likely be improved through sieving to remove the largest particles; however, the purpose of this study is to use commercially available powders as-received from the suppliers.

The size of the substrates used for the depositions was 101.6 mm by 25.4 mm by 6.35 mm. The substrate material used to deposit the pure aluminum and aluminum alloy

Table 2 Pertinent CGDS parameters

Parameter	Value
Gas pressure	3.4 MPa
Gas temperature	500 °C
Standoff distance	10 mm
Traverse velocity	5 to 25 mm/s

powders was as-received 6061-T6511 aluminum alloy cleaned with acetone prior to deposition. The substrate material used to deposit the stainless steel and CoNiCrAlY powders was cold-rolled mild steel (AISI 1020) that was prepared with grit blasting, wire brush scrubbing, and acetone cleaning prior to deposition.

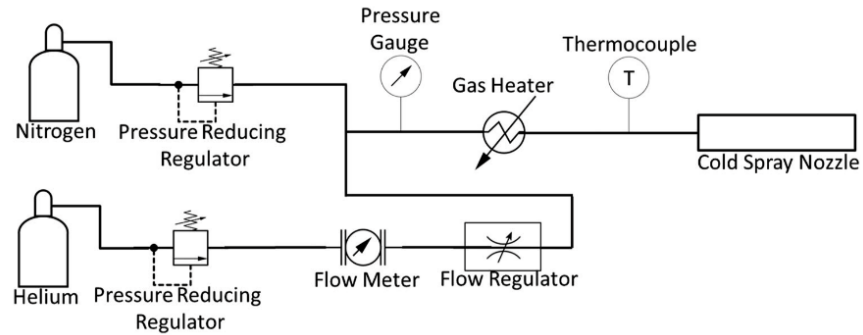
CGDS Process

The metallic powders were deposited using the commercially available SST Series EP Cold Spray System (Centerline Ltd, Windsor, Canada). This system can provide a maximum gas stagnation temperature of 500 °C and a maximum gas pressure of 3.4 MPa, typical of parameters attainable by portable CGDS systems. For the pure aluminum and aluminum alloy powders, an UltiFlowTM polymer nozzle (2-mm-diameter throat, 120-mm-long diverging section, 6.4-mm exit diameter) was used. For the 15-5 PH steel powder, a stainless steel nozzle (2-mm-diameter throat, 120-mm-long diverging section, 6.6-mm exit diameter) was used. For the CoNiCrAlY powder, an Ulti-LifeTM WC nozzle (2-mm-diameter throat, 120-mm-long diverging section, 6.4-mm exit diameter) was used. Powders were fed downstream of the nozzle throat using a commercially available rotary powder feeder (Model AT-1200 Rotary Powder Feeder, Thermach Inc, Appleton, WI, USA).

In order to investigate the effect of the percentage of helium, the spray parameters were held constant and can be found in Table 2. The maximal temperature and pressure of the system were used with a typical standoff distance. Traverse velocities were adjusted for each powder and gas ratio (in the range outlined in Table 2) to ensure that the deposits did not grow excessively thick during deposition due to changes in deposition efficiency.

In-line Nitrogen–Helium Blending

In order for the two gasses to be mixed in-line at controllable ratios, both the pressure and flow rates must be regulated carefully. The process flow diagram in Fig. 3 represents the setup used to achieve this.

Fig. 3 Process flow diagram showing in-line gas mixing

The pressure from the helium storage is first reduced and regulated to a pressure higher than the intended stagnation pressure and suitable for the flow meter. The flow is then regulated using a flow regulator that ensures a constant mass flow [measured in standard cubic feet per minute (SCFM) at the flow meter] regardless of downstream pressures. On the nitrogen side, a pressure regulator then sets the output pressure, which is read by the pressure gauge.

To operate this system, the mass flow rate of helium required for a specific stagnation pressure, temperature, nozzle throat area, and volume percentage of helium must be determined, through calculations. This is done by first finding the overall mass flow rate using,

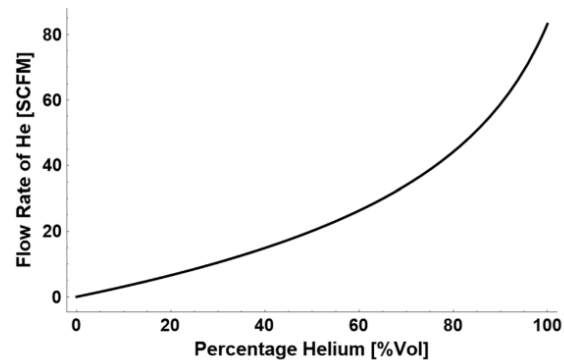
$$\dot{m} = \frac{A * P_o}{\sqrt{T_o}} \sqrt{\frac{k}{R} \left(\frac{k+1}{2} \right)^{-\frac{k+1}{2(k-1)}}} \quad (\text{Eq } 10)$$

where $\dot{m}$ is the mass flow rate, A is the nozzle throat area, P_o is the stagnation pressure measured at the pressure gauge, and T_o is the stagnation temperature measured at the thermocouple. It should be noted here that the k and R values are those of the mixture, calculated in Eq 3 and 4. This mass flow rate can be multiplied by the mass fraction of helium (Eq 7) and adjusted to SCFM. The flow rate of helium required for different volume percentages of helium, for the parameters outlined in Table 1, is plotted in Fig. 4.

The SCFM of helium for various helium percentages can be determined and used to set the flow meter. For this study, the helium rates shown in Table 3 were used. For each set of experimental parameters, three separate samples were deposited.

Particle Velocity Measurement

Particle velocity measurements were taken using the ColdSprayMeter (CSM) eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). This system uses a continuous 2.4 W ($\lambda = 810$ nm) laser with a dual spit photomask in order to perform in-flight diagnostic on individual particles.

**Fig. 4** The flow rate (SCFM) of helium required for a volume percentage of helium (throat diameter = 2 mm, $P_o = 3.4$ MPa and $T_o = 500$ °C)**Table 3** Flow rate of helium for helium percentages at set deposition parameters

Percentage helium, vol. %	Helium flow rate (SCFM)
0	0
25	8.2
50	19.5
75	37.6
100	80.9

It provides the precise velocities of individual particles during flight. In this study, the velocity measurements were taken at a point 10 mm downstream from the center of the cold spray nozzle exit. Testing was run for several minutes to ensure the collection of a robust data set. The data are represented through box and whisker plots of 5000 collected data points.

Sample Characterization

The focus of this study is to characterize the effect of gas mixing on the DE of the coatings. DE was measured by

weighing the samples before and after deposition and comparing the mass gain with the mass of powder fed. The powder feed rate was measured directly at the powder feeder exit in testing separate from the operation of the CGDS system.

The coating quality was investigated through microstructural analysis using a scanning electron microscope (EVO-MA10, Zeiss, UK) and an optical microscope (VHX-2000E, Keyence, Canada). In order to quantify porosity level, entire cross sections of the deposits were stitched together using the software of the VHX-2000 at a magnification of 300x. The porosity was calculated through contrast analysis of the optical images using ImageJ software for three separate cross sections per deposit (9 images per set of parameters). Microhardness testing of the deposits was conducted on polished samples using a Vickers microhardness tester (Struers Duramin-1, Struers Inc., Cleveland, OH, USA) with a 300-g load and a dwell time of 10 s. To avoid the effect of the stress field, the distance between two indentations was kept greater than three times the length of the indentation. The reported values are the average of a minimum of 15 indentations for each set of parameters.

Cost Model

The cost model assumes that the coating quality (porosity and hardness) was found to be adequate for the specific application under all deposition conditions. With this assumption, the cost of the deposited powders is calculated if the DE as a function of helium percentage is known. If some conditions do not meet the quality criteria, they can later be eliminated from the optimization. Conditions can then be identified for the least expensive coatings to deposit.

The cost model aims to incorporate all of the significant cost aspects of the process. In order to have a simple comparative value, the dollar cost per unit mass (in gram) of deposit was calculated. This cost per unit mass of coating is found with the following equation,

$$C = PC + GC + LC + EC \quad (\text{Eq 11})$$

where C is the cost per unit mass of coating, PC is the total cost of powder used, GC is the total cost of gas used, LC is labor costs, and EC is the electricity costs.

The powder cost per gram of deposited coating is calculated simply by dividing the cost for 1 g of powder (available from the manufacturer) by the DE,

$$PC = \frac{P}{DE} \quad (\text{Eq 12})$$

where P is the powder cost (\$/g) and DE is a function of helium percentage determined experimentally. The cost of

gas is dependent on both the length of the spray and the cost of the gas, with the latter varying with the percentage of helium used to produce the coating. The gas costs per second is found with the following equation,

$$GR = w_{He} * \dot{m} * HC + w_3 * \dot{m} * NC \quad (\text{Eq 13})$$

where GR is the gas rate (\$/s), HC is the cost of helium (\$/kg), and NC is the cost of nitrogen (\$/kg).

The time necessary to deposit 1 g of coating is found by dividing the mass of the coating (1 g) by DE and the powder feed rate (PFR),

$$t = \frac{1}{DE * PFR} \quad (\text{Eq 14})$$

where t is time (s) and PFR is the powder feed rate (g/s). The total gas cost is then the gas rate multiplied by the time,

$$GC = GR * t \quad (\text{Eq 15})$$

The labor costs is calculated using,

$$LC = LR * t \quad (\text{Eq 16})$$

where LR is the labor rate (\$/s). For electricity costs, the power is estimated through an analysis of the cold spray gas heater itself using the first law of thermodynamics. Assuming an ideal gas, negligible change in kinetic and potential energies, no work, and minimal heat losses to the surroundings, this reduces to,

$$\dot{Q} = \dot{m} C_P (T_o - T_R) \quad (\text{Eq 17})$$

where $\dot{Q}$ is the heat rate (W) and T_R is the approximate temperature (K) of the gas before heating. The cost of heating then becomes,

$$EC = \dot{Q} * t * ER \quad (\text{Eq 18})$$

where ER is the electricity cost (\$/J).

The costing Eq 11–18 is used with the gas mixing and mass flow Eq 3–10 to determine the actual cost of depositing 1 g of powder for any helium percentage, if DE can be estimated as a function of helium content.

Results and Discussion

Deposition Behavior and Sample Characterization

A plot of the particle velocities is presented in Fig. 5. The velocities are represented by box and whisker plots. This normal distribution of particle velocities matches what is typically seen in cold spray, as varying particle sizes and flow paths result in a range of particle velocities (Ref 15, 29, 30). It can be observed that as the volume percentage of helium is increased, the mean particle velocities

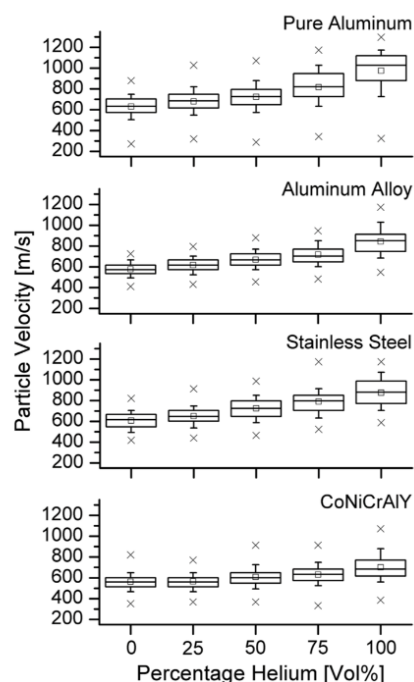


Fig. 5 Particle velocities of the pure aluminum powder for different helium content (box and whisker plot with $\square$ representing the mean, x representing 1–99%, the whiskers representing 10–90%, and the box representing 25–50–75% of all particles)

also increase, as expected (Ref 7–12). This trend also appears to follow a similar path to the gas velocity (shown in Fig. 1 at the nozzle throat). The average velocities found in Fig. 5 for pure aluminum meet or exceed the critical velocity estimated in literature [600–700 m/s (Ref 31)]; however, the critical velocities of the other materials could not be found in the literature.

Figure 6 illustrates the effect of the increase in helium percentage on the DE for all feedstock powders. For the pure aluminum samples, a DE of $53 \pm 3\%$ was found for the pure nitrogen samples, increasing to $98 \pm 2\%$ for the pure helium samples. This high DE, even when using pure nitrogen, was expected as pure aluminum is known to have a low critical velocity and the particle size was suitable for cold spray. The aluminum alloy powder, on the other hand, had a DE of only $3.6 \pm 0.1\%$ for pure nitrogen and increased to $19.7 \pm 2\%$ with pure helium. This low DE is likely due to the strengthening of the alloying elements, resulting in a higher required critical velocity when compared to pure aluminum (Ref 32).

For the stainless steel feedstock powder, the DE started at $8.4 \pm 1.8\%$ when sprayed with pure nitrogen and increased up to $61.3 \pm 1.0\%$ for pure helium. Lastly, the DE of the CoNiCrAlY powders was 0% when sprayed with

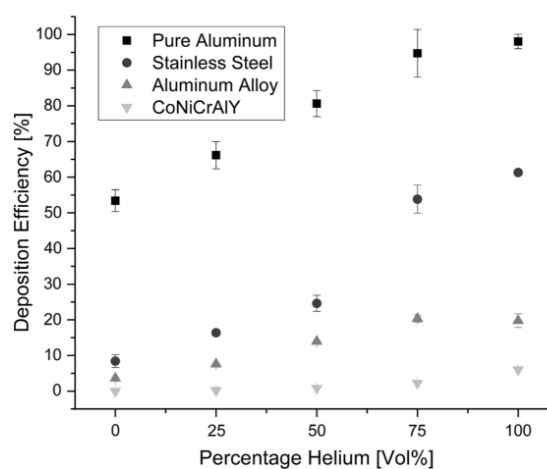


Fig. 6 Deposition efficiency different percentages of helium

pure nitrogen, barely deposited at 25% helium (DE of $0.25 \pm 0.05\%$), and increased to only $6.0 \pm 0.1\%$ for pure helium. Both the stainless steel and the CoNiCrAlY powders are high strength and high melting point materials, resulting in high critical velocities (Ref 32); therefore, low DEs were expected when compared to softer materials (Ref 33). The values for deposition efficiency proved difficult to compare to literature, as the DE varies drastically with spray condition, material composition, and powder morphology/size.

Figure 7 presents the effect of helium content on the porosity level of the depositions. For the pure aluminum, aluminum alloy, and stainless steel coatings, a general downward trend in the porosity is observed. This is expected, since an increase in particle velocity should result in an increase in plastic deformation (upon impact and through impingement of other particles), reducing the size and occurrence of pores. It should be noted that porosity could be measured for the pure helium CoNiCrAlY coatings only, as the DE was so low that a coating thick enough to accurately measure porosity could not be deposited under the conditions prescribed in Table 2.

Sample images of the cross sections used to determine porosity are presented in Fig. 8. It should be noted that these coatings were deposited at different traverse velocities in order to create coatings of roughly similar thickness; therefore, coating thickness is not directly indicative of DE. It is observed from Fig. 8(d) that no CoNiCrAlY particles adhered to the substrate.

The effect of helium content on the coating hardness is shown in Fig. 9. An increase of coating hardness is observed for both the pure aluminum and the stainless steel particles. This increase in hardness can be attributed to the added work hardening with increasing plastic deformation.

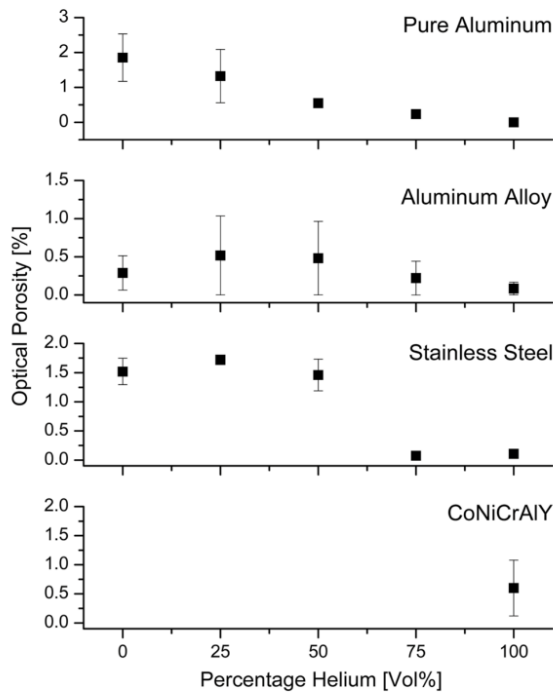


Fig. 7 Apparent porosity (optical) for different percentages of helium for both pure aluminum and 15-5PH steel coatings

This increase is not seen for the aluminum alloy since this alloy gains its strength through precipitates, unlike pure aluminum in which the work hardening would be the dominant factor (Ref 34, 35). It should be noted that hardness of the aluminum alloy coating deposited with pure nitrogen could not be taken, as the DE was so low that a coating thick enough to perform hardness tests could not be deposited under the conditions prescribed in Table 2. For the same reasons as porosity, only the pure helium coating hardness could be measured for the CoNiCrAlY coatings. The hardness values found were in the same range for pure aluminum cold spray coatings as was found by Champagne et al. (Ref 36) and for CoNiCrAlY cold spray coatings as was found by Khanna et al. (Ref 37). As with the DE, it is difficult to compare the hardness with the literature, as it varies with spray conditions, material composition, and powder morphology/size.

For all of the powders in this study, it was clear that an increase in helium content is beneficial for DE, and likely for coating density and hardness. Thus, if these are the only parameters of consideration, then pure helium should be used. However, this does not take into account the reality of helium costs.

Case Study: Cost Optimization

As a case study, the cost model is used to optimize the coating cost using the pricing available as of June 2018 at the University of Ottawa, Canada. The material costs are provided directly from suppliers, labor costs were estimated based on the full burden cost of a skilled employee, and the electricity rate is taken from the 2017 average in Ontario, Canada. For supplier pricing privacy, the pricing (Table 4) has been normalized so that the most expensive cost input is 100 N\$. Please note that the labor and electrical rates are listed in commonly used units and were converted before use in the equations.

In order to do the cost analysis, the DE of the coatings as a function of helium quantity is required. A third-order polynomial was fit to the values shown in Fig. 6, resulting in Eq 19–22,

$$DE_{Al} = -0.596x_{He}^3 + 0.679x_{He}^2 + 0.363x_{He} + 0.534 \quad (\text{Eq 19})$$

$$DE_{AA} = -0.4997x_{He}^3 + 0.6453x_{He}^2 + 0.0158x_{He} + 0.0368 \quad (\text{Eq 20})$$

$$DE_{St} = -0.235x_{He}^3 + 0.594x_{He}^2 + 0.167x_{He} + 0.0888 \quad (\text{Eq 21})$$

$$DE_{CoNiCrAlY} = 0.1061x_{He}^3 - 0.689x_{He}^2 + 0.0231x_{He} - 0.0002 \quad (\text{Eq 22})$$

where DE_{Al} , DE_{AA} , DE_{St} , and $DE_{CoNiCrAlY}$ are the deposition efficiencies for pure aluminum, aluminum alloy, stainless steel, and CoNiCrAlY powders, respectively.

A critical part of this analysis involves PFR as it is required to determine time of spray. This PFR should be maximized at all times to ensure that the time to deposit the coatings is minimized (Eq 14). It has been estimated that the maximum mass flow of powder should be approximately 3% of the nitrogen mass flow and up to 30% of the mass flow of helium (Ref 5). However, physical limitations exist in the feeding and injection systems of commercial CGDS systems. For the experimental setup used in this study, the feed rates at the percentages proposed in the literature were unattainable without clogging of the feeding lines and injection ports. Therefore, this case study was done using the maximum powder feed rate attainable. The values, found in Table 5, were determined experimentally by continually increasing the feed rate until feeding issues arose.

The feed rates possible for the aluminum alloy powder were higher than the pure aluminum likely as a result of its spherical shape (Fig. 2b) and increased flowability. The stainless steel and CoNiCrAlY powder feed rates were also

Fig. 8 Optical images of 0% helium coatings of pure aluminum (a), aluminum alloy (b), stainless steel (c), and CoNiCrAlY (d) and 100% helium coatings of pure aluminum (e), aluminum alloy (f), stainless steel (g), and CoNiCrAlY (h)

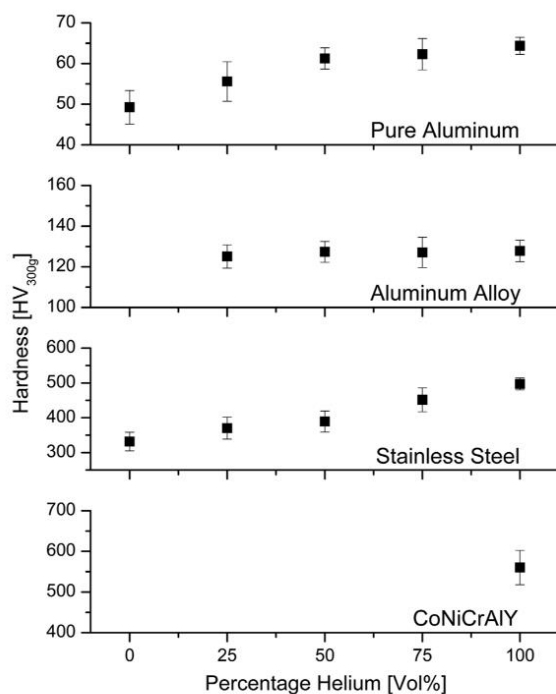
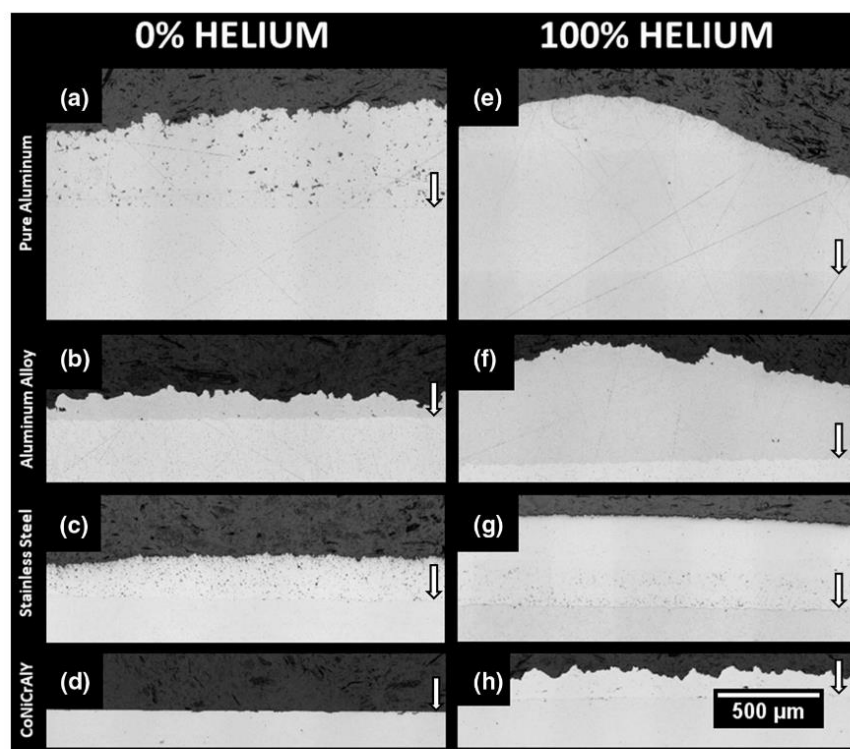


Fig. 9 Vickers hardness measurements for different percentages of helium for the different materials

Table 4 Cost inputs in normalized dollars

Parameter	Symbol	Value
Helium cost	HC	69.1 N\$/kg
Nitrogen cost	NC	1.2 N\$/kg
Aluminum powder	P_{Al}	42.3 N\$/kg
Aluminum alloy powder	P_{AA}	36.6 N\$/kg
Stainless steel powder	P_{St}	100 N\$/kg
CoNiCrAlY powder	$P_{CoNiCrAlY}$	63.8 N\$/kg
Labor rate	LR	29.8 N\$/h
Electricity rate	ER	0.07 N\$/kWh

Table 5 Maximum powder feed rates for different powders

Powder	Maximum powder feed rate, g/min
Pure aluminum	9.8 ± 0.6
Aluminum alloy	17.2 ± 0.5
Stainless steel	31.8 ± 2.5
CoNiCrAlY	32.7 ± 0.2

much higher due to a higher material density (greater than 2 times that of aluminum) and high flowability due to the spherical shapes. Knowing the costs, the maximum PFR, and the equation for DE, the total cost to deposit a coating

for all helium percentages can be calculated from Eq 11, which incorporates Eq 2-22. This relationship is plotted in Fig. 10 for each of the powders as a relative cost, in which 100% represents the most expensive coating of that material that could be produced.

It is observed from Fig. 10(a) that the most expensive pure aluminum coatings were produced with pure helium and the least expensive were deposited using pure nitrogen. This is intuitive since the DE of the pure nitrogen sprays is very high ($> 50\%$); therefore, only small savings in powder costs can be achieved with the use of helium. The powder is also relatively inexpensive and the powder feed rate is low due to low density and poor flowability. The cost of spraying the coatings with nitrogen is only 14% of the cost of depositing them with helium.

In contrast to pure aluminum, the aluminum alloy had a low DE with pure nitrogen and had a higher maximum PFR. A plot of the relative cost of the aluminum alloy coatings is seen in Fig. 10(b), with 100% being the most expensive coating produced. The plot shown in Fig. 10(b) has an interesting shape, it initially increases as

the helium cost outweighs the savings in time (powder, labor, and electricity). As DE continues to increase with the added helium, the cost of the coatings was reduced, reaching a minimum point at 49% helium, which resulted in a coating that was 41% of the cost of a pure helium coating. After this ratio, as seen in Fig. 4, the mass flow of helium increases greatly, raising the cost of gas per second. While a coating deposited at 49% helium is substantially less expensive than spraying with pure helium, spraying with pure nitrogen resulted in a coating of similar cost. For this case, it could be argued that the simplicity of spraying with pure nitrogen could outweigh the added savings; however, from a productivity standpoint, the DE at the optimal point was approximately 14%, compared to 3.7%, a productivity increase of 3.8 times. Therefore, one would have to assess their needs accordingly to see whether the added productivity and a small cost savings are worth the added complication of gas mixing.

The plot of relative coating costs for the stainless steel powder is presented in Fig. 10(c). In this case, the most expensive coating was the one deposited with pure

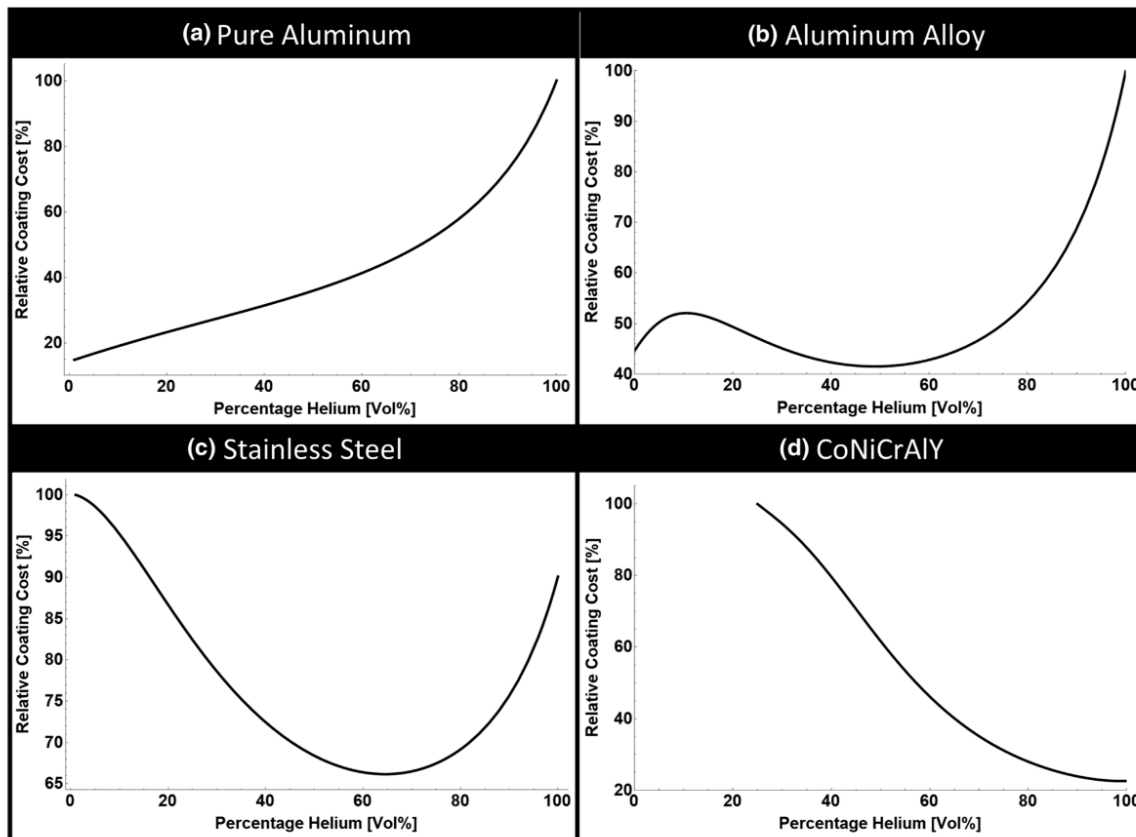


Fig. 10 Relative costs to deposit pure aluminum (a), aluminum alloy (b), stainless steel (c), and CoNiCrAlY (d) as a function of helium content

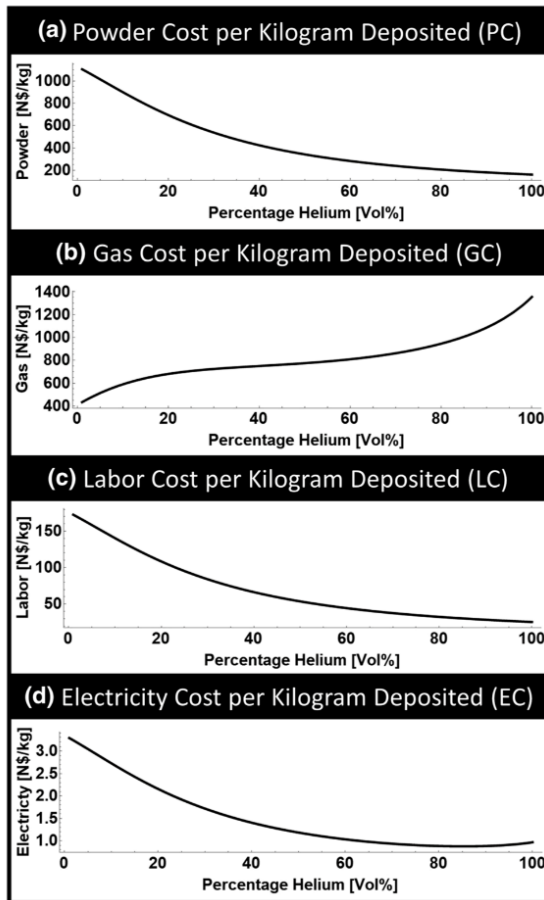


Fig. 11 Powder cost (a), gas cost (b), labor cost (c), and electricity cost (d) to deposit 1 g of stainless steel as a function of helium content

nitrogen. Similar to the aluminum alloy, the powder started with a low DE and had a higher feed rate; however, it was also the most expensive of the powders. All of these factors should push the use of pure helium; however, it can be seen in Fig. 10(c) that is not the optimal point. A coating deposited with pure helium would cost 90% of that of the pure nitrogen cost, a small savings, while a coating deposited at 65% helium would only cost 66% of the pure nitrogen costs, presenting a substantial saving. To further understand why this cost savings occurs, a detailed breakdown of the costs to deposit on kilogram of coating (Eq 11) is shown in Fig. 11.

In Fig. 11(a), it can be observed that the cost of powder decreases as helium content (and DE) is increased as the amount of powder required to deposit 1 kg decreases. The gas costs (shown in Fig. 11b) are more interesting as this curve is influenced by two factors: the length of time required to deposit 1 kg and the gas cost per second of

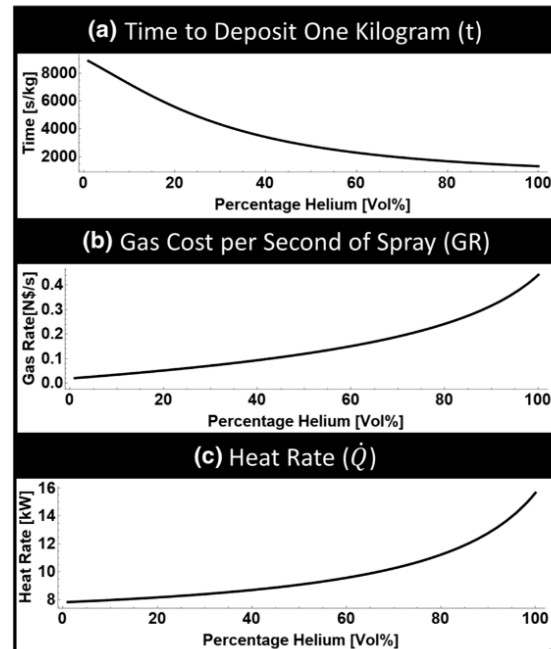


Fig. 12 Time to deposit 1 kg of stainless steel (a), the gas cost per second of spray (b), and the heat rate (c) as a function of helium content

spray. As helium content is increased, the DE increases, and thus the time to deposit a kilogram of coating decreases; this relationship is plotted in Fig. 12(a). However, the cost per second of spray increases substantially with the addition of helium as seen in Fig. 12(b). The combination of these plots results in Fig. 11(b) where at low helium content the addition of helium results in an increase in gas costs higher than savings in reduction in spray time, and at about 20% helium, the increased gas costs are mostly canceled by the spray time reduction, making the gas cost almost constant, while powder costs are still decreasing. At about 70% helium, the cost of gas dominates over the spray time reduction again and the costs rise steeply. It is now evident that the point of maximum cost efficiency should occur at this zone where gas costs have yet to rise steeply, but powder cost is decreasing.

The labor cost (Fig. 11c) is purely time based, so the curve will follow directly the time shown in Fig. 12(a). The electricity cost (Fig. 11d) is also time dependent, but the amount of heat required (thus electricity) per unit time also increases as helium content increases (shown in Fig. 12c). This is the reason for the slight increase in electricity cost at high helium percentages. It can also be observed that cost of electricity is orders of magnitude smaller than powder, gas, and labor costs and could be ignored for future analysis.

The CoNiCrAlY relative cost curve is plotted in Fig. 10(d). Since there was no deposition between pure nitrogen and 25% helium, the curve only starts at this point and is considered the most expensive coating. It is clear for the CoNiCrAlY coatings that they should be deposited with pure helium. The deposition with nitrogen is so low that the powder savings with helium dominate the cost analysis. Depositing these coatings results in only 22% of the cost of the case where a mixture with 25% helium is used.

In this analysis, it is also important to consider the coating quality, as not all coatings are the same. This case study assumed that all coatings produced were acceptable, but in industry, values of acceptable porosity, hardness, etc., are known and can be used as threshold values for determining the optimized gas mixture. In the case where these values are known, the procedure would be the same, but the curves could be truncated to only include acceptable gas ratios during the minimization.

Conclusion

The use of helium in this study was shown to be beneficial for DE, coating density, and hardness. It is concluded that, for the powders and parameters studied, pure helium should be used if cost is not considered. However, if cost is taken into account, it was shown that an optimal helium/nitrogen ratio can be found for maximum economic viability.

For pure aluminum powder, it was found that using pure nitrogen resulted in the least expensive coatings. Although the density and hardness of the nitrogen coatings were not as high as when using pure helium, they were 86% less expensive. The aluminum alloy powder had an optimal point when a gas mixture of 49% helium was used, where the coatings were 59% less expensive than spraying with pure helium. However, these coatings were only marginally less expensive than the pure nitrogen coatings. The stainless steel powder showed the clearest minimum point when a gas mixture of 65% helium was used to produce coatings costing 44% less than pure nitrogen coatings. Lastly, the CoNiCrAlY coatings could not be deposited with pure nitrogen and the least expensive coatings were deposited with pure helium.

In conclusion, it was shown that novel in-line gas mixing allowed for the tailoring of specific gas blends for each unique coating scenario. It was found that the optimal point to deposit powders is the point where the extra cost to spray per second from using helium is balanced by the savings in spray time (gas consumption, powder consumption, electricity use, and labor). As a case study, cost optimized gas blends were found for the specific powders, CGDS system, and costing available. This same procedure

could be applied in an industrial setting, increasing the commercial viability of CGDS coatings or CGDS additively manufactured components.

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5.3 Research Project 3: Effect of Particle Preheating on the CSAM Process

This study aims to build an understanding of how the temperature of the carrier gas affects the LPCS process and to demonstrate that particle temperature can be independently controlled. This understanding paves the way for a potential solution to spraying on temperature sensitive materials that prevents the use of elevated spray parameters. Through CFD modelling and experimentation, the particle temperature was decoupled from the temperature of the carrier gas, and the resulting effects on particle temperature, particle velocity, DE, and deposition quality were investigated. To overcome the potential particle heater clogging problem, this study also introduces a novel powder heater design that allows for particles to be taken closer to their melting temperature without encountering hot metallic walls. This paper addresses Objective 3 presented in Section 3.1.

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**Independent Control of Particle Temperature and Velocity
using a Novel Powder Preheater Design for Low Pressure
Cold Spray**

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Independent Control of Particle Temperature and Velocity using a Novel Powder Preheater Design for Low Pressure Cold Spray

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Abstract

In high pressure cold spray it has been demonstrated that the enthalpy of the particle carrier gas has a significant effect on the propellant gas conditions and resulting particle impact velocities and temperatures. Through modelling and experimentation, this study demonstrates that in low pressure cold spray, the enthalpy of the particle carrier gas has a minimal effect on the particle velocity, therefore particle temperature can be controlled independently from particle velocity. This is a unique feature of downstream injection and a valuable tool when dealing with temperature sensitive substrates and particles.

In this study, particle preheating was used to inject pure aluminum particles up to temperatures of 500°C, about 80% of their melting temperature. This particle preheating was accomplished without clogging because of a novel particle preheater which eliminated the particles exposure to hot metal surfaces. It was found that even after substantial spray time, there was no evidence of wear or clogging. The preheating resulted in a DE increase of 3.6 times when compared to the injection of room temperature particles.

Introduction

Cold spray (CS) is a solid-state thermal spray process which utilizes kinetic energy, as opposed to thermal energy, for particle deposition. In the CS process, particles are accelerated by a high speed gas flow prior to impact with a substrate (Ref 1,2). During impact, the particles experience localized deformation, at rates much higher than those observed in traditional manufacturing processes, resulting in localized heating, material jetting, mechanical interlocking, metallic bonding, and ideally, permanent adhesion. The accumulation of these adhered particles results in the production of a new coating or component (Ref 1,3–6). In CS, two approaches are used to insert particles into the flow that is being accelerated through a converging-diverging nozzle. The most common method is the upstream injection, referred to as high-pressure cold spray or HPCS. In HPCS, a mixture of carrier gas and particles is injected in the high-pressure propellant gas, upstream of the nozzle throat. The other method of particle insertion is downstream injection, commonly known as low-pressure cold spray or LPCS. In LPCS, the carrier gas and particles are injected downstream of the nozzle throat, after the propellant gas has expanded to low pressure. It should be noted that the terms HPCS and LPCS, in this work, refer exclusively to the particle injection point and not the working pressure of the propellant gas.

While CS relies on kinetic energy for particle deposition, the particles temperature also has a substantial effect on the deformation processes during impact. An increase in particle impact temperature is known to decrease the critical velocity required for adhesion to occur (Ref 4). It has also been shown that an increase in the ratio between impact velocity and critical velocity usually improves deposition efficiency (DE), flattening ratio, cohesive strength, and adhesion (Ref 7,8). While this notion is generally accepted, some studies have shown that increasing particle temperatures can actually lower adhesion strength – attributed to either increased particle oxidation (Ref 9), decreased crater depth (Ref 10), or decreased tamping effect of non-adhering particles (Ref 11). While this effect of impact temperature on the deposition process and quality will vary depending on spray conditions and material combinations, in general, increasing particle impact temperature is desirable in CS.

In HPCS, the particles are exposed to the high-temperature and high-pressure gas prior to expansion in the nozzle, raising the initial particle temperature. In some cases, the particle injection point is purposely moved farther upstream, prolonging the exposure of the particles to the hot propellant gas (Ref 12). This extended prechamber can result in higher particle impact temperatures, especially for particles with a large thermal mass, which can maintain their temperature through the diverging section of the nozzle (Ref 12). This form of particle preheating is inherent to the HPCS process and is a major reason that HPCS often results in superior deposition characteristics when compared to LPCS with similar particle impact velocities and spray parameters (Ref 13). However, as this form of particle preheating is inherent to the process, it is difficult to decouple and independently study the effect of particle temperature from the spray parameters.

Another approach to particle preheating is to separately heat the particle carrier gas prior to injection into the nozzle. This type of powder preheating has been shown to result in increased

deposition quality in both HPCS and LPCS. In HPCS, studies have demonstrated that these results are not just due to the increased particle impact temperature but are partially due to the increase in enthalpy of the propellant gas resulting from the injection of high temperature carrier gas. While most studies do not acknowledge this effect, the influence of this added enthalpy cannot be ignored as carrier gas flows can exceed 20% of the overall gas flow (Ref 14). Yin et al demonstrated that preheating copper particles in this way significantly increased the true stagnation temperature of the propellant gas, when compared to using cold carrier gas (Ref 15,16). This resulted in an increased particle velocity as more thermal energy can be converted to kinetic energy, which may have contributed to the substantial increases in coating quality seen in their previous study (Ref 17).

In HPCS, the effective stagnation temperature of the propellant gas is actually the temperature of the mixture of the heated propellant gas and the cool carrier gas. The particles are being exposed to this effective stagnation temperature, influencing their impact temperature. Attempts to raise or lower particle temperature in HPCS necessarily requires the modification of this stagnation temperature, and therefore will affect the resulting particle velocity and substrate temperature. This relationship can be problematic, as there are many situations in which independent and precise control of the particle temperature could be desirable. For situations in which the substrate is temperature sensitive (such as heat-treated aluminum alloys or carbon-fiber reinforced polymers), a low stagnation temperature must be used, but a high particle impact temperature could increase the quality and efficiency of the deposition process. Furthermore, in HPCS the stagnation temperature is limited by the melting/clogging of the particle material in the nozzle, something that could be avoided with the ability to independently control and keep the particle temperature low while maintaining a high impact velocity.

Particle preheating in LPCS also requires the carrier gas to be preheated. While studies have shown that increasing the temperature of the carrier gas results in increases in deposition efficiency (Ref 7,8), it is attributed purely to the increase in particle temperature, and no studies have addressed the additional enthalpy of the gas injected into the main flow. Like HPCS, this carrier gas has energy, however, in LPCS, it is injected in the low temperature/ high velocity section of the nozzle. This injection, downstream of the nozzle throat, cannot affect the stagnation conditions of the propellant gas but may significantly influence the overall gas dynamics of the process downstream of the injection point.

Additionally, an issue that inhibits the widespread preheating of many materials is clogging in the particle preheater itself. Typically, the particles and carrier gas are passed through a high temperature metallic tube, which transfers heat to the gas flow and then to the particles through convection. In most cases, the tube wall temperature is raised through electrical resistance heating, which results in approximate constant heat flux condition along the length of the tube. This heat transfer mode requires the tube inner wall temperature to be substantially higher than the desired particle temperature. When heated particles collide with these high temperature tube walls, weak bonds can be formed - resulting in clogging of the particle preheater. This is especially true for lower melting temperature particles, such as aluminum, for which powder preheating is typically avoided.

This study aims to build an understanding of how the temperature of the carrier gas affects the LPCS process and to demonstrate that particle temperature can be controlled independently of the process stagnation parameters. This understanding paves the way for a potential solution to spraying on temperature sensitive materials that prevents the use of elevated spray parameters. Through CFD modelling and experimentation the effects of carrier gas preheating on particle temperature, particle velocity, DE, and deposition quality were investigated. To overcome the potential clogging of particle heater, this study also introduces a novel powder heater design that allows for particles to be taken closer to their melting temperature without encountering hot metallic walls prior to being injected in the nozzle.

Materials and Methods

Materials

To study the effects of powder preheating, both experimentation and CFD modelling approaches are used. A powder with a spherical shape, high purity, known properties, tight size distribution, and lack of agglomerates/satellite particles is desired. This allows for more accurate modelling and less variability in experimental results. Spherical pure aluminum powder (Equispheres Inc., Canada) was chosen for this purpose. The particle size distribution analysis (Microtrac S3500, Nikkiso, Japan) can be found in Figure 1. The powder has a volume mean (MV) of 49.47 μm and numerical mean (MN) of 44.11 μm . The experimental values used to generate the plot in Figure 1 are used directly in the CFD modelling to ensure accuracy.

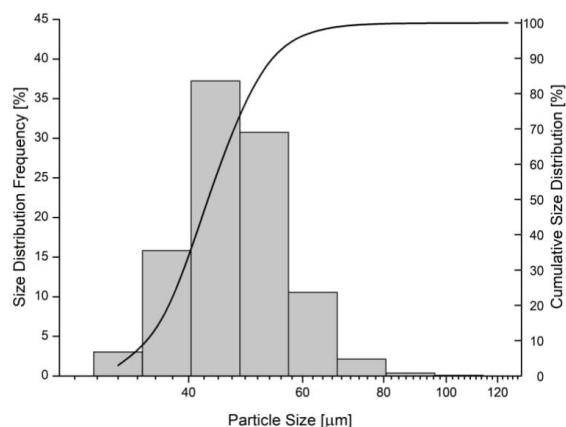


Figure 1: Number-weighted particle size distribution of the aluminum powder.

A typical overview of the particles can be seen in Figure 2. It can be observed in Figure 2(A) that the particles are highly spherical with no agglomeration or satellite particles. The cross section in

Figure 2(B) shows typical density of particles and regular equiaxed grains. This specific powder has a low DE under typical nitrogen cold spray conditions in LPCS, which should allow a large range of observable effects that could be missed if the baseline case is at a high DE. EDS analysis of a particle is shown in Figure 1(C), showing a clear peak at approximately 1.5 keV, which is that of aluminum (Al $K\alpha$ at 1.489 keV). The secondary peak observed at roughly 2.1 keV is that of gold (Au $L\alpha$ at 2.12 keV). The gold is an unlikely contaminant in the aluminum powders and its presence can be explained by the thin gold coating on the samples necessary to discharge the electrons during the SEM examination. Traces of oxygen are also present in the analysis. While it is common for gas atomized aluminum particles to have traces of oxygen, it is usually reserved to the periphery of the particle. In this case, oxygen was present at the center of the particle, which could be the reason for the low DE. The oxygen contamination, however, is not thought to affect the thermal or in-flight characteristics of the particle and the particles will be treated as chemically pure aluminum for the model. The substrates for the study were polished aluminum 6061-T6.

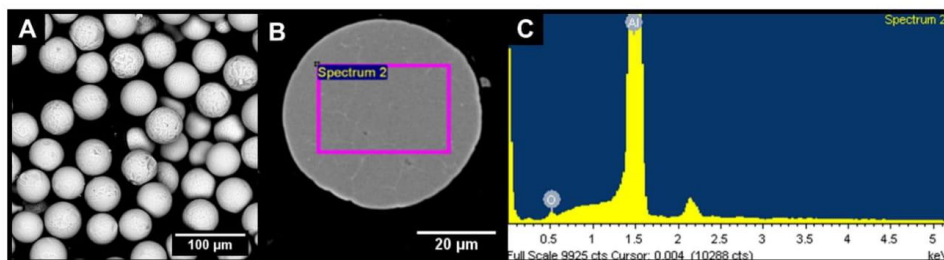


Figure 2: SEM overview image of powder (A), SEM image of powder cross section (B), and EDS results (C).

Cold Spray Process

CS deposition was performed using the commercially available SST Series EP Cold Spray System (Centerline Ltd, Windsor, Canada). This system can provide a maximum gas stagnation temperature of 500°C and a maximum gas pressure of 3.4 MPa. To prevent issues with nozzle clogging that can occur with aluminum powder, a polymer nozzle with a 2 mm diameter throat was used. Powders were fed using a commercially available rotary powder feeder (Model AT-1200 Rotary Powder Feeder, Thermach Inc, Appleton, WI, USA).

The parameters that will be held constant for all trials can be found in Table 1. For this study, nitrogen gas was used exclusively at the maximum temperature and pressure of the system.

Table 1: Pertinent CS Parameters

Parameter	Value
Propellant Gas Temperature	500 °C
Propellant Gas Pressure	3.8 MPa
Nominal Powder Feed Rate	6 g/min
Standoff Distance	10 mm
Traverse velocity	20 mm/s
Passes	20

Particle Preheating Trials

As was described previously, in LPCS particle preheating is achieved by heating the particle carrier gas prior to injection into the propellant gas. To prevent clogging of the powder pre-heating apparatus, a novel device was developed for this work. This device consists of two separate gas flows, one unheated flow carrying the particles and one auxiliary flow which is heated externally with traditional methods. A schematic of the powder preheating system can be found in Figure 3. In this design, particles are carried by room temperature gas and mixed with the heated auxiliary gas inside a two-meter long glass coil - never encountering any hot metal walls. Glass was chosen as the coil material as it is hard, smooth, has low affinity for adhesion with metallic particles, and could be easily manufactured through scientific glass blowing techniques. The injection stem, part of the glass coil, was pressed directly into the injection port of the polymer nozzle. The system was thermally isolated with high temperature refractory ceramic fiber.

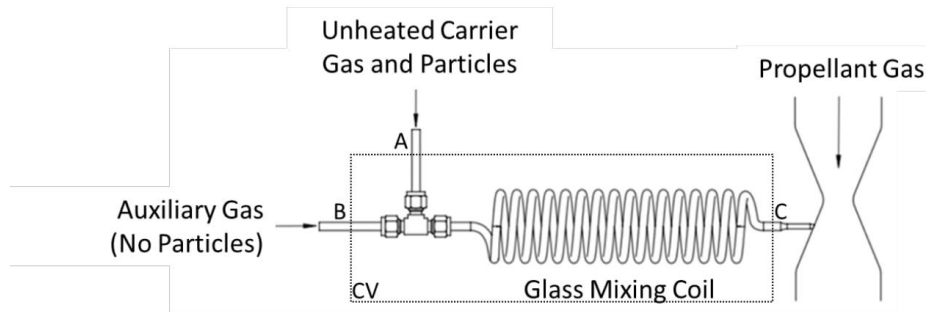


Figure 3: Schematic of particle preheating system.

This configuration allows measuring and controlling the temperatures and flow rates of the two incoming gas flows. Taking the control volume (CV) identified in Figure 3 and assuming this process operates under steady state, a perfectly insulated system, and that thermal equilibrium between the particles and the gas at the exit C has been reached (demonstrated later), the first law of thermodynamics reduces to,

$$\dot{m}_{N_2A} h_{N_2A} + \dot{m}_{N_2B} h_{N_2B} + \dot{m}_P u_{PA} = \dot{m}_{N_2C} h_{N_2C} + \dot{m}_P u_{PC} \quad \text{Eqn. 1}$$

where $\dot{m}_{N_2A}$, $\dot{m}_{N_2B}$, and $\dot{m}_{N_2C}$ are the mass flow rates of nitrogen at A, B, and C, respectively, h_{N_2A} , h_{N_2B} , and h_{N_2C} are the specific enthalpies of nitrogen at A, B, and C, respectively, $\dot{m}_p$ is the mass flow rate of particles, and u_{pA} and u_{pC} are the specific internal energies of the particles at A and C, respectively.

Using mass conservation and assuming constant specific heat, Eqn. 1 can be rearranged to form a useful equation to determine the temperature of the auxiliary gas required at B for a desired particle temperature at C,

$$T_B = \frac{(\dot{m}_{N_2A}C_{pN_2} + \dot{m}_pC_p)(T_C - T_A)}{\dot{m}_{N_2B}C_{pN_2}} + T_C \quad \text{Eqn. 2}$$

where T_A , T_B , and T_C are the temperatures at A, B, and C, respectively, C_{pN_2} is the specific heat of nitrogen at constant pressure, and C_p is the specific heat of the particle material.

To demonstrate the effects of this type of particle preheating and to help validate the model, the particles will be heated to temperatures between 100°C and 500°C, in 100°C increments. The unheated carrier gas will have a mass flow rate of 10 g/min while the mass flow of the auxiliary gas will be five times higher, at 50 g/min. Table 2 shows the temperature intervals for the particles in this study and the corresponding auxiliary gas temperature (T_B).

Table 2: Experimental Particle Temperatures

Desired Particle Temperature (T_C)	Auxiliary Gas Temperature Required (T_B)
Room Temperature	Room Temperature
100°C	126°C
200°C	257°C
300°C	387°C
400°C	518°C
500°C	649°C

Equivalent Enthalpy Trials

In this study, the carrier gas and auxiliary gas mixture makes up about 6% of the total flow, by weight. When the auxiliary gas is heated, it increases the overall enthalpy of the process which may be responsible for a portion of the DE increase experienced in particle preheating through an increase of gas velocity. To determine to what extent this added enthalpy is affecting deposition process, an experiment was designed to keep the particle temperature low while adding the equivalent enthalpy from the heated auxiliary gas. This was done using a custom injection nozzle, shown schematically in Figure 4. In this arrangement, the same auxiliary gas shown in Figure 3 is injected into the nozzle independently from the particle carrier gas.

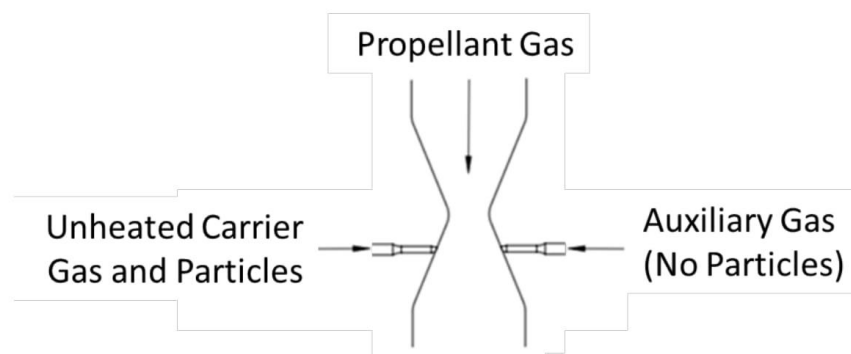


Figure 4: Schematic of custom injection system to inject hot gas without preheating the particles.

To quantify the effect this added enthalpy has on the process, both modelling and spray trials were conducted using the same the flow rates and temperatures employed in the particle preheating trials (Table 2) but with the arrangement shown in Figure 4. This will ensure that the exact same amount of energy enters the system, the only difference being that the particles will not be preheated. Any changes in deposition in these trials can be attributed solely to the enthalpy increase of the system and not particle injection temperature. These trials are referred to as the equivalent enthalpy trials and will be referenced by the corresponding particle preheating temperature to which they have the same enthalpy.

Deposition Characterization and Particle Velocity Measurement

DE was measured by weighing the substrates before and after deposition and comparing the mass gain with the mass of powder fed. Each reported value is an average of 3 samples deposited at each condition. The powder feed rate was measured directly at the powder feeder exit in tests separate from the operation of the CS system, directly before and after spraying.

The deposit quality was investigated through microstructural analysis using a scanning electron microscope (EVO-MA10, Zeiss, UK) and an optical microscope (VHX-2000E, Keyence, Canada). To quantify porosity level, entire cross sections of each deposit was stitched together using the software of the VHX-2000 at a magnification of 1000x. The porosity was calculated through contrast analysis of the optical images using ImageJ software. Microhardness testing of the deposits were conducted on polished samples using a Vickers microhardness tester (Struers Duramin-1, Struers Inc., Cleveland, OH, USA) with a 50g load and a dwell time of 10s. To avoid the effect of the stress field, the distance between two indentations was kept greater than three times the length of the indentation. The reported values are the average of a minimum of 15 indentations for each set of parameters (5 per deposit).

Particle velocity measurements were taken using the ColdSprayMeter (CSM) eVOLUTION (Tecnar Automation Ltd, St-Bruno, Canada). This system uses a continuous 2.4 W ($\lambda=810$ nm) laser with

a dual spit photomask to perform in-flight diagnostic on individual particles. It provides the precise velocities of individual particles during flight. In this study, the velocity measurements were taken at a point 10 mm downstream from the center of the cold spray nozzle exit. Testing was run for several minutes to ensure the collection of a robust data set of over 5000 particle data points.

Computational Fluid Dynamics

The commercially available computation fluid dynamics software, ANSYS Fluent, was used to produce three-dimensional models of the particle preheater, the standard CS nozzle, and the equivalent enthalpy configuration shown in figure 4. A discrete phase of particles was also simulated for each of the models.

Continuous Phase Modelling of the CS Process

The mass, momentum, and energy equations were solved using a pressure-based solver with a coupled algorithm. To account for compressibility effects, nitrogen was assumed to obey the perfect gas law. Due to the high Reynolds number of the flow, and to solve the Reynolds Averaged Navier–Stokes equations, the k-epsilon model was used, which has been shown to provide accurate flow structure in CS (Ref 18). The flow is assumed to be in a steady-state regime. A 2D representation of the 3D domain is shown in Figure 5.

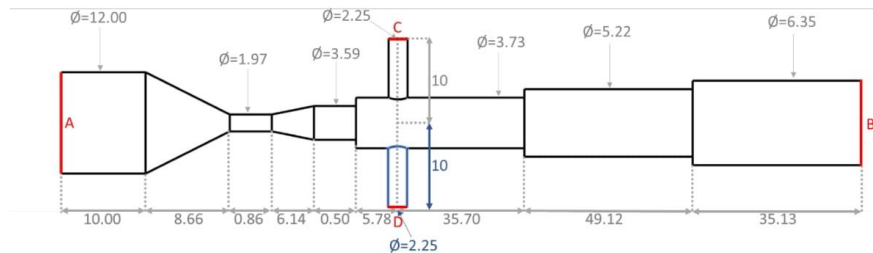


Figure 5: A 2D representation of the 3D computational domain dimensions for the cold spray nozzle. Red shows inlets and outlets. Blue is the auxiliary gas inlet for equivalent enthalpy trials. Not to scale. All dimensions in mm.

All of the surfaces of the domain are taken by default as adiabatic walls, except for the inlets (A, C, and D) and the outlet (B). At the propellant gas inlet (A), the flow was assumed to be uniform and normal to the inlet cross section with a prescribed pressure and temperature. The pressure at the outlet (B) was considered as atmospheric pressure. At the carrier gas inlet (C) and the auxiliary gas inlet (D), the flow was assumed to be uniform and normal to the inlet cross sections a prescribed mass flow and temperature. Table 3 outlines the boundary conditions used in the model, where each row represents a different trial.

Table 3: Boundary Conditions for 12 Different Preheating Scenarios.

Propellant Gas Inlet (A)		Carrier Gas Inlet (C)		Auxiliary Gas Inlet (D)		Outlet (B)
Temperature [°C]	Pressure [MPa]	Temperature [°C]	Mass Flow Rate [g/min]	Temperature [°C]	Mass Flow Rate [g/min]	Pressure [kPa]
500	3.54	15	59.2	NA	NA	101.3
500	3.54	100	59.2	NA	NA	101.3
500	3.54	200	59.2	NA	NA	101.3
500	3.54	300	59.2	NA	NA	101.3
500	3.54	400	59.2	NA	NA	101.3
500	3.54	500	59.2	NA	NA	101.3
500	3.54	15	9.9	15	49.3	101.3
500	3.54	15	9.9	126	49.3	101.3
500	3.54	15	9.9	257	49.3	101.3
500	3.54	15	9.9	388	49.3	101.3
500	3.54	15	9.9	518	49.3	101.3
500	3.54	15	9.9	649	49.3	101.3

The 3D domain was meshed using ANSYS WB meshing tool. Due to the large length scales of the flow, the domain was discretized into an unstructured triangular/tetrahedral mesh. In order to provide higher precision and resolution near the boundaries, inflation was used at the walls with a growth rate of 1.2 and 5 maximum layers. A grid dependency study was performed to determine the appropriate grid size ensuring grid independency. The solutions iterated until convergence was reached by at least 3 orders of magnitude and then by ensuring that net mass and energy imbalances are below 0.001%.

Continuous Phase Modelling of the Particle Preheater

It was assumed that the particles and the gas are injected into the propellant flow at equilibrium conditions, i.e the particles are at the gas exit temperature at the end of the particle preheater. To confirm that the length of the coil in which the two flows mix was adequate for particles to reach the exit gas temperature, a 3D model of the powder preheating system was developed. The mixing coil was modeled as a straight tube, as the curvature radius of the coil was 25.4 mm, orders of magnitude larger than the particles and should not affect the results. Figure 6 is a schematic of the full 3D domain (not to scale). The numerical boundary conditions used for each condition are presented in Table 4, in which each row representing a different trial. The inlet flows are set mass flow rates that match the experiment and the required temperatures of the hot gas were calculated from Eqn. 2. For the pressure at the exit of the preheater, average pressure values were extracted from the solved model of the standard CS process at the point of injection.



Figure 6. Schematic of the 3D computational domain dimensions for the powder preheater model. Red shows inlets and outlets. Not to scale. All dimensions in mm.

Table 4: Boundary Conditions for Particle Preheater Model

Desired at Exit	Auxiliary Gas Inlet (A)		Unheated Carrier Gas Inlet (B)		Preheater Exit (C)
Temperature [°C]	Temperature [°C]	Mass Flow Rate [g/min]	Temperature [°C]	Mass Flow Rate [g/min]	Pressure [kPa]
15	15	49.3	15	9.85	307
100	117	49.3	15	9.85	320
200	237	49.3	15	9.85	333
300	357	49.3	15	9.85	334
400	477	49.3	15	9.85	354
500	597	49.3	15	9.85	365

The mass, momentum, and energy equations were solved using a pressure-based solver with a coupled algorithm. Nitrogen was assumed to obey the perfect gas law and to solve the Reynolds Averaged Navier–Stokes equations, the k-epsilon model was used. The flow was assumed to be in a steady-state regime. The 3D domain was meshed using ANSYS WB meshing tool. Due to the large length scales of the flow, the domain was discretized into an unstructured triangular/tetrahedral mesh. In order to provide higher precision and resolution near the boundaries, inflation was used at the walls with a growth rate of 1.2 and 5 maximum layers. A grid dependency study was performed to determine the appropriate grid size ensuring grid independency. The solution iterated until convergence was reached by at least 3 orders of magnitude and then by ensuring that net mass and energy imbalances are below 0.001%.

Discrete Phase Modelling

For all models, the particles were injected as a discrete phase of inert points in space using a Lagrangian method. In this method, momentum and heat transfer were examined as they pass through each control volume. For the CS model, a high Mach number drag correlation (the Henderson drag correlation), was used. This correlation covers a wide range of particle Mach numbers and Reynolds numbers and has been shown to have accurate results based on experiments in CS (Ref 19,20). For the particle preheater, the default spherical drag law was used

as the relative gas velocities were subsonic. In all cases, the particles are assumed to be at a uniform temperature as the Biot number of the particles is well below the threshold of 0.1 required to use the lumped capacitance method. Heat transfer to or from the particle was assumed to be convective and computed using the Ranz and Marshall correlation for forced flow over spherical particles, which has been shown to have good correlation with experimental results (Ref 19). Additional body forces, such as gravity and lift, were not added as they provide little influence on the particle momentum in CS.

Energy transfer was coupled one way from the gas to the particles, ensuring the steady state solution of the continuous phase was unaffected during the discrete phase calculation. For the standard and equivalent enthalpy cases, the discrete phase only accounts for approximately 0.65% of the overall mass flow rate in the system, which is considered dilute. While particles in the preheater do account for a larger percentage of the total mass flow, it becomes prohibitively expensive computationally to account for the effect of the particles on the gas phase while still accounting for the variation in size distribution in the particle stream.

A discreet random walk (DRW) model was applied to simulate the particles turbulent dispersion. A random eddy lifetime was used with sufficiently large number of tries to ensure that the trajectories include statistical effect of turbulent dispersion. Since the particles are injected radially, some wall/ particle interactions are expected. However, experimental evaluation of the coefficient of restitution for impacts between smooth spherical aluminum particles and the polymer nozzle material could not be found in literature. Consequently, the impacts were assumed to be perfectly elastic, which Ba et al have shown to be adequate for the cold spray process (Ref 21).

To accurately model the particle size distribution in this flow, the particles were injected uniformly across the carrier gas inlet surface of the domain with initial temperature and velocity matching that of the gas stream at that point. Injections of nine different particle sizes were chosen, each matching the particle bin sizes shown in Figure 1. The resulting averages and distributions were weighted to match the true frequency percentage of particle diameters in the powder.

Results and Discussion

Modelling of the Powder Preheater

To ensure that the mixing section of the particle preheater was adequately long, each of the desired preheating temperatures shown in Table 4 was modeled. To verify that the simulation matches the conceptual model, the mass average gas temperature at the exit of the preheater was compared to the gas temperatures predicted from the 1st law of thermodynamics (eqn. 1). The results of this model can be found in Table 5, all with a percentage error of less than 1%.

Table 5: Preheater Model Results: Gas Temperature

Expected Temperature [°C]	Modelled Average Gas Temperature [°C]
15	15.0
100	100.0
200	200.3
300	301.1
400	402.4
500	504.7

In Figure 7(A), an area plot showing the particle temperatures along the length of the mixing tube for the 500°C preheating case can be observed. The smaller particles (30 to 40µm), which make up most of the aluminum powder, reach the gas temperature quite rapidly (<0.5m), while the largest particles (~80µm) take the full 2 meters to approach desired temperature. The average temperatures of the particles exiting the preheater and the mass averaged gas temperature can be seen in Figure 7(B). From this it can be concluded that both the carrier gas and the particles reach the desired temperature before injection into the nozzle.

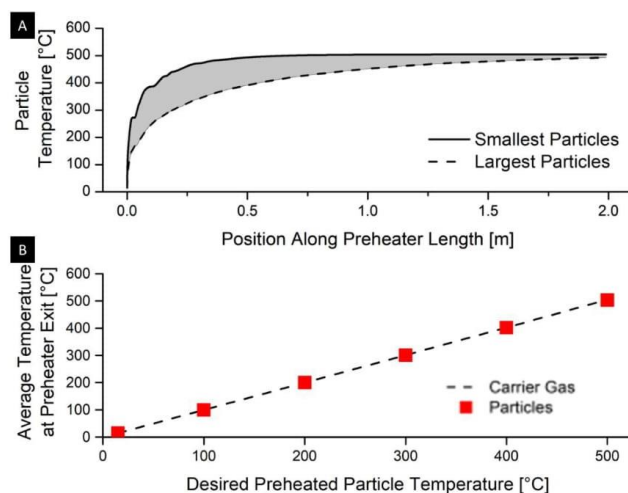


Figure 7: Modelling results of powder preheating process: (A) Area plot of particle temperatures along the heater length for a 500°C desired exit temperature and (B) the average particle and mass averaged gas temperature at the preheater exit.

Continuous Phase Modelling of the CS Process

The process was modelled for various particle preheating temperatures outlined in Table 3. Figure 8 shows the gas temperature contours without particle preheating in Figure 8 (A) and (B)

which can be compared to the case for maximum particle preheating (500°C) in Figure 8 (C) and (D). It can be observed that when preheating the carrier gas, a higher temperature is present around the nozzle wall localized to the injection side. This effect quickly vanishes along the length of the nozzle and there appears to be a minimal difference to the center of the gas flow and at the exit plane.

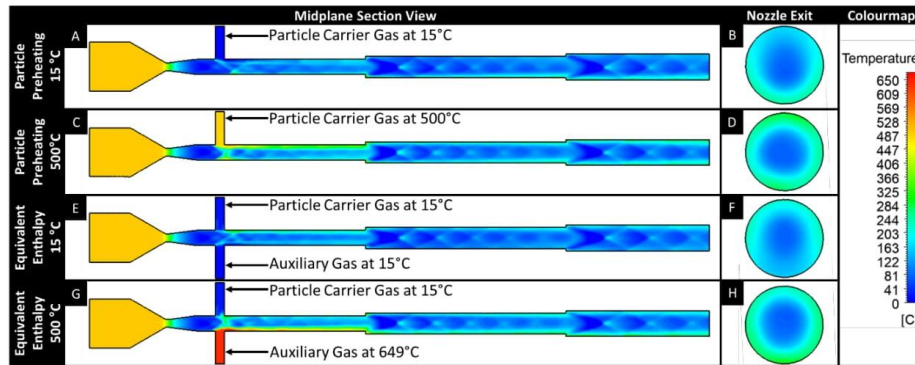


Figure 8: Modelling results: Gas temperature contour maps of the midplane section of the nozzle (A, C, E, and G) and at the nozzle exit (B, D, F, and H), under the different conditions noted in the figure. The midplane section is taken along the length of the nozzle through the center of the injection ports. The nozzle exit cross section is at 3X scale compared to the side sections and oriented in the same direction.

The flow modelling results for the equivalent enthalpy trials can be seen in Figure 8 (E), (F), (G), and (H). In Figure 8 (E) and (F), lower temperatures can be seen along the wall at the bottom, where the auxiliary gas flow is, instead of the top where the particles are injected. When auxiliary gas is heated (Figure 8 (G) and (H)), the effect of temperature can be seen along the length of the nozzle on the side of the auxiliary injection. However, it appears to have minimal effect on the temperature of the center of the flow and at the exit plane.

The velocity contours can be seen in Figure 9. In this case, small differences in velocity can be seen close to the nozzle walls in the midplane sections in Figure 9 (A), (C), (E) and (G). However, when the gas flow reaches the nozzle exit, there does not appear to be a significant difference between any of the arrangements in Figure 9 (B), (D), (F), or (H).

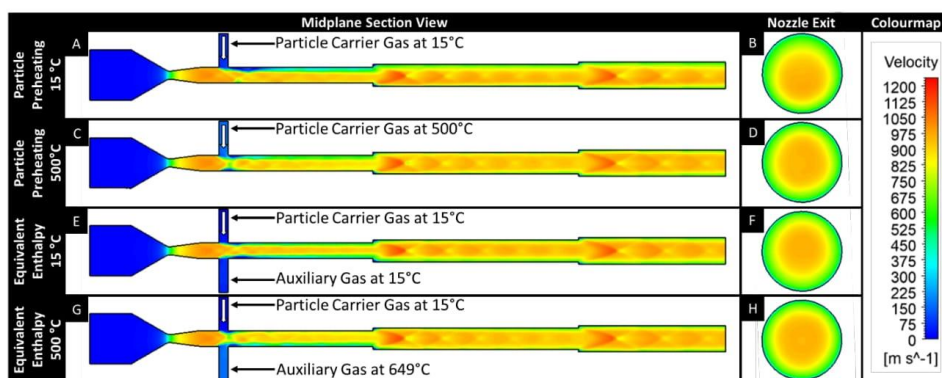


Figure 9: Modelling results: Gas velocity contour maps of the midplane section of the nozzle (A, C, E, and G) and at the nozzle exit (B, D, F, and H), under the conditions noted in the figure. The midplane section is taken along the length of the nozzle through the center of the injection ports. The nozzle exit cross section is at 3X scale compared to the side sections and oriented in the same direction.

The mass averaged gas temperature at the exit for the various cases can be found in Figure 10(A). At this resolution, it can be observed that both the particle preheating trials and the equivalent enthalpy trials have similar values at each carrier gas temperature. These values increase slightly as the temperature of the carrier gas increases. In the particle preheating trials, the exit temperature of the gas raised from 150 °C to 166 °C and in the equivalent enthalpy configuration, the exit gas temperature raised from 146 °C to 166 °C.

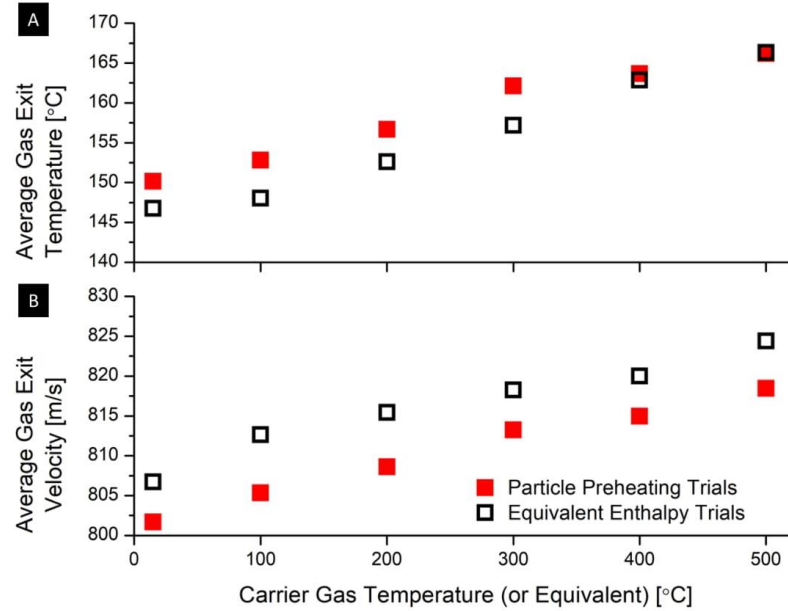


Figure 10: Modelling results of (A) mass averaged gas temperature and (B) mass averaged gas velocity at the exit plane of the nozzle for different carrier gas temperatures.

The mass averaged gas velocity at the exit of the various cases can be found in figure 10 (B). Much like the gas exit temperature, the values for velocity between the two trials are very close. It can be observed that the gas exit velocity increases slightly as the temperature of the carrier gas is increased. In the particle preheating trials, the average exit velocity of the gas raised from 801 m/s to 818 m/s, while in the equivalent enthalpy trials, the velocity raised from 806 m/s to 824 m/s.

The increase in gas exit temperature and velocity are expected, as energy is being added to the flow. This effect on the deposition in HPCS has been demonstrated to be substantial, but the values uncovered by the current model for LPCS show that they are relatively minor, with gas temperature increasing only 3.6% and gas velocity increasing only 2%, when comparing unheated carrier gas to the highest temperatures tested. The differences between the particle preheating trials and the equivalent enthalpy trials at each carrier gas temperature for both the velocity and temperature at the exit is very small (<1.6%), confirming that injecting the auxiliary gas directly into the nozzle instead of premixing with the carrier gas has little effect on the gas dynamics.

Discrete Phase Modelling

The particle exit velocity for the various cases can be found in Figure 11, in the form of box and whisker plots. In this figure, the values obtained from the model can be compared directly to the values measured using the CSM. From this, it can be observed that model results closely matched those from the experiment. Interestingly, in all cases, particles from the particle preheating trials exited the nozzle slightly faster than those of the equivalent enthalpy trials, despite a similar gas velocity field predicted by the model. This small difference is likely due to the particles in the particle preheating trials being injected into the nozzle at a higher initial velocity, since the mass flow rate of carrier gas in the particle preheating trials is six times higher than the mass flow of particle carrier gas used in the equivalent enthalpy trials. This higher initial velocity would allow the particles to penetrate to the fast-moving center of the propellant flow more easily, as well as having a higher amount of kinetic energy to begin their acceleration. While particle preheating in LPCS may slightly increase gas exit velocity through the added enthalpy of the hot carrier gas, its effect on particle velocity at the exit of the nozzle appears to be negligible, as shown in both the experimental and modelled results. This is a very different result that what has been shown by others in HPCS.

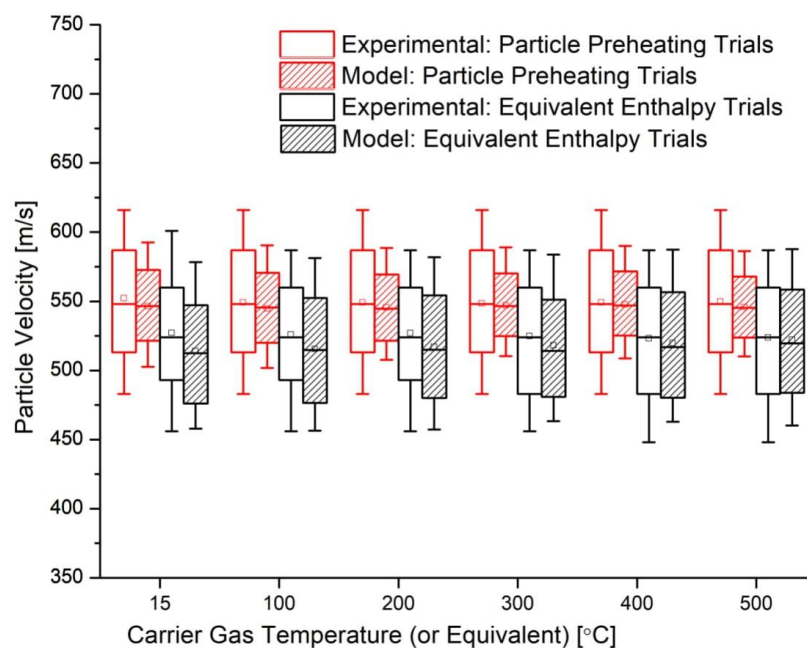


Figure 11: Experimental and modelling results for particle velocity for carrier gas temperatures (box and whisker plots with $\square$ representing the mean, the whiskers representing 10-90%, and the box representing 25-50-70% of all particles).

The model results of the average particle exit temperatures can be found in Fig 12. It can be observed that the preheated particles do not remain at their initial injection temperature, but drift towards the average gas exit gas temperature (shown as the dotted line). However, they do retain most their thermal energy. For example, the particles injected at a temperature of 500°C exited the nozzle at an average temperature of $436 \pm 11^\circ\text{C}$, a drop in temperature of approximately 8%. For the enthalpy equivalent trials, the particle temperature increases slightly, from $33 \pm 3^\circ\text{C}$ to $45 \pm 5^\circ\text{C}$ with the hottest auxiliary gas injection, a 3.8% increase in particle temperature. This small increase in particle temperature is unlikely to result in any significant particle softening or changes in deposition.

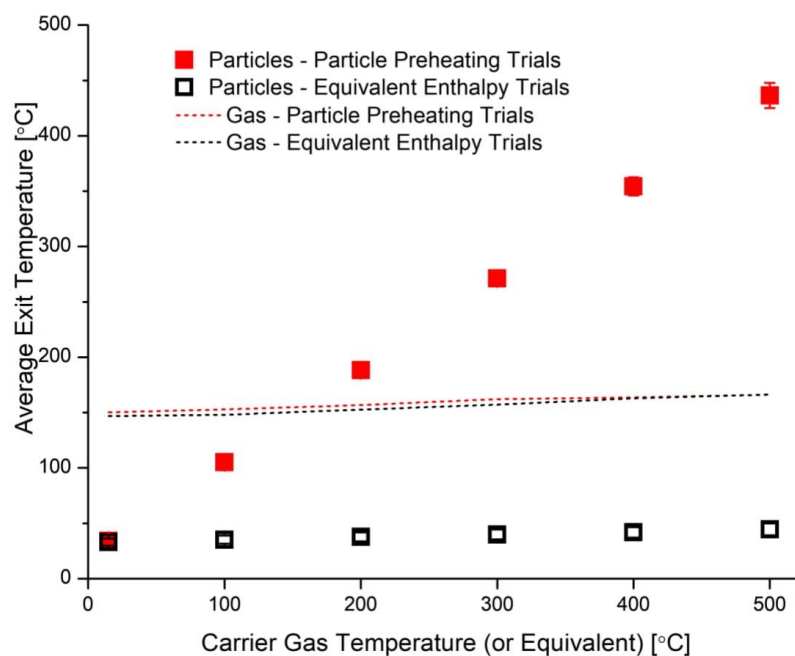


Figure 12: Modelling results of the average particle and gas temperatures at the exit of the nozzle for different carrier gas temperatures. Note: Some error bars hidden by symbols.

Deposition

The results have demonstrated that the particle exit velocity was mostly unaffected by particle preheating, while particle exit temperature was. Figure 13 shows the normalized deposition efficiency for the different trials. In this plot the DE is normalized against the baseline test with unheated particle carrier gas. By increasing the particle preheating temperature, a clear trend of increasing deposition efficiency is seen. In the case of preheating the particles to 500°C, the deposition rate increased by a factor of 3.6 compared to unheated particles.

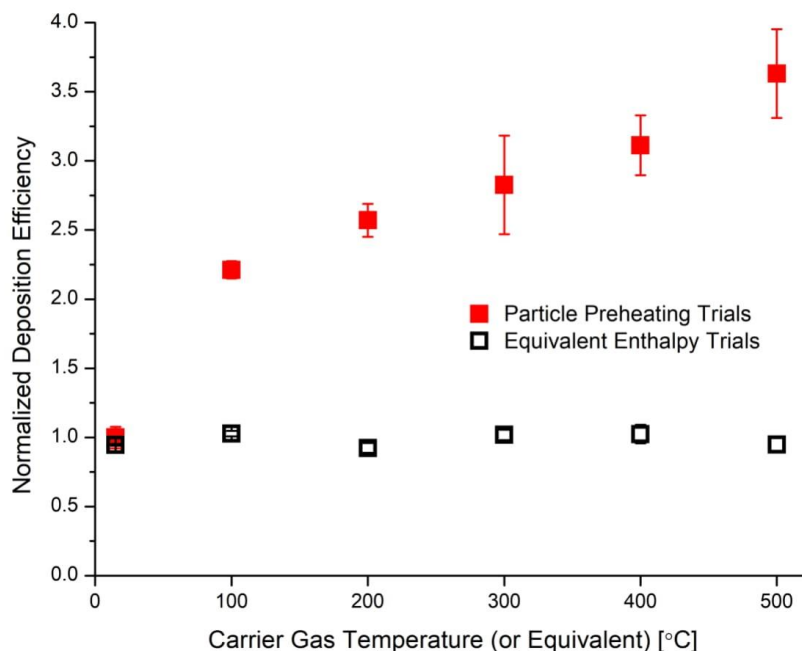


Figure 13: Deposition efficiency, normalized to the unheated conventional case, for different carrier gas temperatures. Note: some error bars hidden by symbols.

It is also clear from Figure 13 that the 3.6% increase gas temperature and 2% increase in gas exit velocity did not increase the deposition efficiency in the equivalent enthalpy trials, as the DE remained unchanged throughout. Therefore, the effect on DE seen in the particle preheating trials can be solely attributed to the increase in particle temperature and not the increased enthalpy of the flow. The effect of this DE increase can be observed in Figure 14. In this figure, the unheated particle sample (A) is much thinner than the sample deposited with particles preheated to 500°C (B).

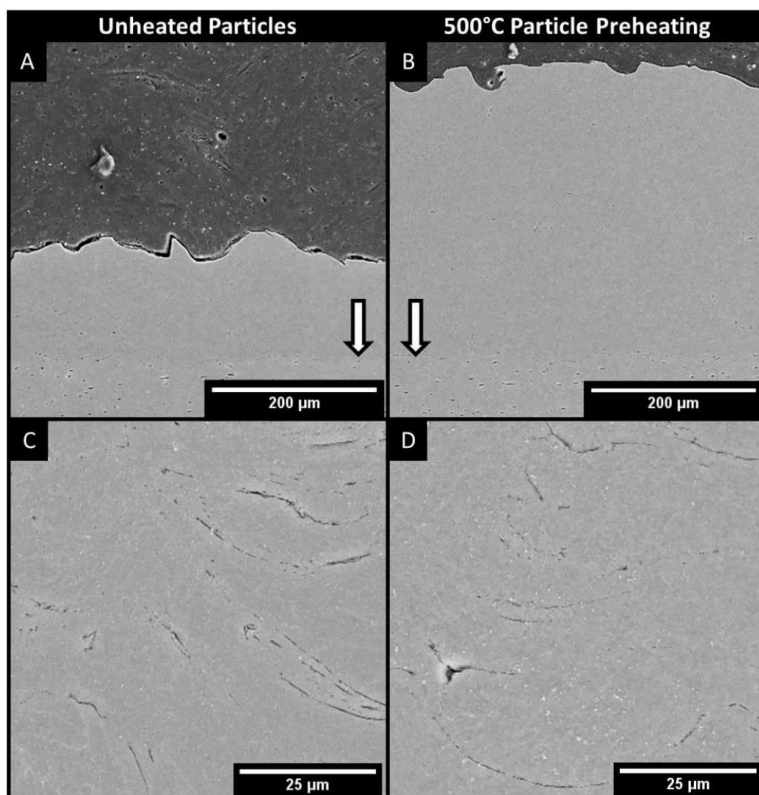


Figure 14: SEM micrographs of etched cross sections of (A) a conventional deposition without particle preheating and (B) a deposition with particles preheated to 500°C prior to injection (arrow indicates the location of the substrate/deposit interface). Higher magnification in (C) and (D).

The SEM micrographs in Figure 14(A) and Figure 14(B) show that the coatings are dense. With the higher magnification in Figure 14(C) and Figure 14(D), it can be observed that the spherical feedstock particles have been heavily deformed during the deposition process for both preheated and non-preheated samples. The extent of the deformation in the samples is substantial and it is not possible to quantify and compare between conditions. This high density of the deposition was verified through porosity measurement, which was found to be well under 0.5%, as seen in Figure 15 (A).

The microhardness values can be found in Figure 15 (B). A decrease in hardness as powder preheating temperature is increased can be observed, from 50 ± 4 HV_{50g} with no powder

preheating to 44 ± 2 HV_{50g} with the particles preheated to 500°C. This decrease in hardness is expected for two reasons. First as the impact temperature of the particle increases, it may approach or exceed the hot working temperature of the material, eliminating the strain hardening that can occur during deformation. Secondly, as DE increases the amount of impingement seen by the previously deposited particles is reduced. This decrease in strain hardening results in a slightly softer deposition. This was not seen in the equivalent enthalpy trials as the samples did not have a change in DE or particle temperature.

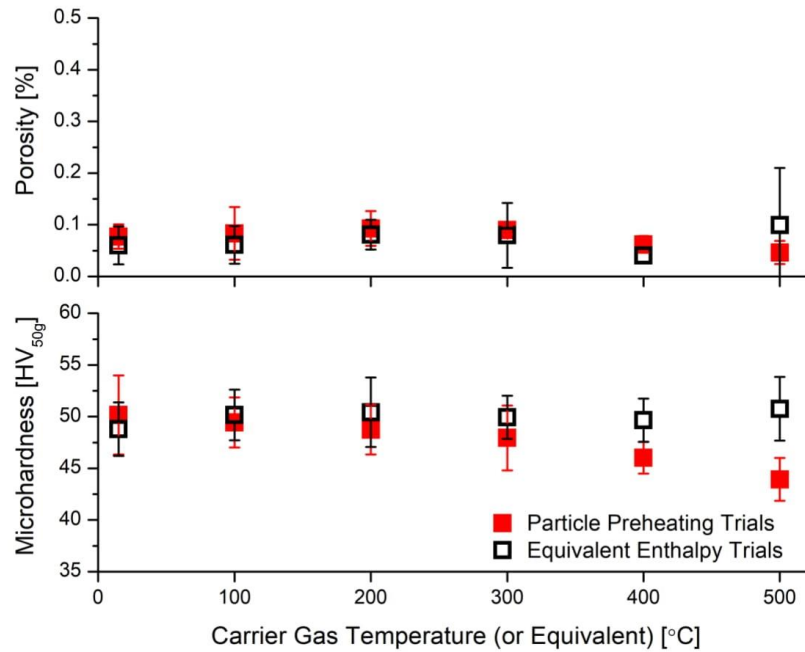


Figure 15: Deposition results of (A) Vickers hardness and (B) optical porosity measurements for different carrier gas temperatures. Note: some error bars hidden by symbols.

Conclusion

This work demonstrated that independent control of particle temperature is possible through particle preheating in LPCS. Unlike HPCS, it has been demonstrated that the enthalpy of the hot carrier gas used in particle preheating has a minimal effect on the propellant gas conditions and resulting particle impact velocities. It was also shown that the particles retain most of their thermal energy throughout the acceleration process in the nozzle. Therefore, increasing or decreasing the particle temperature can be accomplished independently, without increasing or

decreasing the gas stagnation conditions - a unique feature of downstream injection and a valuable tool when dealing with temperature sensitive substrates and particles.

Particle preheating was used to inject pure aluminum particles up to temperatures of 500°C, about 80% of their melting temperature. This particle preheating was accomplished without clogging because of a novel particle preheater which eliminated the particles exposure to hot metal surfaces. It was found that even after substantial spray time, there was no evidence of wear or clogging. These particles retained, on average, 92% of their thermal energy throughout the acceleration process. This resulted in a DE increase of 3.6 times when compared to the injection of room temperature particles. The preheating of this carrier gas does come at a cost. For the 500°C preheating, the overall energy consumption increased 9% compared to not preheating the particles. However, this is a small cost for substantial savings in spray time and powder.

Conclusion

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6 Conclusions and Future Work

The purpose of this investigation was to understand and improve the deposition quality and rates of CSAM in a way that is economically sound and without detrimental temperature effects. It focused on materials that are desired by the AM community and built upon the current knowledge in CS. This motivation was satisfied by pursuing three clear objectives, each addressing a critical roadblock in the adoption of the technology.

The effect of a non-spherical particle morphology was the first objective investigated. Titanium has been shown repeatedly to require pure helium at very high temperatures and pressures to get dense coatings, however, the unique coral-like morphology resulting from the Armstrong Process was revealed as a key to successful deposition with nitrogen. Using LPCS, under conditions that would be considered mild, a DE of 100% and a porosity of nearly 0% was achieved. This is a promising approach for CS as a method for AM of titanium parts. The low powder cost and the advantages of additive manufacturing could allow for a substantial cost savings in titanium part production when compared to traditional manufacturing methods. With these cost saving advantages, AM of titanium using Armstrong process powder and CS could lead to a paradigm shift of titanium production, allowing titanium to enter markets that under traditional methods would be far too expensive.

Unfortunately, this unique powder morphology was not available in other materials. To address the low DE of the other metals of interest, such as aluminum and stainless steel, the concept of mixing the propellant gas was introduced in the second objective. Considering the relative costs of gases, powder, electricity, and labour, the second paper focuses on the concept of optimizing the amount of helium to produce the minimum component cost. It was found that for the specific stainless steel and aluminum alloy powders discussed, costs could be reduced by 44% and 59% respectively using the gas mixing system. However, no cost savings was found for the most inexpensive of the powders, pure aluminum.

For gas mixing to be effective, the cost of helium must be offset by the cost of the powders. Therefore, low-cost powders, such as pure aluminum, resulted in pure nitrogen as their least

expensive option. This however doesn't address the low DE that is preventing its adoption in CSAM. The third objective addresses just this, an improvement in DE without the introduction of expensive helium. In this study, aluminum particles were preheated using a novel particle preheater that does not clog. This resulted in a DE increase of 260% with a minimal increase in electrical costs.

These three objectives, while studied and published separately, all relate to the purpose of this work to improve the process economics without detrimental temperature effects. These findings have been (or will be) published in international peer reviewed journals to add to the collective knowledge.

Future work

Several follow up studies could be proposed to expand upon this work and improve our current understanding.

- It is possible that titanium alloys can be produced using the Armstrong Process. An investigation into the use of nitrogen for the deposition of these alloys could expand the potential reach of CSAM.
- The current work only shows the benefit of raising the particle temperature. Efforts should be made to demonstrate the benefit of independent particle temperature control by demonstrating the potential advantage of cooler particles in a hot flow and hot particles in cooler flows.
- A study on the combination of gas mixing and particle preheating, should in theory, improve the process economics and further expand our understanding.
- Since the particle carrier gas was shown to have minimal effects on the propellant gas velocity and the resulting particle velocity in LPCS, the use of different low-cost gasses as the carrier gas should be investigated.

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