# CHARACTERIZATION AND DEPOSITION BEHAVIORS OF COLD SPRAYED MIXED 316L/FE COATINGS

By

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# Abstract

The focus of this thesis is to explore the effects of powder characteristics on the cold sprayability of mixed 316L and Fe powders. X-ray diffraction (XRD), electron backscatter diffraction (EBSD) were performed to characterize the feedstock powders before and after mixing. In addition to deposition efficiency (DE), porosity, microhardness and bond strength of the coatings were measured and used as metrics for cold sprayability. Experiments were also performed with a dual powder feeder, which therefore eliminated the need for premixing powders, and introduced new factors which added to the understanding of cold spraying of mixed powder feedstocks. Individual particle impact tests were performed to study the different cold spray behaviors of different particle-substrate combinations, e.g. Fe on 316L, Fe on Fe, etc., since these events could take place in mixed powders cold spray.

# Résumé

L'objectif de cette thèse est d'étudier les effets des caractéristiques des poudres sur la projection à froid de poudres mélangées 316L et Fe. Les poudres de charge d'alimentation avant et après le mélange ont été caractérisée par la diffraction des rayons X (XRD) et la diffraction d'électrons rétrodiffusés (EBSD). En plus du rendement de la projection (DE), la porosité, la microdureté et la force d'adhérence des revêtements ont été mesurés et utilisés en tant que paramètres d'évaluation pour la projection à froid de poudres. Des expériences ont également été réalisées avec un doseur de poudre double, qui a éliminé par conséquent la nécessité du prémélange des poudres, et a introduit de nouveaux facteurs qui ont ajouté à la compréhension de projection à froid de poudre mixtes. Des tests d'impact de particules individuelles ont été réalisées pour étudier les différents comportements des différentes combinaisons de particules de substrat, par exemple par pulvérisation à froid Fe sur 316L, Fe sur Fe, etc., étant donné que ces événements ont lieu en poudre mixte pulvérisation à froid.

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# Preface

This thesis is organized into the following seven chapters: Chapter 1 is a brief introduction of cold spray and a description of the research objectives. Chapter 2 presents a literature review on the fundamental and applied aspects of cold spray technology, as well as current findings of the mixing powders effects on cold sprayability. Chapter 3 describes the materials, experimental procedures and methods used in this thesis. Chapter 4 involves further characterizations of samples produced in a previous study, and an analysis of the DE behavior as well as other parameters of cold sprayability. Chapter 5 explores the effects of mixing powders on cold sprayability with new 316L and Fe experiments using different powders and a new cold spray system. Chapter 6 studies the deposition behaviors of single particles depositing on different substrates using individual particle impact tests. Finally, Chapter 7 gives conclusions of the current work and provides suggestions for the future work.

# **Contributions of Authors**

This thesis is completed with contributions of the candidate and many other individuals. The candidate and the supervisor of his Master of Engineering program Prof. Stephen Yue, have defined the projects and have regular meetings on discussions regarding the methodology and progress of this project. Dr. Phuong Vo and Jean-François Alarie at the National Research Council Canada-Industrial Materials Institute (NRC-IMI) assisted in the fabrication of cold sprayed coatings. Rohan Chakrabarty provided the simulated results of single particle impact tests using ABAQUS software. Xingchen Liu helped in measuring the bond strength of cold sprayed coatings. Binhan Sun and Dr. Sriraman Rajagopalan offered guidances in quantitative phase composition analysis of samples using XRD. I, Xin Chu, have performed all of the following tasks: cold spray experiments, measurements of particle impact velocity, deposition efficiency, and particle size distribution. Moreover, I have performed all the metallographic preparations of powders and cold sprayed coatings, including sample sectioning, mounting, polishing, etching, and all sample characterizations such as coating porosity, microhardness, flattening ratio, and surface roughness. I have also taken all the scanning electron, energy dispersive spectrometer and electron backscatter diffraction images. As well, I have conducted heat treatment of the powder samples. Finally, I have performed all the calculations and data analyses.

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# **Chapter 1 Introduction**

Cold spray technology has emerged to become an excellent alternate technique for producing thermal-sensitive, low oxide content coatings instead of the conventional thermal spray methods [1]. Commercial cold spray systems are now able to produce coatings with high density and reproducibility [2]. Some of the current trends in cold spray are to include the production of composite coatings such as Metal Matrix Composites (MMC) [1]. The deposition of metal powder mixtures can combine several functional properties and also expand the range of sprayable materials [1, 3]. To obtain dense and homogenous composite coatings, besides the optimization of process parameters, the selection of appropriate powder blend is also reported to improve the cold sprayability of one powder [1].

However, there is still a great lack of knowledge in understanding the cold spray mechanisms in the case of multimaterial coating deposition [1]. In particular, it is not clear how to model the key cold spray metrics of the mixture. For example, it is not clear that there is a critical velocity that is unique to any specific composition of composite powders, or whether it can be determined from knowledge of the critical velocities of the individual components.

The overall goal is to understand the effect of mixed powder feedstock characteristics on cold sprayability of these powders. The term "cold sprayability" indicates the ease with which the material is deposited. It consists of several parameters such as critical velocity, porosity, deposition efficiency (DE) and other mechanical properties [4]. Specific to composite powders, a further metric is compositional yield, i.e. how close deposited composition is to the initial powder feedstock composition.

#### 1.1 Problem Description and Research Objectives

This research was initiated by observations of DE characteristics of mixed 316L and Fe deposition in a previous PhD thesis [5]. The 316L powder had a pure austenitic FCC structure while the Fe powder featured a pure ferritic BCC structure [5]. In this work, five compositions of 316L/Fe pre-blended powder mixtures (316L, 20wt%Fe, 50wt%Fe, 80wt%Fe, Fe) were produced [5]. Pure 316L had almost double the DE of the Fe coating. It was found that if the DE of the mixed coatings was considered to be the weighted average values according to 316L/Fe ratios in the starting powders, large deviations between the predicted and experimental DE values were seen [5]. In particular, for 80%Fe+20%316L, the DE was almost the same as pure 316L coating [5]. Similarly, 20%Fe mixed with 80% 316L powders gave a DE much closer to pure Fe than pure 316L [5].



Figure 1.1: Theoretical and experimental DE with increasing wt.% of Fe [5].

These findings show that there is a strong but "unpredicted" effect of mixing on deposition efficiency of mixed metal powders. Thus, this research focuses on the cold spray deposition of 316L stainless steel/Commercial purity iron (CP Fe) mixed coatings, and the cold sprayability of the mixed coatings is examined as a function of the powder feedstock composition. Normally 316L stainless steel is harder than commercial purity Fe, but can exhibit better plastic deformability than Fe due to the larger number of slip systems in FCC structure than BCC [6]. Therefore, the objective is to explore the effects of different hardnesses, flow properties and crystallography on cold sprayability. The findings will

ultimately provide concepts determining the cold sprayability of metal powder mixtures in general.

# **Chapter 2 Literature Review**

# 2.1 Cold Gas Dynamic Spray (CGDS)

#### **2.1.1 Introduction**

#### **2.1.1.1 History**

Cold spray (CS) is often considered as a novel and recently emerged spray method, though its basic idea behind the process has already been established at the beginning of the 20th century [2]. Thurston in 1990 filed the first patent of utilizing the impact energy of metal particles driven by compressed gas to produce a coating [2]. However, the technology required was too complicated at that time, and it took another 80 years to put this idea into practical use [2]. It was in 1980's, when studying models related to supersonic two-phase flow (gas+solid particles) in a wind tunnel, Russian scientists observed that solid particles were deposited onto various materials when their velocities were beyond certain values [7]. This finding marks the first practical demonstration of cold spray; since then efforts have been devoted to convert the wind tunnel experiment into a viable industrial coating technique [7]. Till now, a wide range of pure metals, metal alloys, and composite powders can be successfully deposited onto a variety of substrate materials to fabricate reproducible coatings using commercialized cold spray systems [8].

#### 2.1.1.2 General process review

Depending on the pressure level used, cold spray can be divided into two different processes: high-pressure (>1 MPa) cold spray (HPCS) and low-pressure (LPCS) cold spray [9]. The stationary HPCS process generally offers advantages such as the larger selection of materials and high quality of the coatings. While the LPCS being portable allows the possibility of on-site spray, and also it is a typical method to spray mixtures of metal and ceramic powders due to its distinct radial powder injection approach [9]. In this thesis, only the HPCS process is used so it is discussed in detail.

Figure 2.1 (a) shows a schematic illustration of the HPCS process and 2.1 (b) shows the gun details [10]. A compressed gas (usually N<sub>2</sub>; occasionally He) between 1.0 MPa and 4.0

MPa is pre-heated to a temperature ranging from 100 °C to 1000 °C [11, 12]. It flows directly to the nozzle to mix with the powder which is fed by a carrier gas. Then the two-phase flow (gas+powder) is fed through the nozzle where a supersonic velocity is generated [11]. After that, the two-phase flow exits the nozzle and the powder impacts on the substrate to deposit a coating [11].

A de Laval type converging/diverging nozzle is most commonly used in cold spray process to generate high speed gas flow [9]. A supersonic velocity is produced in the nozzle throat and the nozzle diverging part [9]. The colors seen in Figure 2.1 (b) indicate the temperature distribution in different part of the gun, revealing, as designed, that the energy of the heated gas is converted to kinetic energy in the nozzle, literally resulting in a cold spray [9].



Figure 2.1: Schematics of (a) HPCS process; (b) HPCS gun [10].

# 2.1.1.3 Advantages and limitations

As illustrated in Figure 2.2, the major difference of cold spray over other thermal spray processes is the low temperature involved [8, 13].



Figure 2.2: Comparison of cold spray with traditional thermal spray methods [8].

Cold spray utilizes the impact energy of highly kinetic particles to fabricate a coating, and in the meantime particles can remain thermally unaffected, although heavily plastically deformed [2]. Therefore, cold spray becomes an excellent method to produce coatings of oxygen-sensitive materials such as Al and Ti, or temperature-sensitive materials such as amorphous and nanostructured powders [2]. Also, the absence of high temperature during process permits coating deposition without inducing thermal stresses or forming undesirable phases [1]. A dense and thick (up to several centimeters) coating can be obtained using cold spray with wrought microstructure [13]. Moreover, as the spray trace is relatively small (1-25 mm<sup>2</sup>) and well defined, cold spray can realize reasonably precise deposition [1, 6]. Furthermore, the "oversprayed" expensive powder feedstock can be recycled for reprocessing [13].

Despite all its advantages, cold spray has several drawbacks. For instance, cold spray requires the feedstock materials to have certain capability to plastically deform whereas almost all materials can be sprayed through thermal spray techniques [9, 11]. Therefore, cold spray is restricted to ductile metallic materials such as Al, Cu and steels or at best composite powders of ductile matrix materials with other brittle components [2, 11]. As

well, compared with thermal spray methods such as arc spray and wire flame spray, the deposition rate of cold spray is lower, so a large amount of gas is needed for processing and its running costs are in turn higher, especially if He has to be used although it is very rare case in a production run [9]. In addition, cold sprayed coatings are relatively brittle in their as-sprayed state since a large fraction of their particle-particle/substrate interfaces are simply bonded together mechanically, and the particles are heavily work hardened, thus brittle fractures easily occur along these weak interface regions, giving a poor coating ductility [11].

#### **2.1.1.4 Industrial applications of cold spray**

Cold spray is a potential additive manufacturing method to fabricate complex and intricate structures [14]. Moreover, the portable LPCS system permits the field repairing of inservice components [6]. Some typical applications of cold spray coatings are tabulated in Table 2.1 [6, 9].

Applications	Coating Materials	Industry Sectors			
		Aerospace			
Corrosion resistance	Zn, Al	Oil & gas			
		Powder generation			
Wear resistance	WC-Co, CrC-	Oil & gas			
wear resistance	NiCr,W-Cu	On & gas			
Electrical and	Cu Al	Electronics			
thermal conductivity	Cu, Al	Automotive			
Renairing	Stainless Steel, Ti,	Aerospace			
Repairing	Al	Automotive			
Functional coatings	Ti Ni Fe	Medical			
- i unetional coatiligs	11, 141, 10	Electronics			

Table 2.1 Cold spray materials and their applications [6, 9].

#### 2.1.2 Bonding mechanisms

Starting from the early 2000's, cold spray technology has gone through fast commercial development, and today reliable cold spray systems are made available to produce highly dense and reproducible coatings [2]. Ironically, the bonding mechanisms behind the adhesions of particle-particle and particle-substrate in cold spray are still poorly understood [6]. So far, the most widely accepted bonding mechanisms in cold spray are the adiabatic shear instabilities (ASI) leading to "metallurgical" bonding and physical interlocking [15, 16].

As shown in Figure 2.3, during impact the solid particles undergo severe plastic deformation [15]. Due to the local thermal softening effect, particles lose their shear strength and the interface behaves like a viscous fluid to form metal jets [15]. In this way, the particle deformation breaks the oxides film, which, in turn creates intimate conformal contact between interface, promoting the formation of metallurgical bonding [15]. However, the impact evolution process shown in Figure 2.3 is based on numerical simulations, and current experimental methods are limited to verify the evolution process in such a short time scale [15].



Figure 2.3: Simulation of impact between the particle and substrate materials with temporal evolution: (a) 4.4 ns, (b) 13.2 ns, (c) 22.0 ns, and (d) 30.8 ns [15].

Champagne et al. [16] have proposed another theory of bonding mechanism based on the interface mixing. During cold spray deposition, the incoming particles with high kinetic energy could deeply penetrate into the substrate, causing the forced mixing phenomenon of interface materials through the formation of interfacial waves, vortices, and roll-ups [16]. The interface mixing phenomenon is reported to be more obvious when the substrate is softer and particles have higher density [16]. As seen in Figure 2.4, the presence of vortices structures, as well as the metal jets, provide the mechanical interlocking between the particles/substrate or particles/particles in cold sprayed coatings [16].



Figure 2.4: SEM images showing (a) vortices at coating-substrate interface [16] and (b) metal jets on coating surface [17]

The process of coating formation in cold spray is illustrated in Figure 2.5 [18]. Broadly speaking, the coating deposition process can be divided into two main steps: (1) the adhesion of particles with substrate (formation of the breeding layer); and (2) the cohesion between particles (coating deposition) [18]. In the first stage, incident particles shot peen and leave craters to the substrate surface [19]. Cratering activates the substrate surface by removing any surface contamination and help to bond the incoming particles to form the first layer [19]. This stage is critical and largely depends on the material properties of the particle and substrate, and also the substrate conditions (e.g. preheating and roughness) [6]. Then the subsequent particles adhere to the previously deposited layers, deform and realign, and particles start to form metallurgical bonding between each other [18]. After the coating is built up, the continuous peening effect leads to further densification and work-hardening of the coatings [18].



Figure 2.5: Schematic of coating formation in cold spray process [18].

# 2.1.3 Cold sprayability

Cold sprayability is introduced in order to evaluate the ease with which a powder can be cold sprayed [17]. Critical velocity, deposition efficiency, porosity and coating mechanical properties such as hardness and bond strength are the important metrics of cold sprayability [4].

As previously stated, not all particles impinging on the substrate can deposit a coating. Deposition can be facilitated by using higher values of process parameters (temperature and pressure), however, the ease of deposition depends on the physical characteristics of the materials, e.g. the plastic deformability [20].

In general, metals of face-centered cubic (FCC) group such as aluminum, copper and 316L stainless steel are most easy to deposit as the highest number of slip systems provide

excellent deformability; while metals of hexagonal (HCP) group such as magnesium and titanium, and body-centered cubic (BCC) group like tungsten and alpha-iron have the fewer number of slip systems, thus they yield lower deformability and are relatively difficult to deposit [6]. However, there are other factors to consider, as will be described below.

## 2.1.3.1 Critical velocity (V<sub>crit</sub>)

Critical velocity ( $V_{crit}$ ) is defined as the minimum particle impact velocity required for any deposition to occur [20]. Critical velocity depends on the sprayed material itself, but can also be modified by powder quality, particle size and particle impact temperature [20]. Assadi et al. [21] proposed a simple equation based on numerical simulations to calculate the critical velocity of different materials as:

$$v_{\rm crit} = 667 - 0.014\rho + 0.08(T_{\rm m} - T_{\rm R}) + 10^{-7}\sigma_{\rm u} - 0.4(T_{\rm i} - T_{\rm R})$$
 (2.1)

Where  $\rho$  is the particle density,  $T_{\rm m}$  is the melting temperature,  $T_{\rm R}$  is the reference temperature (293 K),  $\sigma_{\rm u}$  is the ultimate tensile strength, and  $T_{\rm i}$  is the impact temperature.

Schmidt et al. [20] improved his equation to incorporate the specific heat, tensile strength, mechanical and thermal calibration factors, as seen in Equation 2.1 [18].

$$v_{\text{crit}}^{\text{th,mech}} = \sqrt{\frac{F_1 \cdot 4 \cdot \sigma_{\text{TS}} \cdot \left(1 - \frac{T_i - T_R}{T_m - T_R}\right)}{\rho}} + F_2 \cdot c_p \cdot (T_m - T_i).$$
(2.2)

Where  $\sigma_{TS}$  is the ultimate tensile strength,  $T_i$  is the impact temperature,  $T_R$  is the reference temperature (293 K),  $T_m$  is the melting temperature,  $\rho$  is the particle density,  $c_p$  is specific heat of the particle, and  $F_1$ ,  $F_2$  are the empirical factors.

Figure 2.6 shows the comparison of experimental critical velocities with the calculated results using Assadi's and Schmidt's equations [20]. The predictions based on Schmidt's equation show more accurate descriptions of  $V_{crit}$  with the measured data for different types of materials than Assadi's equation, especially for tin, copper and tantalum [20, 21]. In addition, it is noticed that for Al and Cu powders, when the larger spheres of 20 mm are used for the impact tests instead of the 25  $\mu$ m particles, their experimental and calculated

 $V_{crit}$  are both seen to decrease [20, 21]. It indicates a negative correlation between the critical velocity with particle size, which can be explained by the high cooling rates of smaller particles during impact to hinder the occurrence of shear instabilities and thus increase  $V_{crit}$ ; or the smaller particles with higher surface to volume ratios usually contains higher impurity levels to affect bonding [20]. Therefore, different empirical factors  $F_1$  and  $F_2$  in Schmidt's equation are used for calculations to consider the size effect [20].



Figure 2.6: Comparison of calculated versus experimental critical velocities for different materials and particle sizes [20].

## 2.1.3.2 Deposition efficiency (DE)

Deposition efficiency (DE) is defined as the weight change of a substrate ( $\Delta ms$ ) over the total weight of as-sprayed particles ( $M_p$ ) [6]:

$$DE = \frac{\Delta ms}{M_p} \times 100\%$$
 (2.3)

As illustrated in Figure 2.7, during cold spray, the particle deposition starts to occur only when the velocity reaches the critical value. The deposition efficiency is reported to rapidly increase to 50–70% as the particle velocity exceeds the critical value, after which DE reaches a peak and starts to decrease due to erosion [6].

As deposition efficiency is a function of the particle impact velocity, therefore, those factors affecting particle velocity will also affect DE, such as powder morphology and particle size [6]. In addition, the substrate temperature as well as the substrate surface conditions like roughness could also affect DE [6].



Figure 2.7: Effect of particle velocity on deposition efficiency [22].

Deposition efficiency is rather difficult to predict since it is the complex interplay of two distinct and highly dynamic processes: (1) formation of the breeding layers; and (2) continuous coating build-up. In the case of very similar deformability between the particle and substrate, Meng et al. [23] employed FEA simulations to introduce a rate parameter  $R_{EQ}$  to calculate DE, which was calculated as the steady-state rate of squared average equivalent plastic strain (**PEEQ**<sup>2</sup>) over time during impact evolution process. An excellent correlation between the rate parameter  $R_{EQ}$  and experimental coating DE was obtained [23].

Individual particle impact tests are commonly used to investigate the deposition behaviors of impacted powders. As an indication of DE, the bond ratio (BR), which is defined as the ratio of the number of bonded particles to the total impinged particles (deposits+craters) in a unit impact area [24]. Fukumoto et al. [25] proposed a modified approach to calculate the bond ratio as the ratio of the number of particles with metal jets to the total particles deposited over the substrate in the measured area. The obtained results of the bond ratios were reported to show a good agreement with the measured coating DE [25].

Wu et al. [24] considered the deposition of particles as a competition between the adhesion and rebound energies. Using the equations shown in Table 2.2, curves of adhesion energy minus rebound energy were plotted and compared with the measured bond ratios as a function of particle velocity [24]. As shown in Figure 2.8, both curves corresponded well and peaked at the same velocity, indicating the deposition of the impacted particles was well modeled by "A–R" [24]. These equations provided a theoretical approach to explain and predict the deposition behaviors of different metal powders on various substrates [24]. However, this model fails to consider the erosion phenomenon and cannot explain the plateau state of DE after reaching the maximum DE velocity in coating deposition process.

 Table 2.2: Mathematical equations to calculate rebound energy (R) and adhesion energy

 (A) [26-28].

Rebound energy (R) [26, 27]	$R = \frac{1}{2} e_{\rm r} m_{\rm p} v_{\rm p}^2, \qquad (2.4)$ $e_{\rm r} = 11.47 \left(\frac{\bar{\sigma}_{\rm Y}}{E^*}\right) \left(\frac{\rho_{\rm p} v_{\rm p}^2}{\bar{\sigma}_{\rm Y}}\right)^{-\frac{1}{4}}, \qquad (2.5)$
Adhesion energy (A) [28]	$a\% = 1 - \exp\left\{-vt_{c} \exp\left[\frac{-E_{a}}{kT_{c} + (1 - e_{r})m_{a}v_{p}^{2}/2}\right]\right\}, (2.6)$ $A = a\%A_{max}  (2.7)$ $A_{max} = S_{c}N_{a}E_{1}  (2.8)$

Table 2.3: Nomenclature of equations to calculate rebound energy (R) and adhesionenergy (A) [24].

m <sub>p</sub>	Mass of particle
Vp	Velocity of particle
$\bar{\sigma}_{\rm Y}$	Effective yield stress during impact
E*	Conventional elastic modulus of particle and substrate
ρ	Density of particle
er	Recoil coefficient
a%	Fraction of bonded atoms per unit interface
A <sub>max</sub>	Maximum adhesion energy of particle to substrate
t <sub>c</sub>	Contact time

Craters



8-8

0

-1 4

200

400

600

Particle velocity (m/sec)

800

1000

Figure 2.8: (a) SEM image showing the bonds and craters of individual particle impact tests; (b) comparison of the bond ratios to "adhesion energy-rebound energy" [24].

# 2.1.3.3 Porosity

(a)

Inadequate particle conformal deformation results in the presence of porosity in the coatings, as illustrated in Figure 2.9 [18]. Porosity is usually measured as the area fraction of pores over the total area of the coating cross-sections, using image analysis software [19]. Coatings with lower porosity levels can exhibit higher hardness, better corrosion resistance and better electrical as well as thermal properties [29].

20 10

1200



Figure 2.9: Schematic of particle shape change during cold spray process [18].

Porosity of cold sprayed coatings varies from less than one to several tens of percents depending on the types of sprayed materials and spray conditions [14]. For instance, cold sprayed Cu coatings are highly dense with less than 1% porosity level, while the porosity of Ti coatings processed with nitrogen can reach as high as 20% [19, 30]. The reason could be the low yield strength and face-centered cubic (FCC) structure of Cu, which facilitate particle plastic deformation and thus create a large particle flattening [31]. The effect of cold spray conditions is simply that increasing velocity decreases porosity by increasing plastic deformation. Thus, for a given pressure and temperature, if helium is used instead of nitrogen to fabricate Ti coatings, the lower molecular weight gas can provide faster acceleration of particles, thus larger particle deformation can be obtained and it is reported the porosity could be reduced to 0.5% [32]. In addition, a higher gas temperature could soften the particles and hence reduce the porosity by decreasing the particle strength [32, 33].

## 2.1.3.4 Mechanical properties

#### 2.1.3.4.1 Hardness

During cold spray, particles undergo intense deformation and are severely work hardened, therefore the as-sprayed coatings possess higher hardness than their corresponding bulk hardness [34, 35]. Increasing hardness can be obtained by increasing impact velocities [9]. Annealing the as-sprayed coatings can remove dislocations by recovery and recrystallization and thus lead to the reduction in coating hardness [36]. The effects of annealing on cold worked materials are shown in Figure 2.10 [9]. Note that the ductility keeps increasing at temperatures at which the hardness is at a steady state. Thus, ductility is not necessarily to be due to softening, but may be due to "sintering" of the particle/particle interfaces.



Figure 2.10: Effects of annealing temperature on cold-worked structure and properties

[9].

#### 2.1.3.4.2 Bond strength

Bond strength reflects the coating property to resist separation within each layer (cohesive strength) or from the base material (adhesive strength) [37]. Although not comparable with the bulk materials or thermal sprayed coatings, cold sprayed metallic coatings can still possess acceptable adherence to the metallic substrate due to various bonding mechanisms [18]. For instance, the bond strength of Cu coating on Al substrate is reported to be around 60 MPa [38]. Methods such as increasing the propellant gas pressure, particle and substrate preheating levels can all raise the bond strength of cold sprayed coatings [4]. Moreover, adhesion can be affected by the substrate surface conditions, e.g. the substrate roughness [39]. In addition, adhesion of coating is reported to be stronger on soft substrate materials with low melting temperature than hard substrate due to the elevated degree of metallurgical bonding and embedding phenomenon [40]. Adhesion between metals and ceramics or polymer are generally poor because there is only mechanical interlocking between particle and substrate [41].

#### 2.2 Cold spray of mixed powders

#### 2.2.1 Advantages of using mixed powders

There are several advantages that might occur of using mixed powders for cold spray. Firstly, using mixed powders is a straightforward method to produce novel composite coatings with improved or multifunctional properties [42]. Moreover, appropriate powder blends can expand the range of sprayable materials and enable the mixed powders to exhibit better cold sprayability than their each component [42]. Furthermore, the insights gained from exploring the distinct deformation behaviors of the mixed powders might help to understand the bonding mechanism in cold spray, by which the finite element models can be used to validate [42].

#### 2.2.2 Methods of mixing powders

Using a preliminarily prepared powder mixture is a simple and low cost approach to deposit composite coatings [1]. However, this approach has several intrinsic drawbacks. The most

outstanding issue is that this is a batch process [43]. Moreover, the distinct deposition behaviors of individual powder component resulting from their difference in physical properties such as density and deformability might lead to the composition deviations of the deposits from the starting powders [4]. Hence, a compromise must be made for each powder component when choosing the process parameters, for instance, the appropriate preheating levels must be selected to suit each powders provided that they have distinct melting temperatures, therefore optimum process parameters are often difficult to reach [43].

Cold spray systems can be equipped with dual/multiple powder feeders, thus each component powder can be fed at different rates to mix before the nozzle for the subsequent deposition. This realizes the convenience of easily changing coating composition by modifying the feed rates of each powder hopper.

Another type of powder dual feeding is applied with the low pressure cold spray system [43]. It permits the separate injection of powders from both axial and radial locations into the nozzle [43]. As the temperature is differently distributed in the nozzle (seen in Figure 2.1(b)), therefore, the powders can be fed into the nozzle and be deposited under their most appropriate spray conditions [43].

#### 2.2.3 The effects of mixing powders on cold sprayability

# 2.2.3.1 Deposition efficiency (DE)

For the cold spray of mixed powders, it is reasonable to expect that an increasing addition of poor DE powder component into the good DE matrix powder would decrease DE of the composite powder since the occurrence probability of impact between the poor DE powder components is higher. Typical examples can be found for spraying powder mixtures such as 316L/Co-Cr and Cu/CNTs [44, 45]. However, it is also found in some cases, the decrease of DE is not that obvious with the addition of poor DE powder component in the mixtures [46]. Luo et al. [46] investigated the DE of Ti6Al4V and Ti particles to separately mix with large shot peening stainless steel particles. It was found that as the content of shot peening particles increases from 0 to 70 vol.%, although almost no shot peening particles could be

deposited in the coatings, only a slight decline in DE of both powder mixtures were measured (12% for Ti, 14% for Ti6Al4V) [46].

Cold spray of metal/ceramic powder mixtures has been commonly applied to fabricate composite coatings and can improve the cold sprayability of the component powders [47-52]. For instance, it is known that the hard Al<sub>2</sub>O<sub>3</sub> powder alone cannot deposit a coating under experimental conditions, but Irissou et al. [47] have discovered that small addition of Al<sub>2</sub>O<sub>3</sub> into the primary Al powder can dramatically stimulate the DE of the mixture. The optimum DE was found at a Al<sub>2</sub>O<sub>3</sub> content of about 30wt. %, and after which the DE started to decrease [47]. It was explained that the brittle Al<sub>2</sub>O<sub>3</sub> particles probably play a role of peening and roughening of the coating top layers, therefore, facilitating the deposition by promoting mechanical interlocking [47]. Some other examples of metal/ceramic combinations are Cu+Al<sub>2</sub>O<sub>3</sub> [48], 316L+Al<sub>2</sub>O<sub>3</sub> [49] and Ni-20Cr+Al<sub>2</sub>O<sub>3</sub> [52].

Besides adding a ceramic component, Yue et al. [42] found that mixing metal powders can also contribute to a better DE. Three powders were used in his study: P1: spherical shape, 25 µm size with hardness 148 HV; P2: irregular shape, 30 µm size with hardness 138 HV; P3: spherical shape, 45 µm size with hardness 124 HV [42]. Two binary mixtures were made by adding 20 wt.% of P1 or P2 to P1 and the DE of pure as well as mixed powders were studied [42]. Yue et al. [42] considered the predicted DE of mixed powders as the weighted average of the DE of each powder component, and it was found both the mixtures of (P1+P2) and (P1+P3) have exhibited significant DE improvements compared with their predicted values. Since there is an influence of particle size and morphology on the impact velocity in cold spray, it is believed in the binary mixtures the smaller particles being the faster ones may exert an effect on the slower and larger particles and thus affect the DE [42].

#### 2.2.3.2 Porosity

Generally speaking, coatings fabricated from smaller powders would exhibit lower porosity level as they are initially denser packed and can also obtain higher impact velocity in the gas stream for deposition [53]. However, using fine powders in cold spray could have several issues such as the unstable powder flow and nozzle fouling, not to mention they are significantly more expensive to manufacture [53].

Spencer et al. [53] investigated the porosity levels of cold sprayed 316L coatings produced from dual mixtures of powders with three different average sizes of 5  $\mu$ m, 10  $\mu$ m and 22  $\mu$ m. Results indicated that as compared to the coatings from larger powders, using the mixtures with smaller size particles for cold spray can lead to improved coating density, and the coating fabricated by powder mixture of 5  $\mu$ m and 10  $\mu$ m was highly dense with a porosity level of less than 1 vol.% [53].

Another practice to reduce coating porosity is to incorporate heavy and large particles in the initial powder mixture. Those particles with high kinetic energy behave as "micro-hammers" during deposition to in-situ tamp the previously deposited layers, therefore, the coatings are densified to exhibit low levels of porosity [4]. Typical examples incorporating tamping effect are the addition of Al<sub>2</sub>O<sub>3</sub> in mixture with soft metals like Al or Cu [47, 48], and Ti-6Al-4V in mixture with pure Ti [42, 46].

#### 2.2.3.4 Mechanical properties

#### 2.2.3.4.1 Hardness

The coating microhardness is the combined result of high particle deformation upon impact and its related work hardening [4]. Coatings fabricated from larger particles are harder than from smaller particles due to the strong peening effect exerted by the higher impact energy of those larger particles [47]. For cold sprayed composite coatings, the hardness increment of each component from their feedstock states are often different, depending on their degree of plastic deformation [4]. A typical example is the reinforcing effect of hard particles in the powder mixture [4]. The intense tamping effect of the hard particle additions such like Al<sub>2</sub>O<sub>3</sub> in the Al-Al<sub>2</sub>O<sub>3</sub> mixture can enable the forced deformation of soft Al particles, thus leading to the higher coating hardness [47].

#### 2.2.3.4.2 Bond strength

Irissou et al. [47] have reported an increased adhesive strength of the coatings with increasing ceramic particle addition, despite the poor cohesion of ceramic-metal bond. This was explained by rebounded ceramic particles erode and create micro-asperities to the previously deposit layers, thus favoring the mechanical anchorage of the incoming particles [47].

# **Chapter 3 Materials and Methods**

This aim of this thesis is to investigate the powder feedstock characteristics on the cold sprayability of 316L/Fe mixed powders. This research was initiated by observations of the DE characteristics of mixed powders 316L and Fe powders by Barua [5], which as reported in the introduction section, could not be easily explained. One of the issues that was presented in his work was reproducibility of the spray conditions, particularly with regard to feed rate. Therefore, a new deposition process was carried out using a PLASMA GIKEN PCS-800 cold spray system, which could reduce nozzle blockage problems. As well, a powder dual feeding was used to provide a comparison with the premixed powders. The as-received and as-deposited new 316L/Fe coatings were characterized to determine the influence of feedstock characteristics and powder composition on cold sprayability of the mixtures. Previous approaches to analyse the cold sprayability of mixed powders were based on using the cold spray metrics of single component spray experiments and determining the behavior of the mixture by a simple law of averages. Since this proved ineffective, it was thought that data were required that characterized behavior of mixed powders. Thus, individual particle impact tests generated by very low feed rate spraying of single component powders on single component or mixed 316L/Fe substrates were performed to help understand the impact behaviors.

#### 3.1 Materials

The 316L stainless steel and "commercial purity" Fe feedstock powders used in this study are all commercially available. As the powders used by Barua were unavailable, so new powder batches were obtained. The 316L powder was purchased from Sandvik Osprey Limited (Neath Port Talbot, UK), while the Fe powder was provided by Quebec Metal Powders Limited (Sorel-Tracy, QC, Canada). The chemical compositions of the powders were validated using inductively coupled plasma optical emission spectroscopy (ICP-OES). The volume-weighted powder size distributions were measured using a laser diffraction particle size distribution analyzer LA-920 HORIBA (Horiba Ltd., Tokyo, Japan).

# **3.2 Cold Spray Process**

All cold spray deposition was carried out using the cold spray facilities in the McGill-NRC cold spray facility at NRC (Boucherville, QC, Canada). The average in-flight velocity of particles was measured by a time-of-flight particle diagnostic system DPV-2000 (Tecnar Automation Ltd., St. Bruno, QC, Canada).

# 3.2.1 Cold spray deposition through powder dual feeding

The coating deposition was performed using the PLASMA GIKEN PCS-800 cold spray system (Plasma Giken Company Ltd., Tokyo, Japan) with a PNFC2-010-30S carbide nozzle and dual powder feeder.

Prior to the spray process, the 316L and Fe powders were loaded into separate powder hoppers. The two powders were fed through separate powder lines that joined before entering the gun so the powders were mixed. Then the powder mixture was axially injected into high pressure region of the gun for subsequent deposition of composite coatings. By setting the feed rate of each powder hopper, the powder mixing compositions can be easily varied for each spray process. A schematic diagram of a Plasma Giken cold spray system with powder dual feeding is shown in Figure 3.1 [54].



Figure 3.1: Schematic diagram of a Plasma Giken cold spray system with powder dual feeding [54].

Calibration procedures were performed before the spray process to convert the feed rate of each powder to the corresponding rotary speed (RPM) of each powder feeder and the correlations are shown in Figure 3.2. It is seen that in general the feed rate of each powder increases linearly with the rotary speed of powder hopper, and the 316L powder is much easier to feed compared to Fe.



Figure 3.2: Correlations between the feed rate of each powder with rotary speed (RPM) of each powder feeder.

In order to establish comparisons with Barua's experiments, all the spray conditions (except for feed rate) were the same. Besides the five compositions used in his PhD thesis, two more samples with 10wt%Fe and 90wt%Fe compositions were also sprayed to further explore the mixing effect with smaller powder additions. The substrates used were mild steel plates with dimensions of 7.62 mm×7.62 mm×0.64 mm. Prior to coating deposition, a sandblast procedure was performed with 24 grit alumina to roughen the substrate surface and promote coating adhesion. The detailed spray conditions are shown in Table 3.1. It should be noticed that notations of powder samples such as 10wt%Fe simply indicate the designed powder mixing compositions from the calibrated correlations. As seen in Figure 3.3, feedings of rotary powder feeders were sometimes not stable and the actual feed rate might differ from the calibrated values. Therefore, deviations are to expect between the actual composite compositions and the designed ones. In fact, Figure 3.3 suggests that there is a time required for the feeder to reach the relative steady state.

Table 3.1: Cold spray conditions used to produce 316L/Fe coatings.

Samples	Gun speed	Propellant	Gas temperature	Gas pressure	No. of	Rotary (RF	y speed PM)	Standoff distance
	(mm/s)	gas	(°C)	(MPa)	Passes	316L	Fe	(mm)
316L	300	$N_2$	700	4	12	0.6	0	80
10wt%Fe	300	$N_2$	700	4	12	0.5	0.1	80
20wt%Fe	300	$N_2$	700	4	12	0.5	0.2	80
50wt%Fe	300	$N_2$	700	4	12	0.2	0.6	80
80wt%Fe	300	$N_2$	700	4	12	0.1	1	80
90wt%Fe	300	N <sub>2</sub>	700	4	12	0.08	1.2	80
Fe	300	$N_2$	700	4	12	0	1.2	80



Figure 3.3: Correlation of the average feed rate as a function of spray time (316L powder, RP=0.6).

# 3.2.2 Individual particle impact tests

To investigate the deposition behaviors of single particles on a single component or mixed "substrate", individual particle impact tests were performed. Coatings of single component 316L and Fe, and a mixed 50-50 316L/Fe, with the thickness of around 1 mm were generated by cold spray conditions as described above. These coatings were polished through standard metallographic preparation procedures in order to be used as the
substrates for the impact tests. Six different particle on substrate impact combinations (316L on 316L, 316L on Fe, 316L on 50Fe; Fe on 316L, Fe on Fe, Fe on 50Fe) were carried out. The detailed cold spray conditions, shown in Table 3.2, reveal that the only differences from those conditions of Table 3.1 are the much higher gun traverse speed and much lower feed rates, designed to generate "single splats".

Samples	Gun speed	Propellant gas	Gas temperature (°C)	Gas pressure (MPa)	No. of Passes	Rotary speed (RPM)		Standoff distance
	(mm/s)					316L	Fe	(mm)
316L on 316L	1000	$N_2$	700	4	1	0.2	0	80
316L on Fe	1000	$N_2$	700	4	1	0.2	0	80
316L on 50Fe	1000	$N_2$	700	4	1	0.2	0	80
Fe on 316L	1000	$N_2$	700	4	1	0	0.6	80
Fe on Fe	1000	$N_2$	700	4	1	0	0.6	80
Fe on 50Fe	1000	$N_2$	700	4	1	0	0.6	80

Table 3.2: Cold spray conditions used to perform single splat impact tests.

## 3.3 Metallographic Preparation and Microstructural Characterization

#### **3.3.1 Metallographic preparation**

To investigate the powder microstructure and microhardness, a small amount of powder was cold mounted in an epoxy resin and ground using silicon-carbide paper from 600, 800 and 1200 grit, and then polished using 3  $\mu$ m and 1  $\mu$ m colloidal silica suspension through standard metallographic preparation procedures.

To investigate the coating microstructure and microhardness, the coatings were crosssectioned transversely to the spray direction with a coolant-assisted diamond wheel cutter. Samples were hot mounted in Bakelite and ground and metallographically prepared as above, except the three extra SiC grits used (240, 320 and 400 grit) prior to polishing.

Both powders and coatings were etched to reveal the interparticle and interphase boundaries. 316L stainless steel samples were electrolytically etched using 10% oxalic acid for 28s, while the commercial purity iron samples were immersed into Viella's solution (5 mL HCl, 2 g picric acid and 100 mL alcohol) for 7s to reveal the boundaries.

#### **3.3.2 Light optical microscopy (LOM)**

Images of both powders and coatings were examined for microstructural observations using a light optical microscope (LOM) equipped with Clemex Vision Professional 5.0 software (Clemex Technologies Inc., Longueuil, QC, Canada). Porosity was measured by analyzing optical images of the coating central regions using ImageJ 1.48v software (NIH, Bethesda, MD, USA). A minimum of 10 images were taken and the average value was calculated to estimate the level of coating porosity.

Coating flattening ratio is a measure of the degree of particle deformation in the coatings and is described in Equation 3.1 as the width over height of the deformed particle. As shown in Figure 3.4, optical images of the coating cross-sections at 200X magnification were used to measure the width and height of the single particle in the cold sprayed 316L/Fe coatings. For each powder component in the coatings, more than 100 particles in a single image were recorded and the average values were calculated.

Flattening ratio = FR = 
$$\frac{w}{h}$$
 (3.1)



Figure 3.4: Optical image of the as-polished cross-section of the 316L/Fe coating.

Surface roughness was measured through the optical images of as-polished coating top surface cross-sections. Images at 500X magnification were used and the image width of around 0.21mm was considered as the sampling length (lr) for roughness measurements in order to correlate with the particle size and to avoid the influence of waviness. These images, which illustrated the representative surface profiles, were analyzed for the 2D arithmetic roughness (Ra). Using image analysis software, the lowest valley and highest peak were determined and the distance between them were defined as the sampling height h. Then a mean reference line at the height of h/2 was determined and the distance between surface profiles to the reference line were calculated, as shown in Figure 3.5 [55]. More than 100 lines were drawn along the sampling length for each image and the method to calculate 2D arithmetic roughness (Ra) was described in Equation 3.2.



Figure 3.5: Schematic diagram of the method to measure 2D surface arithmetic roughness (Ra) [55].

$$R_a = \frac{1}{n} \sum_{i=1}^n h_i, \, n > 100 \qquad (3.2)$$

#### 3.3.3 X-ray diffraction (XRD)

XRD phase identification of both powders and coatings were performed with a Bruker D8 Discover X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany). Scans were performed at a voltage and current of 40 kV and 40 mA with 0.02  $^{0}$ /sec scan rate. The x-ray source used was Co K $\alpha$ . Quantitative phase compositions of both powders and coatings were calculated by means of Rietveld refinement analysis with a TOPAS software (Bruker AXS GmbH, Karlsruhe, Germany).

#### **3.3.4 Scanning electron microscopy (SEM)**

A tungsten filament source scanning electron microscope Hitachi SU3500 (Hitachi High-Technologies Co., Tokyo, Japan) was used to characterize the morphologies of the feedstock powders and as-sprayed coatings. The SEM was equipped with X-ray energy dispersive spectrometer (SEM/EDS), which was used to investigate the elemental line profile at particle-substrate or particle-particle interface regions. The metallographically prepared powder cross-sections were characterized by electron backscatter diffraction (EBSD) for phase mapping. The accelerating voltage chosen was

20 kV and the step size was 0.1  $\mu$ m. For EBSD characterization, the powder samples were additionally polished on a vibratory polisher using 0.05  $\mu$ m colloidal silica for 4 hours to remove the deformed surface layers.

#### 3.4 Mechanical Characterization

#### 3.4.1 Microindentation

Microhardness measurements were performed on the mounted and as-polished powder and coating cross-sections using a Clark CM-100AT Microhardness Tester (Sun-Tec Corp., Novi, MI, USA) with a Vickers diamond indenter. For the powders, microindentations were conducted for a penetration time of 15 s under 10 g load, while 50 g load was used to measure the coating microhardness. For each specimen, a minimum of 15 indentations were performed and the average value as well as the standard deviation were reported.

#### 3.4.3 Bond strength

The adhesive/cohesive strength of cold sprayed 316L/Fe coatings were investigated according to ASTM C633-01 standard [56]. Due to the small coating areas, relatively small test coupons with diameters of 1 mm and 2 mm were fabricated for experiments. The surfaces of both the samples and aluminium cylinder couplings were roughened with a file to enhance the interface adhesion before they were joined together with HTK Ultrabond 100 (HTK Hamburg GmbH, Hamburg-Sasel, Germany) epoxy glue. To ensure proper adhesion, the joined coupons were heated in air at 190 °C for 35 mins under a load of 100 N for curing purpose. The maximum adhesion strength of epoxy obtained was 68.54 MPa. The samples were then cooled down in the air to room temperature and loaded in a computer controlled servo-hydraulic materials testing system (MTS) (MTS Systems Corp., Eden Prairie, MN, USA) for tensile pull-off tests at a constant strain rate of 1 mm/min. Images of the test coupons joined with aluminium screw couplings and the set-up of pull-off experiments are shown in Figure 3.6.



Figure 3.6: (a) test coupons joined with aluminium screw couplings (b) set-up of pull-off experiments.

# 3.5 Heat treatment

To investigate the existence of martensite, powders were heat treated in a Type F21100 tube furnace (Barnstead/Thermolyne Corp., Iowa, USA) with argon atmosphere. The powders were wrapped in steel sheets for oxidation protection. The heat treatment was carried out at 900°C for the hold time of 30 mins and 1 h, then samples were air cooled to room temperature.

# Chapter 4 Characterization of Feedstock and Coatings Fabricated Through Spraying Preblended 316L/Fe Powder Mixtures

#### 4.1 Introduction

This part of the thesis is an in-depth study of the coatings of mixed 316L and Fe powders in a previous PhD thesis by Barua [5] as discussed in the introduction section. As reported, both the as-received 316L and Fe powders were found to have potential existence of martensite through metallographic or XRD observations [5]. As well, since he used preblended powder mixtures to fabricate mixed coatings, during the powder rolling mix and coating deposition processes, the austenitic 316L powder was suspected to undergo a strain induced transformation to form martensite according to the XRD quantitative analysis [5]. Martensite in the feedstock powders could affect DE in different manners. For instance, any quenched martensite formed during powder processing is a brittle phase and has little deformability, its presence in feedstock powders could hinder deposition and increase the critical velocities [57]. However, the formation of martensite during deposition may be beneficial to cold sprayability, since the transformation induced plasticity could increase the level of plastic deformation during spraying, and thus be equivalent to increasing velocity. Hence, the characterization techniques of etching, XRD, and EBSD were performed to detect the presence of martensite.

Optical microscopy of the coating microstructure was used to study the different deposition behaviors of different particle-substrate impact combinations (e.g., Fe on 316L and 316L on Fe) during mixed powders deposition. XRD analyses of coatings were performed to investigate the phase evolution during deposition process. Coating flattening ratios were calculated to investigate the different deformation behaviors of mixed powders. Coating surface roughness were recorded by means of the optical microscopy to study the influence of powder composition on coating surface conditions. Bond strength of the 316L/Fe coatings were measured and the bonding behaviors as well as fractography was conducted as additional cold sprayability indicators.

#### 4.2 Feedstock powders

The 316L and Fe powders used by Barua were both manufactured through gas atomization process. The measured chemical compositions of powders are shown in Table 4.1 [5].

Powders	Fe	Cr	Ni	Mo	Mn	Si	С
316L	68.71	16.36	10.90	2.33	1.41	0.28	0.014
Fe	99.29	0.07	0.11	0.02	0.37	0.14	0.032

Table 4.1: Chemical compositions of 316L and Fe powders (wt. %) [5].

The 316L powder has a microhardness of 226.4±31.66 HV<sub>0.01</sub>, while the Fe powder with relatively high carbon content (0.032% vs 0.014%) is slightly harder with a microhardness of 287.71±33.35 HV<sub>0.01</sub> [5]. As shown in Figure 4.1, the 316L powder has an average diameter of 43.74  $\mu$ m, while the Fe powder is much smaller with a size of 23.21  $\mu$ m [5]. Due to the negative correlation between particle size and in-flight velocity, the finer Fe powder can obtain a higher impact velocity than the coarser 316L powder for deposition [20]. It is also noted that Fe powder exhibits a wider particle size range, which is reported to cause heterogeneous powder feed flow and deteriorate deposition efficiency as well as coating density [58].



Figure 4.1: Particle size distributions of the 316L and Fe powders.

#### 4.3 Results

## 4.3.1 Characterization of feedstock powders

## 4.3.1.1 Morphology and microstructure

SEM images of the feedstock powders are shown in Figure 4.2 (a, d). It is seen that overall both the gas atomized 316L and Fe powder are spherical in shape. But the 316L powder seems to be rougher than Fe powder, with considerable ultrafine particles sticking to its surface. Optical images of the as-polished powder cross-sections are seen in Figure 4.2 (b, e). No obvious substructure can be seen. The etched cross-sectional optical images of both powders are shown in Figure 4.2 (c, f). Etching reveals the grain boundaries, both powders display the typical quenched microstructure with ultrafine crystal grains. No martensite phase with needle-like or lath-like structure is identified, indicating both 316L and Fe powders could exhibit the single-phase structure.



Figure 4.2: SEM micrographs (a, d), as-polished OM images (b, e), and as-etched OM images (c, f) of the as-received 316L (a, b, c) and Fe (d, e, f) powders.

EBSD image quality mapping of the as-received feedstock powders was performed. As seen in Figure 4.3 (a, b), powder regions with single colors indicate the 316L and Fe powders are both of single phase.



Figure 4.3: EBSD image quality (IQ) map of the as-received feedstock powders: (a) Fe (b) 316L.

## 4.3.1.2 Phase transformation during powder mixing

It is commonly reported that during ball milling process the austenitic 316L powder can undergo a strain induced martensitic transformation [59]. As well, the bcc-Fe powder is also as reported to form bct martensite structure after high energy ball milling [60]. Since the powder mixtures used were mixed by "rolling" (i.e. ball milling but without any balls) for 1 hour for deposition, it is possible that a martensitic transformation could occur, although the relatively low intensity of mixing powder would seem to make an FCC to BCT transformation unlikely.

In order to determine the effect of "rolling" on any transformations, the powders were subjected to "rolling" without mixing the two powders. The pure 316L and Fe powders were characterized for phases before and after the "rolling" step, as seen by the XRD patterns in Figure 4.4 (a, b). The ICDD pattern #00-065-4150 is found to match with peaks of 316L powder, which represents the FCC austenite phase. And the ICDD pattern #03-065-4899 matches with Fe powder, showing the typical BCC ferrite structure. For both the 316L and Fe powders, XRD patterns confirm they both present as single-phase structure. As well, the XRD patterns of both powders are found to be respectively identical before

and after mixing steps, indicating no phase changes have taken place during 1 hour rolling mix.



Figure 4.4: XRD patterns of powders before and after mixing: (a) 316L and (b) Fe.

Having shown that the rolling stage does not lead to any phase transformation, the next step was to examine the influence of rolling and mixing. Quantitative phase compositions of austenite and ferrite in each powder sample by Rietveld refinement are seen in Table 4.2. The results of powder mixture samples (20Fe, 50Fe and 80Fe) show that for the 20 and 50Fe specimens there is approximately a 10% decrease in austenite after mixing, but for the 80Fe this rises dramatically to 50%. It seems to indicate an occurrence of FCC to BCC phase transformation in the powder mixtures during rolling mix, which more specifically is the strain induced martensitic transformation in austenitic 316L powder. Moreover, it indicates that the effect increases with increasing Fe/316L contacts, somewhat analogous to Fe acting as the balls in "milling" 316L.

Table 4.2: Phase compositions in the as-mixed feedstock powders.

Powders	Austenite ( $\gamma$ )	Ferrite (a)
20wt% Fe	71.19%	28.81%
50wt% Fe	45.22%	54.78%
80wt% Fe	10.01%	89.99%

To confirm the existence of phase transformation, the as-mixed powder samples are heat treated to study evolutions of the austenite phase fraction ( $f_A$ ) as a function of heat treatment time. As suggested by Foroozmehr et al. [61], the heat treatment to completely retransform any martensite in 316L was carried out at 900°C for the hold time of 30 mins and 1 h, then samples were air cooled to room temperature. The quantitative phase composition of austenite are shown in Table 4.3. It can be seen that there is no significant effect of heat treatment, which indicates there is no martensite.

Table 4.3: Austenite phase fraction  $(f_A)$  as a function of heat treatment time.

Powders	f <sub>A</sub> before HT	f <sub>A</sub> : 30 mins HT	f <sub>A</sub> : 1h HT
20Fe	71.19%	75.15%	74.31%
50Fe	45.22%	40.20%	43.09%
80Fe	10.01%	9.85%	12.07%

Furthermore, EBSD image quality mapping of a 50-50 316L/Fe powder mixture sample was also performed. As seen in Figure 4.6, powder regions with single colors indicate the 316L and Fe powders are both of single phase. No martensite is identified in the FCC region which is the 316L powder. Hence, it confirms no phase transformation to occur during the 1 h powder rolling mixing process. The loss of austenite from powder XRD quantitative analysis might only be due to the errors during measurements, e.g., powder sampling variation.



Figure 4.6: EBSD image quality (IQ) map of a 50-50 316L/Fe powder mixture.

## 4.3.2 Characterization of coatings

## **4.3.2.1 Microstructure**

The optical images of as-polished coating cross-sections are shown in Figure 4.7. The dark regions in the coatings represent the Fe powder, the light regions are the 316L powder, and the black spots in the coatings indicate the porosity. It can be seen that both Fe and 316L powders are no longer spherical and are somewhat flattened and are definitely no longer spherical.

Chapter 4 – Characterization of feedstock and coatings fabricated through spraying preblended 316L/Fe powder mixtures



Figure 4.7: Optical images of coating cross-sections: (a) 316L, (b) 20wt%Fe, (c) 50wt%Fe, (d) 80wt%Fe and (e) Fe.

The higher magnification coating microstructure for 20Fe and 80Fe is shown in Figure 4.8. The images are oriented such that the impact direction is as indicated by the white arrows. Cracks, which indicate poor interparticle bonding or strong particle rebound trend, can be seen at the mixed particle interfaces as well as the non-mixed interfaces; the Fe/Fe interfaces appear to be more susceptible to cracks, which supports the observation that the DE of pure Fe is significantly inferior to that of 316L. For clarity, the mixed particle

interface cracks are indicated by the red arrows. It seems in both 20Fe and 80Fe coatings, the cracks of mixed particle interfaces would preferably locate at the interfaces between the top of Fe and bottom of 316L. Considering the particle impact direction is from top to bottom of the image, this implies that the impact of Fe on 316L leads to a better cold sprayability than 316L on Fe. This result will be discussed in the single particle impact section in Chapter 6.



Figure 4.8: Optical images of coating cross-sections at 500X magnification: (a) 20Fe and (b) 80Fe.

## 4.3.2.2 Phase transformation

XRD patterns of the feedstock powders along with their corresponding coatings are shown in Figure 4.9. For single component coatings, only the typical austenite or ferrite peaks are present before and after coating deposition, indicating no phase transformation during the process. 316L austenitic stainless steel is reported to undergo strain induced martensitic transformation during cold work [59, 62]. The stability of 316L powder under such intense deformation during the deposition process might be due to the relatively elevated temperatures at the deformation localized regions [62].



Figure 4.9: XRD patterns of feedstock powders and their corresponding coatings.

For the mixed coatings, XRD peaks corresponding to austenite and ferrite are present as expected. It is noted that peaks at high  $2\theta$  angles are always decreased in the coatings. This may be due to the preferred orientation during deformation or peak broadening [45]. In terms of any martensitic transformation, as for the mixed powders, quantitative analysis of the XRD results was performed.

Powders	Austenite (γ)	Ferrite (a)
316L	100%	0%
20wt% Fe	68.4%	31.6%
50wt% Fe	40.4%	59.6%
80wt% Fe	9.6%	93.8%
Fe	0 %	100%

Table 4.3: Phase compositions in the as-sprayed coatings.

Compared with powder phase composition in Table 4.1, no obvious change can be seen, showing no phase transformation during coating deposition process.

## 4.3.2.3 Coating flattening ratio

Flattening ratio (FR) is calculated as the width over height of a deformed particle and indicates the degree of particle deformation in the coatings [63]. Since the 316L and Fe powders differ significantly regarding the crystalline structure, particle size and velocity, distinct deformation behaviors of the two powders are to be expected in the coatings. The average FR of each powder is plotted in Figure 4.10.

For single component coatings, despite a lower particle impact velocity, 316L powder still exhibits a higher FR than Fe powder in the coatings (3 vs 2.4). The result is consistent with the DE values where 316L has almost double the DE of Fe, therefore it implies some positive correlation between FR and DE. The possible reasons for the difference in FR of 316L and Fe powders are similar to those for the DE, e.g., softer and easier plastic flow of 316L than Fe.

In the 20Fe coatings, the FR of Fe powder (3.3) is higher than that of the 316L powder (2.7). This is possibly due to the impact of large 316L powder with high kinetic energy, thus the small Fe powder is forced to deform more in the coatings. In the 80Fe mixed coatings, the FR of both powders decrease but 316L powder exhibits a larger degree of deformation than Fe powder (2.5 vs 2.2), which possibly results from the continuous tamping of high speed and relatively hard Fe powder in large amount. In the 50Fe mixed coatings, both powders displaying the same FR value of 2.8, due to a combination of the above-mentioned mechanisms.

For the cold spray deposition of single component coatings, it is often reported that coatings with larger FR can exhibit better DE [64]. However, this conclusion seems not applicable in the case of the mixed coatings. For instance, the 20Fe coating with high FR presents low level of DE (42%), while a high DE (66%) occurs at 80Fe where the FR of both powders are relatively small.

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Figure 4.10: Flattening ratios of 316L and Fe powders in the coatings.

#### 4.3.2.4 Porosity

The porosity of cold sprayed coatings are a result of the incomplete conformal deformation of the particles. As shown in Figure 4.11, the porosity levels of single component coatings are found to correlate with the FR values, but for the mixed coatings, there is a much better correlation with the difference in FR values. The coating of 20Fe has a larger FR difference (0.6) between the 316L and Fe powders, hence the dissimilar particle deformation creates more gaps between each powder and leads to the highest coating porosity of 4.5%. While in 80Fe coating the FR difference is smaller (0.3), therefore the porosity level of 2% is also lower than 20Fe. As well, in 50Fe coating as both powders have the maximum contact area with each other and their deformation levels are similar (same FR), thus the coating yields the lowest porosity.

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Figure 4.11: Average porosity levels of as-sprayed coatings.

#### 4.3.2.5 Microhardness

The average microhardness of as-sprayed mixed coatings are shown in Figure 4.12. After cold spray the feedstock powders are severely hardened, the hardness increment is mainly due to plastic deformation and its related strain hardening [4]. The as-received 316L powder has a lower microhardness compared to Fe powder (226  $HV_{0.01}$  vs 287  $HV_{0.01}$ ). However, in the coatings the deformed 316L particle exhibits a higher microhardness than Fe, even in the 20Fe coating where a larger degree of deformation (FR) of Fe than 316L has been identified. Thus, it implies a more dominant strain hardening exponent of the 316L powder leading to a high microhardness in the coatings. In the mixed coatings, microhardness of both powder component are measured and plotted, respectively. For the same powder materials in different mixed coatings, the microhardness increment is seen to mainly relate with the degree of deformation (FR). For instance, similar to FR, the microhardness decreases with a higher Fe content in the starting powders. Moreover, it is also noticed that the Fe powder in general exhibits a larger deviation of microhardness than 316L powder, which is possibly due to its wide particle size distribution.



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Figure 4.12: Average microhardness of as-sprayed coatings.

## 4.3.2.6 Coating roughness

Low magnification optical images of each coating surface are shown in Figure 4.13. The 316L coating is seen to yield a smooth coating surface. While along with a higher Fe content in the starting powders, the coating surface becomes rougher and large craters (2 mm) as well as small waviness are clearly visible in 80Fe and Fe coatings. These qualitative observations are further confirmed with the microroughness measurements.

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Figure 4.13: Low magnification optical images of coating surfaces: (a) 316L, (b) 20Fe, (c) 50Fe, (d) 80Fe, and (e) Fe.

Optical images of the coating top surface cross-sections were taken to measure the coating microroughness, as shown in Figure 4.14. Images at 500X magnification were used and the image width of around 0.21mm was considered as the sampling length (lr) for roughness measurements in order to correlate with the particle size of 23~43 µm and to eliminate the influence of waviness. The calculated arithmetical average microroughness (Ra) of each coating is tabulated in Table 4.4.



Figure 4.14: Optical images of the coating top surface cross-sections: (a) 316L, (b) 20Fe, (c) 50Fe, (d) 80Fe, and (e) Fe.

The coating microroughness Ra are found to correlate well with the observations from the coating top surfaces. The 316L single component coating with a smoother surface finish also exhibits a smaller microroughness value (Ra) than Fe coating (4.37 vs 6.96). Similarly, as the surface finish deteriorates with a higher Fe content in the coatings, the microroughness Ra also continues to increase and end ups with the highest value of 7.29 in 80Fe.

Coatings	Ra
316L	4.37
20Fe	4.86
50Fe	5.89
80Fe	7.29
Fe	6.96

Table 4.4: Arithmetic average roughness (Ra) of as-sprayed coatings.

This might be explained by Fe powder having a poor flow through the nozzle and thus deteriorates deposition and also the surface integrity; or the Fe powder with relatively weak cohesion is easy to debond by high pressure gas plume to leave craters to the surface. Thus increasing Fe increases roughness. However, there is an exception with the 80Fe specimen which exhibits the highest roughness, indicating that a small amount of 316L increases roughness. At present, this phenomenon cannot be explained.

## 4.3.2.7 Bond strength

Bond strength of the as-sprayed coatings are shown in Figure 4.15. The 316L coating is seen to exhibit epoxy failure, indicating a higher cohesive and adhesive strength of the coating than the epoxy strength of about 53 MPa. While with a higher Fe content in the starting powders, the fracture type switches to the cohesive failure and the coating bond strength exhibits a very wide range of cohesive strength values with minima between 2-10 MPa, although the maximum values decrease with increasing Fe from about 50 to 35 MPa.



Figure 4.15: Bond strength of the as-sprayed coatings.

The bonding behaviors of both the interface and coatings were studied to explain the bond strength results. The 316L coating interface regions were investigated by SEM as shown in Figure 4.15. The dark regions indicate the Al substrate, and the bright regions are the 316L particles. The 316L particles seldom deform and remain almost spherical, indicating a strong embedding phenomenon into soft Al substrate. Moreover, some transitional layers are found at the periphery of the 316L particle boundaries with the Al substrate. SEM/EDS line scan is performed at these regions for elements profile analysis.

As seen in Figure 4.16 (b) and (c), the EDS result shows an obvious gradient distribution of Al element at the transitional layers which is possibly due to Al interatomic diffusion, and the diffusion distance as measured is around 3  $\mu$ m. It implies strong metallurgical bonding has formed during coating deposition process. As well, the red arrow in Figure 4.16 (a) shows the Al "extrusion" between two embedded 316L particles, the presence of Al at interparticle region may act as a physical interlocking bond or possibly a solder thus promote adhesion between the adjacent particles [65].

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Figure 4.16: (a) SEM images of the 316L coating interface region. Light region-316L particles, dark region-Al substrate, (b) high magnification view of selected area, and (c) EDS line scan of selected area.

In the coatings, the etched microstructure of single component 316L and Fe coatings are shown in Figure 4.17. Etching reveals the particle boundaries (black regions) in the coatings and also the grain boundaries (grey regions) within the single particles.

Particles are not embedded to each other in the coatings but have deformed to create a selfinterlocking scheme. The coatings are relatively dense, but after etching the majority of the particle boundaries are clearly revealed. It indicates that in cold sprayed 316L and Fe coatings, particles are in general poorly bonded through mechanical interlocking. Note that there are still particle boundaries that appear to have transformed into grain boundaries, since they cannot be clearly etched, as revealed by the arrows. These regions are as reported to be strongly metallurgically bonded [18, 40]. Over the areas of Figure 4.17, percentage of interparticle boundaries that were transformed to metallurgically bonded interfaces was measured and calculated using image analysis software. The fraction for 316L coating is 26.7% while Fe coating has a lower value of 19.6%. The possible reason for the difference could be relatively thick oxide films on Fe particles preventing the formation of metallurgical bonding. In any case, the higher metallurgical bonding component in 316L coating could contribute to the higher cohesive strength compared with Fe coating.



Figure 4.17: Optical images of the as-etched coating cross-sections: (a) 316L coating and (b) Fe coating.

For the mixed coatings, as the 316L and Fe particles were difficult to etch at the same time, therefore, SEM characteristics of the coating pull-off fractures were studied as shown in Figure 4.18.

The majority of the fracture surfaces are seen to be rather smooth, indicating a brittle fracture which is simply through the physical detachment of the mechanically interlocked interface. However, dimples are identified for each coating fracture surface (outlined in red), where metallurgical bonds have formed and ductile fracture has occurred. The degree of metallurgical bonding in each coating is approximated by the area of dimple structures as outlined in red in Figure 4.18. It is seen that the area of dimple sites decrease with a higher Fe content in the starting powders. The observation correspond with the bond strength results, indicating the 316L powder is more prone to form metallurgical bonding during impact than Fe, and thus coatings with higher 316L content would yield the higher cohesive strength.

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Figure 4.18: SEM fractography of: (a) 20Fe, (b) 50Fe, (c) 80Fe, and (d) Fe.

## 4.4 Discussions

To explain the DE characteristics reported by Barua [5], the first approach is to determine the potential existence of martensite in powders and martensitic transformation during powder premixing or deposition processes. However, all the characterization results negate such an idea.

Cracks at particle/particle interfaces are an indication of the bonding behaviors of particle/particle interfaces. As seen in Figure 4.8, the bonds at 316L/Fe interfaces appear to be better than Fe/Fe interfaces bonds but worse than 316L/316L interfaces bonds. Therefore, addition of Fe to 316L will be unfavorable in terms of DE, since it is like adding "weak links" of 316L/Fe and Fe/Fe bonds to 316L/316L bonds. The DE prediction used by Barua [5] was based on a weighted average contribution of each single component powder, thus it didn't consider the influence of 316L/Fe interfaces on the DE of mixed powders. For the 20Fe coating, the high pancaking of Fe (highest FR) leads to relatively large 316L/Fe interface areas in 316L/316L interfaces which could contribute to the low

DE. While for the 80Fe coating, other factors need to be considered, e.g., tamping and surface roughness.

As the 316L/Fe powder mixtures used by Barua [5] have bimodal size distribution, this may have an influence on DE. Figure 4.19 shows a schematic diagram of depositing bimodal powder mixtures by cold spray [66]. The mixed powders having different velocities in the gas stream can form clusters prior to deposition [66]. Luo et al. [46] reported that the large core particles with high kinetic energy can tamp the small particles and facilitate the particle deposition. Hence, for the 80Fe coating, considering the easy deposition of Fe particles hitting 316L (fewer cracks in Figure 4.8), it is possible that high DE can be obtained by the continuous tamping of large 316L particles to the small Fe. As well, a similar phenomenon was observed by Yue et al. [42] when spraying bimodal tantalum powders that addition of 20% large particles to the small particles can significantly increase the DE by about 25%.



Figure 4.19: Schematic of cold spraying bimodal powder mixtures [66].

Regarding surface roughness, it has been reported that for single component coatings, a better coating surface finish could indicate a better DE [31]. But in this mixed case, as shown in Table 4.4, with a higher Fe content, the DE and the coating surface roughness both continue to increase. Generally, a roughened substrate could facilitate the mechanical interlocking of incoming particles for the first a few particle layers and thus slightly improve DE [67]. Since the coating surface can be considered as the newly formed substrate, therefore, it is believed that a rougher coating surface (e.g. 80Fe) can also lead to a better DE, as such improvement can occur layer by layer during continuous deposition.

Examples can be found in spraying of Al-Al<sub>2</sub>O<sub>3</sub> powder mixtures [47]. Although the brittle ceramic is prone to bounce off upon impact, they leave micro-asperities to the coating surface which promote the mechanical interlocking of Al particles [47]. The DE as reported could be maximally improved by 25% with about 30 wt.% ceramic addition [47, 68]. In this case of spraying 316L/Fe mixed powders, variations of the coating surface roughness are a result of the packing of bimodal particles with different mixing ratios, thus the DE is affected.

## 4.5 Conclusions

- Both the as-received 316L and Fe feedstock powders are of single phase with no martensite. During rolling mixing and the cold spray deposition process, no martensitic transformation is observed in either the 316L or Fe powder.
- 2. The bonds at 316L/Fe interfaces appear to be better than Fe/Fe interfaces bonds but worse than 316L/316L interfaces bonds. Therefore, addition of Fe to 316L will be unfavorable in terms of DE. The high pancaking of Fe in 20Fe leads to relatively large 316L/Fe interfaces areas in 316L/316L interfaces which could contribute to the low DE.
- 3. The surface roughness of mixed 316L/Fe coatings increases with increasing Fe content, which is believed to be beneficial for particle deposition due to the enhancement of mechanical anchorage effect. The high surface roughness, as well as tamping of the large 316L particle, could result in the high DE of 80Fe.
- 4. The flattening ratio of each powder component in the mixed coatings depends on the incorporated amount of large 316L powder. More than 50% 316L powder in mixtures can considerably tamp the Fe powder as the 316L is larger and also works hardens faster, thus leading to a very large Fe FR.
- 5. The microhardness of the as-received Fe powder is higher than that of the 316L. However, the microhardness of the Fe in the coating is always lower than that of the 316L, almost certainly because the work hardening rate of the 316L is higher. The microhardness of each component in the coatings is directly related to the coating flattening ratio. A higher FR indicates a higher degree of work hardening and thus leads to higher coating microhardness.

- 6. The coating porosity is also directly related to the coating flattening ratio. For single component coatings, a larger FR could lead to a lower porosity level. For the mixed coatings, a similar FR (degree of deformation) of each powder component could result in a reduced porosity level.
- 7. All coatings exhibit a relatively high adhesive bond strength due to combined effect of embedding, Al diffusion, and "cold weld" of extruded Al. The cohesive bond strength of coatings exhibits a very wide range, but the maximum values decrease with a higher Fe content, probably because of increasing Fe/Fe interfaces which are the weakest interfaces in the mixture.
- The etching of coating cross-sections indicates that 316L powder is more likely to form metallurgical bonding than Fe particle during deposition. The fractions of metallurgically bonded interfaces in 316L/Fe coatings are between 19.6%~26.7%.

# **Chapter 5 Cold Spray Deposition of 316L/Fe Coatings Through Powder Dual Feeding**

#### **5.1 Introduction**

Nozzle clogging issues in the KINETIKS 4000 system were identified in the previous PhD thesis [5] which could affect the feed rate capability and thus affect the reproducibility of the process. Moreover, spraying preblended powders slows down the composition optimization. Therefore, an new cold spray process was carried out using a PLASMA GIKEN PCS-800 system, which is reported to reduce the nozzle blockage issue [5]. As well, the dual powder feeder which increases the rate of composition optimization was utilized.

As shown previously in Figure 3.1, with dual powder feeder, the 316L and Fe powder were fed through different powder lines and thus separate controls of their feed rates could be realized. The two powder lines joined before entering the gun and powders were mixed, after which the mixtures were axially injected into the cold spray gun for codeposition. Compared with powder preblending, dual powder feeding utilized a different powder mixing approach and thus could permit the convenient variation of powder mixing compositions for each spray process. In this work, apart from the 5 compositions used previously [5], two more samples with compositions of 10%Fe and 90%Fe were also fabricated to study the mixing effect of smaller powder additions. Similar characterization methods as in previous chapter were performed on both powders and coatings to investigate the evolution of microstructure and mechanical behaviors. New batches of 316L and Fe powders were sourced because the previous powder grades were unavailable. The cold sprayability of these new 316L/Fe powders were examined as a function of Fe mixing ratio and were also compared with those of the powders used previously [5], despite the difference in powder such as size and hardness.

#### 5.2 Results

## 5.2.1 Characterization of feedstock powders

#### 5.2.1.1 Chemical composition

The chemical compositions of feedstock powders are shown in Table 5.1. Compared with powders used previously [5], the new 316L powder indicates basically the same composition, but has slightly higher content of Cr, Ni and C elements. While the new Fe powder is much different, having a lower carbon content and no Mn.

Table 5.1: Chemical compositions of 316L and Fe powders (wt. %).

Powder	Fe	Cr	Ni	Mo	Mn	Si	Р	С	S
316L	67.005	17.3	12.1	2.4	0.57	0.58	0.02	0.02	0.005
	Powde	er l	Fe	Р	С	S	(	)	
	Fe	99	.908	0.001	0.005	0.00	06 0.	08	

#### **5.2.1.2 Microstructure**

SEM morphologies of the feedstock powders are shown in Figure 5.2 (a, d). The 316L powder is spherical in shape, while the Fe powder exhibits a mixture of both spherical and irregular shapes. Optical images of as-polished powder cross-sections indicate no obvious structure, as seen in Figure 5.2 (b, e). As well, the etched microstructure of both powders shown in Figure 5.2 (c, f) only reveal the presence of typical quenched microstructure with ultrafine crystal grains. Hence, it implies that both the 316L and Fe powders are single phase.



Figure 5.2: SEM micrographs (a, d), as-polished OM images (b, e), and as-etched OM images (c, f) of as-received 316L (a, b, c) and Fe (d, e, f) powders.

# 5.2.1.3 Particle size distribution

The average particle size of feedstock powders are plotted in Figure 5.3. The Fe powder has an average diameter of 29.04  $\mu$ m, while the 316L powder is smaller with the size of 22.22  $\mu$ m. Note that laser particle size analyzer records the longest dimension as the average size for irregularly shaped Fe powder.



Figure 5.3: Particle size distribution of 316L and Fe powders.

#### 5.2.1.4 Microhardness

Microhardness values of 316L and Fe powders are shown in Figure 5.4. The 316L powder has a higher microhardness of  $262.61\pm10.99$  HV<sub>0.01</sub> compared to  $141.28\pm16.85$  HV<sub>0.01</sub> for the Fe.



Figure 5.4: Average microhardness of feedstock powders.

#### 5.2.1.5 Phase identification

Figure 5.5 (a, b) are the XRD patterns obtained for the 316L and Fe powders. Again, the ICDD pattern #00-065-4150 is used to indicate the FCC austenite, while the ICDD pattern #03-065-4899 represents the BCC ferrite. Both FCC and BCC peaks are identified in the XRD pattern of 316L powder. Quantitative Rietveld analysis shows the fraction of BCC phase to be 10-15%, although its microstructure is not revealed in Figure 5.2 (b, c). According to the Schaeffler-Delong diagram, the 316L stainless steel with a composition such as the one given in this work could have around 10% ferrite in the as-solidified condition [69]. Moreover, it is well known that retained ferrite can be found after welding 316L type austenitic steels as welding ensures a sufficiently large cooling rate [70, 71]. Since the gas atomized 316L powder especially those smaller ones have gone through fast heat extraction during processing, thus the resulting large undercoolings are sufficient to

quench in metastable ferrite phase [72]. While the XRD pattern of new Fe powder shows the only presence of ferrite phase.



Figure 5.5 XRD patterns of feedstock powders: (a) 316L and (b) Fe.

#### 5.2.2 Characterization of process

#### 5.2.2.1 Particle impact velocity

The average particle velocities are plotted as a function of the designed Fe mixing ratio as illustrated in Figure 5.6. The Fe powder, despite a larger size, exhibits a higher average velocity of 600.48 m/s as compared with 583.35 m/s of the 316L powder. It is probably due to the irregular morphology of particles having larger drag force in the gas stream and thus obtaining higher velocity [48]. A relationship, y=0.1812x+584.01, was established to describe the correlation between average particle velocity and Fe mixing ratio. This linear correlation implies the mixing of powders exerts no effect on the velocity of each component at least before exit of the nozzle since the average velocity of powder mixtures is simply the weighted average of the velocity of each powder component.



Figure 5.6: Average particle velocities of each powder sample.

## 5.2.2.2 Deposition efficiency

The deposition efficiency of each powder sample is shown in Figure 5.7. The pure 316L powder has a slightly higher DE than the pure Fe. And for the mixed powders, the DE increases along with increasing Fe. However, a small addition of Fe to 316L, i.e. 10Fe, gives the lowest DE, and the 90Fe actually exhibits a DE that is higher than 316L.



Figure 5.7: Deposition efficiencies of each powder sample.
# 5.2.3 Characterization of coatings

# 5.2.3.1 Microstructure

The cross-sectional views of as-polished coatings are shown in Figure 5.8. The dark regions are the Fe powder, the light regions represent the 316L powder, and the black spots indicate the porosity. However, inhomogeneity issues have been identified in some of the mixed coatings such as 10Fe along the build-up direction (from bottom to top of the image), which is due to the unstable feed rate of each powder component with the dual feeder system.



Figure 5.8: Optical images of coating cross-sections: (a) 316L, (b) 10Fe, (c) 20Fe, (d) 50Fe, (e) 80Fe, (f) 90Fe, and (g) Fe.

### 5.2.3.2 Porosity

The average coating porosity levels are plotted in Figure 5.9. The 316L coating has a porosity level of 1.7%. While for the Fe and mixed coatings, the porosity levels all seem negligible (< 1%). Considering the Fe powder used in this work is much softer than the 316L, during deposition it probably forms a continuous network in the coatings to fill in the porosity. This result indicates that the porosity levels of cold sprayed coatings can be significantly reduced by spraying softer powder alone or in a mixture.



Figure 5.9: Average porosity levels of each coating.

# 5.2.3.3 Coating composition

The coating compositions are estimated by the area fraction of each powder in a unit area of coating cross-sections using imageJ software. The results are tabulated in Table 5.4. Notations of coating samples (e.g.10Fe) indicate the designed powder mixing ratios calculated based on the calibrated feed rates of each powder feeder. In general, the actual Fe composition in the coating increases along with a higher designed Fe mixing ratio. However, despite the calibrations prior to coating deposition, feed rate of each powder feeder is still not stable and can be influenced by factors such as powder refilling and runtime. Therefore, the actual compositions in the coatings often exhibit deviations, occasionally very large deviations, from the designed powder mixing ratios.

Coatings	Fe	316L
316L	0%	100%
10Fe	21.6%	78.4%
20Fe	28.3%	71.7%
50Fe	81.0%	19.0%
80Fe	89.4%	10.6%
90Fe	96.4%	3.6%
Fe	100%	0%

Table 5.4: Fractions of Fe and 316L powders in each coating.

# 5.2.3.4 Microhardness

The average coating microhardness is plotted as a function of Fe mixing ratio as shown in Figure 5.10. A general decrease of both coating microhardness of 316L and Fe components with increasing Fe is identified. The effect of Fe can be attributed to tamping of the relatively hard 316L powder. As a higher amount of soft Fe powder is incorporated in the starting mixtures, the less occurrence probability of the tamping of the hard 316L powder, hence the coating microhardness continues to decrease.



Figure 5.10: Average microhardness of each coating.

## 5.2.3.5 Phase identification

XRD patterns of the as-sprayed coatings are shown in Figure 5.11. The 316L stainless steel powder is reported above to exhibit both the FCC and BCC phases, but in the coatings only the typical FCC peaks are identified. The loss of BCC structure implies an BCC to FCC phase transformation which is induced by the high compressive strains during deposition [13]. It is reported that in 316L stainless steel powder, the metastable ferrite resulting from large undercoolings is in metastable state, when under strong pressure pulses, can undergo diffusionless transformation to form the more stable austenite [72]. For the Fe coating, same as for the Fe powder, only the typical ferrite peaks are presented in the XRD pattern, indicating its high stability. For the mixed coatings, qualitatively, it is reasonable to consider the strain induced ferrite to austenite transformation taking place since the kinetic impact energy for mixed powders deposition process is comparable to that for pure 316L.



Figure 5.11: XRD patterns of each as-sprayed coating.

# **5.2.3.6 Coating roughness**

The low magnification optical image of each coating surface is shown in Figure 5.12. The single component 316L coating has a smoother surface than Fe coating. For the mixed coatings, an increasing surface roughness and presence of large craters can be seen along

with a higher Fe content in the starting powders. Especially for 90Fe, it has the roughest surface, even rougher than the pure Fe.



Figure 5.12: Low magnification optical images of coating surfaces: (a) 316L, (b) 10Fe, (c) 20Fe, (d) 50Fe, (e) 80Fe, (f) 90Fe, and (g) Fe.

Optical images of the coating top surface cross-sections were taken to measure the coating microroughness, as shown in Figure 5.13. Similar as the previous chapter, images at 500X magnification were used and the image width of around 0.21mm was chosen as the sampling length (lr) for roughness measurements in order to relate with the particle size of  $22\sim29 \ \mu\text{m}$  and to eliminate the influence of waviness. The calculated arithmetical average roughness (Ra) of each coating are tabulated in Table 5.5.



Figure 5.13: Optical images of the coating top surface cross-sections: (a) 316L, (b) 10Fe, (c) 20Fe, (d) 50Fe, (e) 80Fe, (f) 90Fe, and (g) Fe.

The coating microroughness Ra are found to correlate well with the observations from the coating surfaces. For single component coatings, the 316L coating with a smoother surface

finish also exhibits a smaller microroughness value (Ra) than Fe coating (4.35 vs 6.33). For the mixed coatings, along with a higher Fe content, Ra continues to increase and ends up with the highest value in 90Fe.

Coatings	Ra
316L	4.35
10Fe	4.67
20Fe	5.70
50Fe	5.78
80Fe	6.12
90Fe	7.57
Fe	6.33

Table 5.5: Arithmetic average roughness (Ra) of each coating.

# 5.2.3.7 Bond strength

The bond strength of as-sprayed coatings are shown in Figure 5.18. The coatings all exhibit the adhesive failure, indicating a weaker bond strength of the interface with grit-blasted mild steel substrate than the coatings. The coating adhesive bond strength decreases along with a higher Fe mixing ratio, indicating that 316L powder generally exhibits a higher bond strength than Fe powder after deposition in the coatings.



Figure 5.18: Bond strength of each as-sprayed coating.

# 5.3 Discussions

This discussion is essentially a comparison with the previous work to understand the effect of powder changes on the mixed powders behaviors.

Compared with powders used by Barua [5], the new 316L powder is slightly harder, much smaller and with a similar spherical shape, while the Fe powder is much softer, slightly larger and has a different irregular morphology. As for the particle velocity, both new powders have lower velocity than powders used by Barua [5]. Therefore, as expected the DE of new powders are lower than the previous powders, expect for Fe, which instead has a higher DE as it is much softer and thus more beneficial for deposition than the previous Fe.

Despite the significant difference from the powders used by Barua [5], a similar trend of increasing Fe increases DE can still be seen for the mixed powders used in this work. As for the new batches of 316L and Fe powders, since they are comparable in density, size and velocity, the effect of tamping is not sufficient to result in such a significant change in DE with regards to Fe. Moreover, assuming the transformation induced plasticity of BCC to FCC in the 316L powder is beneficial for deposition, again it fails to explain that mixed coatings with relatively high DE (e.g. 80Fe and 90Fe) in turn have lower content of 316L.

It is noted that the coating surface roughness is also found to increase with increasing Fe in the mixed coatings, similar as the previous work. In general, irregularly shaped Fe particles in this work do not feed as easily as the spherical particles due to its large specific surface area and high surface friction coefficient, hence could lead to the poor surface conditions [4, 64]. Moreover, the irregular morphology of Fe particles could also create more micro-asperities to the coating surface. Therefore, since a rough surface could facilitate the particle deposition, it is believed that the increase of DE with increasing Fe is most likely to be due to the increase of coating roughness.

# **5.4 Conclusions**

- 1. During cold spray deposition, the metastable ferrite resulting from large undercooling in 316L powder undergoes a strain induced transformation to form the more stable austenite.
- The porosity level of 316L coating can be significantly reduced by incorporating the soft Fe powder for codeposition.
- The microhardness of 316L/Fe mixed coatings depend on the amount of relatively hard 316L powder. The strong tamping effect provided by large amount of 316L powder during deposition would contribute to high coating microhardness.
- 4. Despite the different morphology, microhardness and size of the powders used in this work and by Barua [5], increasing Fe increases both the DE and surface roughness of 316L/Fe coatings. And it is believed that the increase of coating roughness will promote mechanical interlocking of the incoming particles and is most likely to contribute to the elevated DE at high Fe content.
- 5. The coatings deposited onto mild steel substrate exhibit a relatively weak adhesive strength of the interface than coatings. The coating adhesive strength decreases along with a higher Fe mixing ratio, indicating the 316L powder can lead to a higher bond strength than Fe during impact deposition.

# **Chapter 6 Individual Particle Impact Tests**

# **6.1 Introduction**

Based on the discussions in Chapter 4, it is believed that difference in deposition behaviors of 316L on 316L, 316L on Fe, Fe on 316L and Fe on Fe could be a way to rationalize the DE as a function of Fe content, since the occurrence probability of each impact combination depends on composition. Therefore, individual particle impact tests to investigate the above impact combinations were generated by very low feed rate spraying of single component powders onto polished substrates. Besides the above combinations, 316L on 50Fe and Fe on 50Fe were also performed; the 50Fe substrate was produced subjected to the cold spray conditions for 50Fe coating and the optical metallography specimen preparation as described in Chapter 3. The bond ratio (BR) for each impact combination was calculated.

### 6.2 Results

#### **6.2.1 Impacts on single component substrates**

SEM images of the coating surface morphology after individual particle impact tests are shown in Figure 6.1. The Fe coatings have a stronger tendency to rebound the impacting powders since more craters than deposits are revealed compared with 316L coatings as seen in Figure 6.1 (a, b) or (c, d). As well, 316L powder with higher rebound trend exhibit fewer deposits than Fe powder during deposition, as seen in Figure 6.1 (a, c) or (b, d).



Figure 6.1: SEM morphology of the individual particle impact tests of: (a) 316L on 316L, (b) 316L on Fe, (c) Fe on 316L, and (d) Fe on Fe.

Higher magnification SEM images of the four combinations of individual particle impact tests are shown in Figure 6.2. Both powders are seen to be flattened after impact; the 316L powders in Figure 6.2 (a, b) exhibit the "hemisphere" shape while the Fe powder in Figure 6.2 (c, d) are more irregular. The 316L coatings in Figure 6.2 (a, c) have certain levels of porosity while the Fe coatings in Figure 6.2 (b, d) are much denser.

Comparing Figure 6.2 (a, c) with (b, d), it is confirmed that Fe substrate has a higher tendency to rebound the impacting powders. Particles deposited on the 316L coatings show the more intimate contact, while depositions on Fe coatings exhibit the peripheral regions detaching from the substrate. Moreover, comparing Figure 6.2 (b) with (d) in which powders are deposited on the same Fe coatings, it seems the 316L powder shows a stronger rebound tendency than the Fe powder.



Figure 6.2: SEM images of the individual particle impact tests of: (a) 316L on 316L, (b) 316L on Fe, (c) Fe on 316L, and (d) Fe on Fe.

# 6.2.2 Bond ratios (BR) of impacts on single component substrates

The bond ratio (BR), defined as the fraction of bonded particles (deposits) to the total incident particles (craters+deposits), was calculated from images such as Figure 6.1 [65]. It is noted that in Figure 6.1 (a) some ultrafine 316L deposits are identified on the 316L coating, such particles with negligible masses were not considered for BR calculations. The results of bond ratios (BR) are tabulated in Table 6.1. This quantitatively confirms the qualitative observations that Fe as the powder material is easier to deposit, while 316L as the coating material can better facilitate powder deposition. Also it implies that material type of powder or coating will play different roles on the particle deposition behaviors. This result will be discussed later in the discussion section.

Bond ratio	$\sum \frac{N_{bond}}{N_{bond} + N_{crater}}$
316L on 316L	35.6%
316L on Fe	7.8%
Fe on 316L	73.9%
Fe on Fe	23.4%

Table 6.1: Bond ratios (BR) of four combinations of individual particle impact tests.

# 6.2.3 Bond ratios (BR) of impacts on mixed substrates

The results of impacts on mixed substrates are shown in Figure 6.4.

Figure 6.4: SEM morphology of individual particle impact onto mixed coatings: (a) 316L on 50Fe and (b) Fe on 50Fe

The bond ratios (BR) were determined as described above and the results were compared to "predicted" values. The "predicted" BR on 50Fe were calculated as the weighted average of the BR of impacts onto each single component substrate using the coating composition shown in Table 5.4. The "predicted" BR of 316L on 50Fe was calculated as:  $35.6\% \times 0.19 + 7.8\% \times 0.81 = 13.1\%$ ; for Fe on 50Fe was:  $73.9\% \times 0.19 + 23.4\% \times 0.81 = 33.0\%$ . As indicated in Table 6.2, both the "predicted" and measured BR correspond well.

Bond ratios	Predicted	Measured
316L on 50Fe	13.1%	13.5%
Fe on 50Fe	33%	32%

Table 6.2: Comparisons of the "predicted" and measured BR onto 50Fe coatings.

### **6.3 Discussions**

#### 6.3.1 Rebound energy

To explain the different BR of each impact combination, as mentioned in the literature review section, an empirical equation is introduced to describe the rebound energy (also named as recoverable strain energy) of impacting particles in the kinetic spray process [24]:

$$R_e = \frac{1}{2} e_r m_p v_p^2 \quad (6.1)$$

And the recoil coefficient  $e_r$  is given as:

$$e_r = 11.47 (\frac{\overline{\sigma}_Y}{E^*}) (\frac{\rho_P v_P^2}{\overline{\sigma}_Y})^{-\frac{1}{4}} = 11.47 (\frac{\overline{\sigma}_Y^{\frac{5}{4}}}{E^*}) \rho_P^{-\frac{1}{4}} v_p^{-\frac{1}{2}}$$
(6.2)

Where  $\rho_p$ ,  $m_p$  and  $v_p$  are respectively, the density, particle weight, and velocity of impinging particles.  $e_r$  is the recoil coefficient.  $\overline{\sigma}_Y$  is the effective yield stress during impact, and  $E^*$  is the conventional elastic modulus of particle and substrate [24]. The strain-hardening, strain-rate sensitive, thermal-softening, and deformation localization are considered for the calculation of effective yield stress  $\overline{\sigma}_Y$ , which is provided from the Johnson-Cook plasticity model [24].

Table 6.3: Physical properties of 316L and Fe feedstock powders [73].

Powders	Hardness (GPa)	Elastic modulus (GPa)	Particle velocity (m/s)	Particle size (µm)	Density (g/cm <sup>3</sup> )
316L	2.57	193	583.35	23	8
Fe	1.38	200	600.48	29	7.86

The physical properties of the 316L and Fe powders tabulated in Table 6.3 were provided from experiments as well as from literature [73]. The most significant difference between the 316L and Fe powders is the hardness. For metals, usually a higher hardness implies a higher yield strength or tensile strength [74].

The rebound energy  $R_e$  stands for the rebound tendency of the impacting powder in the kinetic spray process [24]. According to equation 6.1 and 6.2, the rebound energy  $R_e$  is proportional to the recoil coefficient  $e_r$  and thus to the effective yield stress  $\overline{\sigma}_Y$  of the impacting powder. The effective yield stress  $\overline{\sigma}_Y$  calculated from ABAQUS simulations are about 650 MPa for the Fe powder and about 1095 MPa for the 316L powder. Therefore, a higher  $\overline{\sigma}_Y$  value of the 316L powder indicates a higher rebound energy and thus explains why the Fe powder generally exhibits a higher BR than the 316L powder. Note that, comparing Figure 5.16 (b) with (c), impacts are both taking place between two materials (316L and Fe) but in different combinations (Fe on 316L and 316L on Fe). But the BR of Fe on 316L is much higher than that of 316L on Fe as seen in Table 6.1. Again, this is explained by the higher effective yield stress  $\overline{\sigma}_Y$  of 316L powder leading to a higher rebound energy, but also it explains why the role of powder or coating during impact could contribute differently to the particle deposition behaviors as described in Equation 6.2.

However, the theory of rebound energy fails to explain why Fe as the substrate material is more prone to rebound the impacting powders than 316L as shown in Figure 5.16 (a, c) or (b, d). Clearly more factors should be considered for explanations such as the high oxidation degree of the Fe coating.

#### 6.3.2 Correlation between BR with DE

In order to establish correlation between BR and DE, two assumptions are made:

(1) deposition behaviors of single particles are only related to the layers that they directly impact onto;

(2) during deposition of 316L/Fe coatings, all the individual particle impact behaviors can be categorized into four basic particle-substrate impact combinations: 316L on 316L, 316L on Fe, Fe on 316L and Fe on Fe, as illustrated in Figure 6.5. Those particle impacts taking place onto the mixed substrates can be analysed on the basis of the relative contact area of the particle and each single component substrate, which has already been confirmed in Chapter 6.2.3.



Figure 6.5: Schematic illustrations of the particle-substrate impact combinations during 316L/Fe coating deposition. Type 1: 316L on Fe; Type 2: Fe on 316L; Type 3: 316L on 316L; Type 4: Fe on Fe.

For single component coatings of 316L and Fe, BR values of 316L on 316L and Fe on Fe are directly compared with DE. For the mixed coatings, in order to correlate with DE, the BR, which is initially calculated from single component particle impacts, needs to be converted to the BR of mixed particles impacts. Hence, the probability of the occurrence of each impact combination during mixed powders deposition is introduced. For instance, 20Fe coating has an estimated composition of Fe for 27.84% and 316L for 72.16%. Thus,

the probability of the occurrence of each impact combination during deposition of 20Fe coating was calculated by multiplying the composition of each component as:

316L on 316L: 72.16%×72.16%=52.07%
316L on Fe: 72.16%×27.84%=20.09%
Fe on 316L: 27.84%×72.16%=20.09%
Fe on Fe: 27.84%×27.84%=7.75%

Then the BR of 20Fe powders on the 20Fe mixed substrate was calculated by multiplying the BR of each impact combination with their respective probability of occurrence during 20Fe coating deposition as:

35.6%×52.07%+7.8%×20.09%+73.9%×20.09%+23.4%×7.75%=36.8%. With this method, the BR for all the mixed coatings were calculated and comparisons with the measured DE were plotted in Figure 6.6.



Figure 6.6: Comparisons of the measured DE with the calculated BR.

For pure coatings and coatings with low Fe content, the trend of the BR prediction follows that of the actual DE measurements, but as the Fe is further increased, the trends are totally opposite. It seems that other factors need to be considered.

The individual particle impact tests used polished coatings as the substrate, therefore, effects of successive particle impact (tamping) and surface roughness (mechanical interlocking) that occur during coating deposition are excluded [65]. Therefore, the deviations between DE with BR could be attributed to those combined effects. While in this work, the effect of tamping should not result in such a significant change of DE with regards to Fe, since the 316L and Fe powders used are comparable in density, size and velocity. Therefore, as both the DE and coating surface roughness increase with increasing Fe, it is most likely that the DE of mixed powders are enhanced as the increase in surface roughness facilitating the particle mechanical interlocking.

### **6.4 Conclusions**

- The individual particle impact tests indicate that the material type of powder or coating will play different roles on the particle deposition behaviors. The 316L powder has a higher rebound tendency than Fe powder, while the coating of 316L can better facilitate particle deposition than Fe.
- 2. The BR calculated from individual particle impact tests corresponds well with the DE of Fe up to 20%, but exhibits the opposite trend with further increases in Fe. The deviations at the higher Fe content may be due to the surface roughness, which has not been considered in the BR model.

# 7 Conclusions and Future Work

# 7.1 Conclusions

- For the single phase 316L and Fe powders, during powder rolling mixing and cold spray deposition process, no martensitic transformation will take place. For the metastable ferrite existed in as-received 316L powder, during cold spray deposition it undergoes a strain induced phase transformation to form the more stable austenite.
- Despite the significant difference in microhardness, size and morphology of the powders used in this work and by Barua [5], the 316L and Fe mixed powders would exhibit an elevated DE at high Fe content. It is mostly likely to be due to the addition of Fe powder increases coating surface roughness and thus promotes the mechanical interlocking of incoming particles.
- The porosity levels of 316L/Fe mixed coatings depend on the relative hardness of the Fe with the 316L. In the case of comparable hardness, coating porosity is related to the deformation behaviors (flattening ratio) of each powder component, and a similar deformation behavior (flattening ratio) could lead to a reduced porosity level. In the case of a much softer Fe powder in mixtures, coating porosity is significantly reduced even with a small addition of Fe.
- The microhardness of 316L/Fe mixed coatings depend on the incorporated amount of large and heavy particles. The strong tamping effect provided by the high quantity of large and heavy particles in the mixtures can considerably increase the coating microhardness.
- Bond strength of 316L/Fe mixed coatings are only related to the coating composition and decrease with a high Fe content.

# 7.2 Future Work

- Investigate the effect of powder dual feeding approach on the DE of mixed 316L/Fe powders.
- Further study of the XRD quantitative analysis to obtain the more accurate composition measurements of the mixed powders.
- Perform EBSD phase mapping on the cold sprayed coatings to investigate the presence of martensite after cold spray deposition.
- Use nanoindentation to experimentally determine the materials properties such as elastic modulus and yield strength of the feedstock powders used for ABAQUS simulations.
- Perform ABAQUS simulations to examine the effect of different substrate roughness scales on particle deposition.
- Further investigate the phenomenon of the higher rebound tendency of Fe coatings to rebound the impacting powders.

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