Micromechanical testing of cold sprayed Ti splats and coatings

by

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Abstract

Cold spray is a thermo-mechanical process where powder deposition is achieved through particle acceleration to supersonic velocities using a preheated and pressurized gas and a deLeval nozzle. The operating temperatures are typically below the melting point of most metals, which limits the material oxidation and phase transformations. Thick, dense coatings can be produced at fast deposition rates (20 g/min), making cold spray a candidate for near net shape production and part repair technology for aerospace applications. However, the cold-spray process is not as well documented as thermal spray techniques and the lack of the reliable experimental data limits the use of the cold spray, especially in load bearing applications.

The present study explored the mechanical and microstructural properties of the cold spray titanium splats and coatings with novel micro-mechanical testing techniques coupled with high resolution microscopy. Electron channelling contrast imaging and nanoindentation mapping were used to examine the evolution of the microstructure and hardness of individual cold spray splats. The grain refinement and recrystallization were observed at particle interfaces which contributed to the strain hardening of the material. Splats deposited above critical velocity (700 - 900 m/s) exhibited nanometer scale grains with average grain diameters in the range of 50 to 200 nm at the splat/substrate interface with regions of metallurgical bonding. A modified ball bond shear test was implemented to measure the adhesion strength of individual cold spray splats. Deposition conditions under which the adhesion strength of splats reached the theoretical shear strength of titanium were identified. Coatings, produced at the same deposition conditions as strongly bonded splats, showed strong particle cohesion strength and low coating porosity. The coating porosity and poor particle cohesion strength affected the microindentation hardness measurements and tensile properties of the titanium coating. A new multi-scale indentation method was developed, where the comparison between the nanoindentation and microindentation and the definition of a “hardness loss parameter” was used to quantify the effect of the coating defects on hardness measurements. Titanium coatings that demonstrated hardness loss parameter approaching that of the bulk titanium were also coatings that demonstrated tensile properties, measured with microtensile testing technique, of fully dense material. The splat adhesion and
multi-scale indentation testing techniques developed in the present research were shown to provide new methods that can be used towards optimization of the cold spray process for deposition of titanium coatings with properties of commercially manufactured material.
**Résumé**

La projection à froid est un processus thermomécanique où la déposition du revêtement est accomplie en accélérant les particules de la poudre, avec un gaz préchauffé et en pression, vers la vitesse supersonique. La température opérationnelle est, d'habitude, plus petite que le point de fusion de la plupart des métaux, ce qui limite l’oxydation et la transformation de phase. Des revêtements épais et denses peuvent être produits avec un taux de déposition rapide (20 g/min) permettant l’utilisation de la projection à froid pour la réparation des pièces et la formation des pièces proche de la forme finale pour les applications aérospatiales. Néanmoins, le processus de la projection à froid n’est pas aussi bien documenté que la projection thermique et manque de données expérimentales fiables, ce qui empêche l’application de la projection à froid aux pièces de portance.

Le travail accompli dans cette thèse est basé sur l’exploration des propriétés mécaniques et microstructurales des trempes et des revêtements par projection à froid de titane avec les nouvelles techniques micromécaniques et à l’aide de la microscopie à haute résolution. L’imagerie de contraste par canalisation et la cartographie par nanoindentation ont été utilisées pour examiner l’évolution de la microstructure et la dureté des trempes du titane. La diminution de taille des grains et la recristallisation des grains ont été observés à l’interface des particules ce qui a contribué à la hausse de dureté dans cette région. Les trempes, qui ont été déposées à une vitesse plus hautes que la vitesse critique (700 - 900 m/s), avaient des grains à l’échelle nanométrique (de 50 à 200 nm) à l’interface de trempé/substrat et présentaient des liaisons métallurgiques. Une nouvelle technique de balle au cisaillement modifié a été utilisée pour mesurer la force d’adhérence de ces trempes. Les conditions de la projection à froid, pour lesquelles les trempes ont démontré la force d’adhésion s’approchant de la force de cisaillement théorique du titane, ont été identifiées. Les revêtements, déposés aux mêmes conditions que les trempes démontrant une adhérence supérieure, ont présenté une forte cohésion des particules et une porosité du revêtement réduite. La porosité et la force de cohésion des particules avaient un effet sur les mesures de dureté et les propriétés de traction des revêtements. Une nouvelle méthode d’indentation multi-échelle a été développée dans laquelle la comparaison entre les mesures faites par nanoindentation et microindentation, défini comme le paramètre de perte de dureté, a été
utilisé pour quantifier l’effet des défauts sur la mesure de dureté du revêtement. Les revêtements de titane qui avait un paramètre de perte de dureté s’approchant de celui du titane massif, ont démontré également les propriétés de traction du titane massif. Les techniques micromécaniques développées dans cette thèse, présente les nouvelles méthodes qui peuvent être utilisées envers l’optimisation du processus de projection à froid et le dépôt des revêtements de titane ayant des propriétés mécaniques de matériaux commerciaux.
Acknowledgement

The work presented in this thesis was made possible through collaboration of different research groups and facilities but I would like to, first, acknowledge the help and support from my supervisor Prof. Richard R. Chromik who gave me the opportunity to work on the cold spray project. Prof. Richard R. Chromik supported my research, contributed to discussion of the results, helped me organize and review the publications and this thesis dissertation while giving me the opportunity and freedom to realize my research ideas. With his help I was able to make valuable contacts with people working in my field and was able to travel and present my work at different international conferences. He helped me develop my research skills, made me be a better presenter, writer and also gave me the opportunity to direct and supervise the research on other projects than my own, thus expanding my horizons.

I would like to also acknowledge Prof. Stephen Yue who is the founder of the McGill Aerospace Materials and Alloy Development Center (MAMADC) cold spray facilities at the Industrial Material Institute (CNRC-NRC IMI) in Boucherville. Many of the experiments achieved in this study would not be possible without his support. Special thanks must be also given to Dr. Eric Irissou and Dr. Jean-Gabriel Legoux from IMI NRC-CNRC Boucherville who provided the access to the cold spray facilities and who also helped in the revisions of manuscripts. Their help with the experimental section and the interpretation of the results is greatly appreciated. I would like to also thank Bernard Harvey, Mario Lamontagne, Jean-Francois Alarie and Frederic Belval for the technical contribution as well as J. Michael Shockley, Jihane Ajaja, Phuong Vo, David Walker, Wilson Wong, Ahmad Rezaeian, and Yu Zou for providing me with some of the coatings, their help with experimental procedures and experimental results. Additional thanks are due to Jolanta Klemberg Sapieha at École Polytechnique and Nicolas X. Randall from CSM Instruments for the access to the MicroCombi Scratch Tester, and to Mathieu Brochu for the access to his furnace at McGill University. Finally, the work would not be possible without the financial support of equipment that was provided by Canadian Foundation for Innovation – CFI fund (McGill University), funding from NSERC, McGill Engineering Doctoral Award (MEDA) and Hydro Quebec Scholarship.
On a personal note, I would like to thank all the people who supported me through my years of research including Pantcho Stoyanov, Holger Strauss and my best friend Tasneem Shariff. Last but not least, I would like to thank my father - Abram Goldbaum for always being there to support me.
Contributions of Authors

The present work is based on a collection of papers that were published in the peer reviewed journals or are in the process of being published. The manuscripts were produced in collaboration with people from different groups and facilities and are listed according to the chapter in which they appear. The contribution of each co-author is provided below the description of each manuscript.


Prof. Richard R. Chromik supervised, reviewed and directed the course of the research. Prof. Chromik contributed to writing and submission processes of all the manuscripts and helped in the analysis of the results. Prof. Stephen Yue, Eric Irissou and Jean-Gabriel Legoux provided the access to the cold spray facilities and the technical support from Bernard Harvey, Mario Lamontagne, Jean-Francois Alarie and Frederic Belval from Industrial Materials Institute, National Research Council of Canada. All the cold spray samples used throughout this dissertation were produced with their help.

Chapter 5: Dina Goldbaum, Richard R. Chromik, Nicolas Brodusch and Prof. Raynald Gauvin, “Microstructure and mechanical properties of Ti cold spray splats determined by high resolution channelling contrast SEM imaging, EBSD and nanoindentation mapping techniques”, to be submitted.

The splats produced in the previous chapter where analyzed with SU8000 microscope with help of Nicolas Brodusch who contributed to the image collection and Prof. Raynald Gauvin from McGill University who contributed to the access to the SU8000 microscope.

James Michael Shockley, as an undergraduate student and also under my co-supervision, developed the splat adhesion testing for cold spray splats. He also did the adhesion testing on most Ti and Ti6Al64V splats deposited with nitrogen gas on as received Ti or Ti6Al4V substrates. In the same publication Dr. Ahmad Rezaeian provided the measurements of the velocity of Ti6Al4V particles accelerated with helium gas.


Wilson Wong carried the measurements of the particle velocities and provided cold spray coatings used in the publication on “Mechanical Behavior of Ti Cold Spray Coatings Determined by a Multi-Scale Indentation Method”. In the same publication Jihane Aajaja, an undergraduate student working under my co-supervision, did most of the sample polishing and helped with micro-hardness testing.

**Chapter 8:** Dina Goldbaum, Richard R. Chromik, Phuong Vo and Stephen Yue, “Tensile Testing of As Deposited and Annealed Titanium Cold Spray Coatings”, to be submitted.

In chapter 8, Phuong Vo helped with the tensile testing while Prof. Yue contributed to the access to his facilities. Not included in the list of authors are Nicolas Brodusch and Prof. Raynald Gauvin who contributed to collection of high resolution images of the coatings with the SU8000 microscope. In the same chapter David Walker performed the annealing of the cold spray coatings.

The author of this Ph.D. thesis was the first author of all the publications and was responsible for the development and planning of the experimental testing. Most of the experimental testing, with the exception of the listed, was performed by the author of this Ph.D. who is also responsible for the data analysis and interpretation of the results.
Disclaimer

The manuscripts presented in the Ph.D. are listed by the topic and do not follow the order at which they were published. The experimental procedures used in the manuscripts were removed and combined into one single Chapter 3.
Chapter 1. Introduction

Cold spray process consists of powder acceleration to supersonic speed with preheated and pressurized gas through a de-Laval type nozzle [1]. The powder deposition results from the powder impact with the substrate material placed some distance away from the nozzle. High velocity impact leads to feedstock powder deformation and spreading resulting in the conformal particle adhesion. The velocity at which particles deposit is termed critical particle velocity which is material dependent [2]. Above the critical velocity, most of the impact stress is converted to heat leading to adiabatic shear and formation of the metallurgical bond [2-4]. Adiabatic shear was first observed during high strain rate material deformation [5]. A formation of adiabatic shear bands consisting of grain refined and recrystallized grains were reported [5-8]. The mechanism by which the adiabatic shear contributes to the metallurgical bonding is not well understood but some propose that the mechanical interlocking and temperature are keys in answering this question [8-10].

Cold spray has several advantages over other deposition techniques such as plasma spraying and high velocity oxygen fuel techniques [11]. In cold spray, the process temperatures are typically below the melting temperature of most metals, which minimizes the material microstructural changes and limits material oxidation [11]. Due to low process temperatures, the cold spray deposited materials are not subjected to the thermal stresses fluctuation which limits coating delamination frequent in other thermal spray techniques [12]. The deposition rate for cold spray coating is high and thick coatings can be produced in relatively short amount of time [12, 13]. The cold spray coating deposition efficiency can reach 99 % which translates into low material waste [13, 14]. Furthermore, cold spray can be used as near net shape technology and most of the costs associated with part casting, machining and tool wear can be circumvented [15].

Currently, cold spray is used for deposition of corrosion-resistant coatings, thermal barrier coatings and abradable coatings [15]. The cold spray deposition was used in the aerospace applications [15] such as cold spray copper coatings in the aircraft engines for heat removal in the combustion chamber. The coatings demonstrated better adhesion and required less process time than the coatings deposited with more conventional electrolytic technique [15, 16]. Recent studies also investigated the applicability of the cold spray process for part
repair [17]. Cold spray was applied in the repair of turbine blades and vanes. The vanes are typically repaired by welding that induced severe oxidation and hot cracking in the repaired part. With the cold spray, these issues were bypassed [17]. High deposition rates, low temperature and the ability to deposit coatings of various shapes, makes cold spray method ideal for various aerospace and automotive applications [18].

There are some limitations to the cold spray technique. Materials that do not exhibit plastic deformation cannot be cold sprayed [19]. For that reason cold spray cannot be used for deposition of hard and brittle materials like ceramics or glasses unless ductile materials are co-sprayed or special powders are used [19]. Also, the production of fully dense cold spray coatings from high strength and high melting point materials requires high deposition velocity [2]. For this case, the processing costs associated with the gas consumption can be high, especially when helium gas is used [19] and some cold spray systems may require a gas recycling system [19, 20]. In addition, cold spray coatings are known to be highly strain hardened and have poor tensile properties [15]. In order to improve the ductility of cold-spray coatings, the coatings have to be annealed [19, 21]. Finally, the cold-spray technique is not as well documented as other thermal spray techniques [19]. The lack of the reliable experimental data limits the use of the cold spray in load bearing applications [15].

Cold spray coatings differ from the conventionally manufactured materials. The coatings contain grain refined microstructure, are strain hardened but at the same time have regions of thermal softening, poorly bounded particles and demonstrate varied degree of porosity. These structural features can either increase or decrease the coating hardness and tensile properties making the comparison between the mechanical properties of the coatings and the commercially manufactured materials challenging. The present work develops or expands on new micromechanical testing techniques such as nanoindentation mapping, splat adhesion and varied load indentation testing. The effect of the cold spray deposition parameters including: gas temperature, pressure, powder size and morphology as well as deposition velocity on the microstructure, hardness and bond strength of the coatings were investigated. The conditions required for the deposition of cold spray titanium coatings with properties of the commercially manufactured titanium were derived based on the experimental results.
The work was divided into nine main chapters. The objective of the present chapter was to familiarise the reader with the cold spray process, its advantages, applications and limitations, while giving a brief overview of the work that was undertaken.

In Chapter 2, a literature review of the principles governing cold spray coating deposition were researched and a number of approaches used by the researchers to understand the effect of the cold spray deposition process on the microstructural and mechanical properties of the cold spray coatings were listed. New microstructural and mechanical testing techniques were explored.

In Chapter 3, different process parameters used for deposition of cold spray splats and coatings in the present work were listed. A detailed description of the testing procedures for optical and scanning electron microscopy, microindentation and nanoindentation testing, splat adhesion, annealing and tensile testing were given.

The subsequent chapters consist of separate publications, evaluating the mechanical and microstructural properties of the cold spray splats and coatings. Some of the chapters were published in the scientific journals and include Chapter 4, Chapter 6 and Chapter 7.

In Chapter 4, the effect of the particle velocity on the deformation and deposition mechanisms of the cold spray splats and coatings was explored. The mechanical properties of the coatings were investigated with nanoindentation and microindentation testing techniques. Nanoindentation mapping of the splats was implemented to determine the effect of the deposition velocity on the hardness distribution within the splats and coatings.

In Chapter 5 the hardness distribution within the titanium splat determined by nanoindentation mapping was correlated to the splat microstructure. High resolution channelling contrast imaging and EBSD mapping were used to define the microstructure in different regions within the splats. The combined information from mechanical and microstructural properties was used to explore the regions of strain hardening and thermal softening. The deposition and adhesion mechanisms of Ti splats impacted onto Ti substrate at increasing deposition velocity and substrate temperature conditions were examined.

In Chapter 6 a new splat adhesion testing technique was used to measure the effect of the deposition velocity and temperature on the Ti and Ti6Al4V splat adhesion strength. The effects of the particle size and the particle interaction with the gas jet on the splat adhesion strength were explored. The deposition conditions with optimal splat adhesion strength were
determined. The splat adhesion strength was compared to cohesion strength of particles in the coatings previously reported in the literature.

In Chapter 7 a new multi-scale indentation testing technique was implemented. A percent difference between nanoindentation and microindentation hardness (termed hardness loss parameter) was used to determine the effect of coating defects, such as particle cohesion and coating porosity, on the hardness measurements. Titanium coatings that demonstrated low hardness loss parameter did not demonstrate particle debonding during high load indentation, had low porosity and had similar response to the indentation load as fully dense, bulk titanium plate. The multi-scale indentation was shown to be a viable method for comparison of the mechanical behavior of coatings and the commercially manufactured materials.

In Chapter 8, the tensile testing of as deposited and annealed cold spray Ti coatings was carried. A good correlation was found between the cold spray deposition condition at which coatings demonstrated good tensile properties and deposition conditions at which splat demonstrated near theoretical adhesion strength and hardness loss parameter. The deposition conditions and heat treatment procedure required to produce titanium cold spray with properties of commercially manufactured titanium were determined.

The conclusions reached from the results obtained in the course of the study are enumerated in the final chapter. The recommendations for future studies are also provided.
Chapter 2. Background and Literature Review

2.1 – Introduction to Cold Spray Process

Cold spray is a process where the coating deposition is achieved by powder impact at supersonic velocities with a substrate material [15]. The powder is accelerated to supersonic velocities with preheated and pressurized nitrogen or helium gas passing through a de-Laval nozzle, as can be seen in Figure 2.1[15]. The gas exerts drag forces onto the feedstock powder (introduced into the gas stream at the throat of the nozzle) and accelerates the powder to a velocity that is slightly lower than the velocity of gas at the exit of the nozzle [22, 23].

\[ V_e = \sqrt{\left(\frac{TR}{M} \times \frac{2c_k}{c_k-1} \times [1 - (P_e/P)^{(c_k-1)/c_k}]\right)} \]  \hspace{1cm} \text{Eq.2.1}

In Eq. 2.1, the gas temperature at the inlet of the de Laval nozzle, shown in Figure 2.1, is denoted as \( T \) while \( R \) is a gas constant, \( M \) is the gas molecular weight, \( c_k \) is isotropic expansion factor or \( c_p/c_v \) where \( c_p \) is specific heat of gas at constant pressure and \( c_v \) is specific heat of gas at constant volume [22]. Finally, \( P_e \) is the exhaust gas pressure and \( P \) is inlet gas pressure [22]. For helium the isotropic expansion factor, \( c_k \), is 1.66 while for nitrogen it is 1.4.
The gas with higher expansion factor, such as helium, reaches greater gas velocities and therefore accelerates the feedstock powder particles to greater velocity [15]. The particle velocity decreases as particles travel some distance away from the nozzle. The optimal particle velocity for the cold spray deposition is therefore achieved some distance (between 40 and 120 mm) away from the nozzle [25], this distance is typically used for substrate positioning. Figure 2.2 shows the effect of the gas preheat temperature, pressure and distance from the cold spray nozzle on particle velocity [25].

![Figure 2.2](image)

**Figure 2.2:** Commercially pure titanium particle velocity, Vp, measured with particle image velocimetry - PIV system as a function of the distance away from the cold spray nozzle, gas temperature and pressure [25].

The particles impact the substrate material at temperature below the melting point of most metals, however the cold spray deposition is not cold as its name infers. During cold spray deposition some of the heat is transferred from the gas into the feedstock powder as well as into the substrate [15, 26]. For example, the temperature rise in the copper particles and steel substrates was reported to reach 200 - 400°C with gas preheat temperature of 500°C [15, 26]. The computer simulated effect of the gas temperature on the temperature of the in-
flight aluminum powder is shown in Figure 2.3. The particle temperature was predicted to vary from 475 to 350ºC depending of the distance traveled away from the nozzle [15].

![Graph showing temperature variation](image)

*Figure 2.3: The effect of the gas temperature on the temperature of the 10µm aluminum feedstock powder temperature through the flight trajectory away from the cold spray nozzle [15]*

2.2 – Cold Spray Deposition Mechanisms

The particle velocity and temperature upon the impact are the two main parameters that govern the deposition of the cold spray particles [2, 3]. The deposition and bonding mechanisms of cold spray particles, while thermo-mechanical in nature [2], are not well understood and are still researched.

2.2.1 – Plastic deformation and conformal adhesion

The general consensus among the researchers is that the deposition of the metallic feedstock powder is achieved through high strain rate deformation of the powder particles [2, 3]. One of the mechanisms of bonding is a formation of a conformal interface between the splat and the substrate upon a supersonic impact. Figure 2.4 illustrates H. Assadi et al. [3], model of supersonic impact of an individual copper particle, also known as splat, with a
copper substrate. According to Assadi et al. model [3], in the first stage of the impact, a crater is produced within the substrate material. Over a period of nanoseconds, the crater diameter increases while the particle deforms, flattens and forms an increasingly conformal interface with the substrate [3]. The material deformation and the formation of a conformal interface between the splat and the substrate become more prominent with increasing deposition velocity [3]. The force of the impact dislodges and removes the oxide layer from the splat/substrate interface and provides a metal to metal contact [3].

Figure 2.4: Particle spreading behavior with increasing deposition velocity [3].

The extent of plastic deformation is highly dependent of the dislocation mobility in the materials [27]. Cu and Al have an FCC structure and contain 12 slip systems, four (111) slip planes and 3 slip directions, by which the dislocations can propagate. Consequently, materials with FCC structure can undergo numerous dislocation events and extensive plastic
deformation under relatively low stresses [27]. The BCC materials, like iron, also have 12 slip systems but have a lower packing density and coordination number. The deformation ability of BCC structured materials is therefore lower than that of FCC materials [27]. Metals with HCP structure, such as Ti, have only 3 slip systems at room temperature. HCP materials do not exhibit extensive material deformation which is therefore restricted to twin formation at room temperature conditions [5, 27-29]. Despite this fact, a successful deformation and deposition of cold spray Ti was achieved [13, 14, 27] indicating that other bonding mechanisms are at play [2, 3, 30, 31].

2.2.2 – Adiabatic shear

During cold spray deposition, the material deformation occurs at high strain rates, up to $5 \times 10^9$ s$^{-1}$, and at very high impact stresses, 5 - 10 GPa [2, 3, 8, 32]. The impact stresses are sufficient to induce dislocation nucleation, grain refinement and recrystallization in the cold spray deposited materials. The stages leading to the grain refinement and recrystallization are illustrated in Figure 2.5 [8].

![Figure 2.5: Grain refinement mechanism with a) pre-impact feedstock powder, b) entanglement of dislocations, c) formation of persistent dislocation cells and re-elongation and d) brake-up, rotation and recrystallization of sub-grains [8]](image)

Prior to the particle impact, the microstructure is shown to contain coarse grains
During the impact, the material is subjected to dislocation nucleation and entanglement (b), the dislocations agglomerate into lower energy sub grains which lead to the grain refinement (c) [8, 32, 33]. 95% of the kinetic energy of the impact is believed to dissipate as heat [34]. The increase in the temperature leads to visco-elastic material flow (often characterized by material jetting) and dynamic rotational recrystallization (d) [8, 35]. This phenomenon is referred to as “adiabatic shear” [5, 19, 28, 29, 36].

The adiabatic shear contributes to a metallurgical bonding [37, 38]; however, the mechanisms by which the bonding takes place are unclear. Some researchers believe that the metallurgical bonding occurs due to the material melting in the adiabatic shear instability region [3, 27, 37, 39, 40] while others believe that the bonding occurs through mechanical interlocking [8, 19].

The temperature in the adiabatic shear instability region cannot be measured using the conventional methods due to the heat localization and the small scale of the adiabatic shear instability region [15, 19]. For that reason, most studies use finite element modeling of temperature distribution within the splats that is based on Johnson-Cook plasticity model [3, 27, 34, 41]. H. Assadi et al. [3] and T. Schmidt et al. [2], used finite element modeling on copper splats and suggested that the temperature in the adiabatic shear instability in copper can reach the melting point (1200ºC) at deposition velocity of 600 m/s. The temperature rise up to the melting point (1660ºC) in the adiabatic shear instability region was also predicted for cold spray titanium [37, 41].

The splat impact simulations provide valuable information on heat distribution during the cold spray splat impact, however the temperature rise in the adiabatic shear instability region was found to be overestimated [8]. The TEM observation of Ti splats did not demonstrate α to β phase transformation expected to take place at high cooling rates and at temperatures above 855ºC. The melting in the adiabatic shear instability region was therefore ruled out [8]. In light of the microstructural evidence, the bonding mechanism in cold spray process was tied to the removal of the oxide layer during the splat impact and formation of a very conformal metal to metal interface [40] with possibility of the mechanical interlocking illustrated in Figure 2.6 [19].
Figure 2.6: Mechanical interlocking between the substrate (Material 1) and coating (Material 2) [19].

The velocity at which the particles exhibit adiabatic shear instability is termed “critical velocity” [18]. T. Schmidt et al. [2] as well as H. Assadi et al. [3], used Johnson-Cook plasticity model to derive the critical velocity required to induce adiabatic shear for different metals. According to T. Schmidt et al. [2], the critical velocity of the particles is a function of the particle size in addition to the particle mechanical and thermal properties, Eq.2.2.

\[
V_{cr} = \sqrt{\frac{F_1}{\rho} \frac{4\sigma_{TS} \left(1 - \frac{T_m - T_R}{T_{m-R}}\right)}{F_2 C_p (T_m - T_i)}} \quad \text{Eq.2.2}
\]

In Eq.2.2, F1 and F2 are empirical factors. \( F_1 \) is a material mechanical calibration factor found to be 1.2 for 25 \( \mu \)m particles and 3.8 for 20 \( \mu \)m particles; \( F_2 \) is part of the
material thermal correlation factor and has a magnitude of 0.3 [2]. The critical velocity of the material was shown to also depend on the material tensile strength - $\sigma_{TS}$, heat capacity - $c_p$, material melting temperature - $T_m$, reference temperature - $T_R$ and the temperature of the particle upon the impact - $T_i$ [2]. Figure 2.7 demonstrates the critical velocity for different metals determined from Eq.2.2 [2]. For pure Ti and Ti alloys the critical velocity ranges between 700 and 900 m/s. The dark regions in Figure 2.7 represent the regions of uncertainty [2]. The critical velocity was measured for the particles, 25 μm in size but could be lower or higher depending on the particle size [2].

![Figure 2.7: Critical velocity for various metals [2].](image)

Studies on high strain rate deformation of materials have demonstrated that by increasing the temperature of the powder, the critical velocity required to induce adiabatic shear in the material can be reduced (see Figure 2.8) [2, 5, 21, 28, 36]. During cold spray deposition, the temperature can be increased by preheating the powder within the cold spray nozzle [9]. In most high velocity cold spray systems, however, the powder heating can occur in flight, through the interaction of heated gas with powder as was shown in Figure 2.3 [15]. In Figure 2.8, the critical velocity was defined as velocity at which the particle deposition was achieved [21].
Figure 2.8: The effect of the gas temperature on the critical velocity of the bronze powder [21].

2.3 – Microstructure

The microstructure of the cold spray splats and coatings deposited above critical velocity typically consists of a mixture of the original microstructure and fine, recrystallized equiaxed grains [8, 10, 42]. The size of the grains range from 50 nm - 1 μm [8, 10, 42]. Up to date, the microstructural analysis was performed with transmission electron microscopy (TEM) [8, 10, 42]. K.H. Kim et al. [8, 10] observed the formation of defect free nanograins in the TEM images of individual cold spray Ti splats deposited above 700 m/s and shown in Figure 2.9a and b. The grain refinement occurred mainly at the splat and the substrate interface [8, 42]. In single impact event, the upper region of the splat retained its original microstructure while very fine, 50 nm grains, were found directly at the splat impact site (region B) and in the jetting region (region C) [8, 10]. The subsequent splat impacts onto the deposited splats induced grain refinement in the un-deformed regions [9]. In titanium cold spray splats deposited at 700 m/s, the grain refinement was observed in 40% of the splat cross-section. Full grain refinement was reported in splats deposited after powder preheating to ~800ºC [10]. In most studies, the grain growth was ruled out based on the assumption that the cooling rates within the adiabatic shear instability region was high, up to $10^9$ K/s [10, 42], however the conclusion made was not sufficiently supported with experimental results [10, 42]. No known studies were undertaken investigating the effect of the temperature on the
splat microstructure arising from a combined effect of adiabatic shear, preheated gas interaction with the powder and substrate as well as particle and substrate preheating during cold spray deposition process. Furthermore, the region of analysis using TEM is narrow [33, 43] and other characterization techniques are required to investigated the size distribution of the grains within the splats as whole [33].

![Figure 2.9: a) TEM image of titanium splat with b) corresponding diffraction patterns taken at the splat upper region. A, impact site – B, jetting region – C[8].](image)

Kim et al. [9], showed grain refinement to be an important mechanism in cold spray particle deformation and adhesion. Particles exhibiting high degree of grain refinement demonstrated high degree of spreading which contributed to an increase in the surface of the metal to metal contact and bonding [9]. In Figure 2.10, a metallurgical bonding between the splat and the substrate was observed at the splat/substrate interface near the jetting region of titanium splat [9]. The bonded interface consisted of roughly 40% of the splat/substrate interface but was predicted to increase with increase in the deposition velocity or with preheating of the feedstock powder [10, 40]. For unheated splats, the center of the splat/substrate interface was unbounded [9, 38]. Poor bonding between the splat and the substrate in the middle of the splat/substrate interface was explained by the elastic strain energy stored in the material that counteracts the impact forces and induces the particle debonding in that region [38, 40]. In the coatings, incomplete particle bonding contributes to the coating porosity, poor inter-particle cohesion strength in the coating and/or poor particle adhesion to the substrate [37, 44].
Figure 2.10: TEM image of a) titanium splat cross-section on the steel substrate and b) the metallurgically bonded splat/substrate interface [38].

2.4 – Adhesion and Cohesion Strength

The bonding for cold spray takes place at the “splat level” [8-10, 37, 38, 41], however, there are only a few reports in the literature of methods for measuring the adhesion of splats on the substrate or cohesion strength of particles in the coatings [30, 45, 46]. S. Guetta et al. [30] measured the adhesion strength of splats with a laser shock adhesion test (LASAT). LASAT measures the tensile stress required to de-bond splats over a 1 cm x 1 cm area in the substrate and was, therefore, not sensitive to the adhesion strength of individual splats or to their position on the substrate [30].

Other adhesion testing techniques were designed for measuring the bond strength of coating to substrate and were based on the ASTM C-633-99 standard. One of such adhesion testing techniques consists of a hydraulic adhesion/tensile test, where the coatings are typically glued to a circular element with a heat cured epoxy and then pulled apart [37, 47]. Using hydraulic adhesion/tensile test, T. S. Price et al. [47] measured the bond strength of Ti coating deposited on as-received and grit blasted Ti6Al4V substrate. The coatings were deposited at 500 m/s and the bond strength was measured to be 32 - 37 MPa [47]. Using similar methods, Morrocco et al. [48] measured the bond strength Ti coatings on polished, grit blasted or ground Ti6Al4V substrates. Better bonding was observed on the polished and ground substrates than on the grit blasted substrates at 5 and 25 MPa. G. Bae et al. [37] measured the bond strength of Ti coatings deposited at 650 m/s on steel substrates. The bond strength was measured to be between 49 and 69 MPa. In most of these cases, the failure
occurred in the epoxy, failing at 85 MPa, and the bond strength of the coatings deposited at higher deposition velocities could only be reported as greater than 85 MPa [37, 47].

Recently, T. Schmidt et al. [49] developed a tubular coating tensile (TCT) test for the measurement of the cohesive strength of copper cold spray particles in the coating deposited on the aluminum substrate. TCT test was used by Binder et al. [50] to measure the cohesive strength of cold sprayed Ti particles. In Figure 2.11, the cohesion strength of particles in the coatings was plotted as a function of gas preheat temperature which directly affects the particle deposition velocity and particle impact temperature [50].

![Figure 2.11: Cohesion strength of Ti coatings as a function of the gas pre-heat temperature [50].](image)

The coating cohesion strength measures the overall bond strength of the particles within the coating. The particle bond strength varies depending of the particle impact angle, the position of the particle within the cold spray jet and the particle size, all of which affect the particle deposition velocity and adiabatic shear [25, 31, 51, 52]. The impact temperature is another parameter that contributes to the particle bonding [21]. Identification of the effect of processing parameters on the underlying mechanism of adiabatic shear instability and the extent to which bonding occurs at the splat level is one viable way to gather information useful to optimizing the cold spray process.
2.5 – Tensile properties

The microstructure and the bond strength of particles affect the tensile properties of the coatings. Due to the grain refinement and strain hardening, the tensile strength of the coatings is typically greater than that of the feedstock material [15, 35]. The coatings demonstrate poor ductility and fail in the brittle manner [15, 35, 53-55]. Poor particle cohesion strength and high coating porosity contribute to the premature coating failure and decrease the ultimate tensile strength of the coatings [35, 53-55].

Up to date, little information can be found on the tensile properties of the cold spray Ti coatings. Most of the tensile testing was performed on the coatings with existing defects such as porosity and poor particle cohesion strength and little importance was placed into the characterization of the coating grain size [15]. The ultimate tensile strength of the coatings was shown to range between 10 MPa and 800 MPa, depending of the deposition conditions and extent of the coating defects [15, 35]. The ductility of the coatings was low, at best reaching 0.02 % (see Figure 2.12) [35].

![Stress vs. Strain curves of cold spray Ti coatings](image)

*Figure 2.12: Stress vs. Strain curves of cold spray Ti coatings [35].*

The annealing of the cold spray coating was performed in order to reduce the strain hardening and improve the coating ductility [15, 35]. The annealing induces grain recrystallization, grain growth and reduces the hardness of the strain hardened material as can be seen in Figure 2.13a and b [55-57]. Previous studies of the cold worked titanium sheets,
demonstrated that full recrystallization of titanium grains can be obtained by heating the sample at 700°C for 1 hour [58].

Figure 2.13: a) The effect of temperature of time on the grain size of the commercially pure titanium [59] and b) the effect of the grain size of microindentation hardness in the titanium [58].

Zahiri et al. [35] carried tensile testing on cold spray titanium coatings annealed at 550°C which was below the temperature required for the full recrystallization. Nevertheless, the annealing contributed to the decrease in the tensile strength of the coatings from 200 MPa to 600 MPa and increased the coating ductility to 8% as can be seen in Figure 2.12 [35]. The tensile properties measured were inferior to the tensile properties of commercially manufactured, coarse grained titanium listed in Table 2.1 and indicated that the cold spray deposition condition and/or heat treatment procedure used were not sufficient for the production of fully dense titanium coatings.

Table 2.1: Mechanical properties of commercially pure – cp titanium.

<table>
<thead>
<tr>
<th>Material/Property</th>
<th>Cp Titanium (coarse grained, &gt;15μm)</th>
<th>Cp Titanium (ultra-fine grained, &lt;300nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness - HV&lt;sub&gt;200&lt;/sub&gt;</td>
<td>170 [59]</td>
<td>265 [59]</td>
</tr>
<tr>
<td>Ultimate Tensile Strength (MPa)</td>
<td>310 [35, 60]</td>
<td>700-1000 [60, 61]</td>
</tr>
<tr>
<td>Strain (%)</td>
<td>28</td>
<td>8-15 [60, 61]</td>
</tr>
</tbody>
</table>

Cold spray deposition of the fully dense cold spray aluminum and copper coatings demonstrating properties of the commercially manufactured, bulk, materials was previously
reported in a number of publications [53-55]. The research on Ti cold spray coatings is more sparse and only a small number of titanium coatings and deposition conditions were investigated [15, 35]. High processing prices associated with deposition of high critical velocity metals like titanium could explain the limited research on this topic [20]. Further studies and more cost effective testing techniques are therefore required to demonstrate whether fully dense Ti coatings can be produced using cold spray process.

2.6 – Indentation Testing

In the cold spray coatings, the strain hardening attributed to the cold spray deposition was measured by different indentation testing techniques and at different indentation loads [13, 14, 33, 35, 37, 42, 62-64]. The hardness of coatings was mostly estimated with Vickers hardness test [13, 14, 35, 37, 42, 65], while other studies used Pharr and Oliver nanoindentation method to measure the hardness [33, 62-64]. The indentation testing principle is based on the measurement of the area beneath the indenter at the applied loads [66]. An assumption is made that the area beneath the indenter is affected only by the indentation load and the resistance of the material to the deformation [66]. The hardness measurements obtained by indentation are, however, not only sensitive to the material strain hardening but are also affected by the composition, microstructure, texture and grain size, as well as the material defects like surface roughness, dislocation density, porosity, cracking and delamination in the coatings [28, 66-78]. The effect of these parameters on the hardness measurement will be more or less pronounced depending of the indentation loads [66, 79-93]. The understanding of how different parameters affect the indentation hardness measurements is important, and may provide new, more comprehensive approach to the characterization of the mechanical and microstructural properties of the cold spray splats and coatings.

2.6.1 - The effect of the grain size and dislocation density on hardness measurement.

The indentation hardness of any material is affected by the material microstructure and grain size. The hardness typically increases with grain refinement, a phenomenon that is attributed to the grain boundary strengthening mechanism [94-98]. The increase in the
hardness with decrease in the grain size is often described by Hall-Petch relationship shown in Eq.2.3 [99].

\[ H = H_\infty + kd_g^{-\frac{1}{2}} \]  

Eq.2.3

According Hall-Petch relationship, the hardness is a function of the inverse square root of the grain size, \( d_g \), the initial material hardness \( H_\infty \) which is a hardness at infinitely large grain size and a constant \( k \) [94-99]. The constant \( k \) contains both the effect of the grain boundary strengthening and the length of the dislocations produced per unit area of the grain boundary [95] and is determined from the slope of the hardness vs. grain size plot similar to the one shown in Figure 2.14 [98].

![Figure 2.14: The effect of the grain size – \( l \), on the diamond pyramid hardness - DPH in titanium [98, 100-102].](image)

The effect of the grain size on the hardness measurements within the cold sprayed particles was previously investigated [42]. M.P. Dewar et al. [42] used a microindentation at 10 g load to measure the distribution of hardness within the cold spray deposited aluminum particles. The hardness was measured to be highest (72 HV) at the particles interfaces where grain refinement was more extensive. Lower hardness (48 HV) was measured at the particle center where the original feedstock microstructure with coarse grains was observed [42].
The microindentation technique is difficult to apply for the measurement of hardness at the cold spray particle interfaces. The indent, produced at typically lowest microindentation load of 10g and shown in Figure 2.15, revealed to be roughly 10 μm in size and are too large for the indentation within a single particle interface. The microindentation was, therefore, carried on multiple particles resulting in the indenter interaction with pores [42].

![Indent](image)

*Figure 2.15: Vickers indent at 10g load in aluminum cold spray coating at the particle interface [42].*

### 2.6.2 - The effect of the coating porosity and particle debonding.

In cold spray coatings, the coating porosity was shown to have a significant effect on the microindentation hardness measurements [65]. In titanium cold spray coatings the hardness was measured to drop from 300 HV to 100 HV with increase in coating porosity from 1 to 14% (see Figure 2.16) [65].

![Porosity vs Hardness](image)

*Figure 2.16: The effect of coating porosity on Vickers hardness measurements in cold spray titanium coatings [65]*
The hardness measurements in the coatings can be also affected by the high load indentation induced defects like cracking and de-lamination [44, 67]. The particle cracking within the cold spray coatings was recently reported by X. Meng et al. [57], during the indentation of stainless steel cold spray coatings however the effect of the cracking on the hardness measurements was not investigated. W. –Y., Li et al. [103] observed a hardness decrease due to cracking in titanium cold spray coatings and attributed low hardness measurements to poor particle cohesion strength and high porosity content in the cold spray coatings.

As opposed to most microindentation testing techniques, the nanoindentation testing is a depth sensing method where hardness is measured from the load/unload curves according to Oliver and Pharr method [66, 104]. The indentation into the pores increased the indentation depth and affected the load/unload curves in the manner shown in Figure 2.17 [105] thus, providing a powerful tool for data filtering and the determination of the material hardness that is not affect by the coating porosity or particle de-bonding.

![Figure 2.17: The effect of coating porosity on nanoindentation load displacement curves coatings with increasing porosity of a) 8%, b) 19%, c) 22% and d) 28% respectively [105].](image)

The nanoindentation is performed at significantly lower loads than in the microindentation, typically at indentation depths below a micron. The indent interaction region with the material is small (see Figure 2.18) [106] and the nanoindentation hardness measurements are less affected by the microscopic defects.
Figure 2.18: Nanoindentation mark at 500 nm indentation depth in the Al 5083 powder particle [106].

2.6.3 – Nanoindentation testing techniques

The small scale of nanoindentation testing is ideal for measuring the mechanical properties of thin films and coatings, small microstructural features like nanograins, phases, oxide layers and precipitates [66-71, 75, 106] and was used to define the mechanical properties of phases as small as 50 nm [68, 70, 71]. Nanoindentation was also used as a mapping technique to define the distribution of the material microstructure and phases [70].

In addition to the hardness measurement of the material, nanoindentation testing provides information on the elastic modulus of the material [66, 70, 104]. For example, profile nanoindentation was used by J. Xia et al. [107] to examine the hardness and reduced modulus across the thermal oxidation treated titanium aluminide (see Figure 2.19).

Figure 2.19: Nanoindentation hardness and elastic modulus profile across the titanium aluminide oxidized surface [107].
As can be seen in Figure 2.19, the hardness and elastic modulus were higher at the surface, a phenomenon that was attributed to the presence of the TiO$_2$ and Al$_2$O$_3$ oxides [107]. The measurement of the hardness and elastic modulus with nanoindentation profile and mapping techniques can be potentially used to observe the changes in the microstructure and composition within the cold spray splats and coatings.

2.6.4 – *Indentation size effect*

Nanoindentation, while a powerful mechanical characterization technique, has its own disadvantages. Previous studies revealed that the nanoindentation hardness was not constant but increased with decrease in the indentation load or size demonstrating behavior similar to one shown in Figure 2.20 [80, 83, 87, 89, 93, 108-110]. Originally this effect was attributed to a poor sample preparation, sample roughness and contamination as well as the indenter defects and poor system calibration. Over time, the technological development helped improve the system calibration problems and the extensive research perfected the sample preparation methodology. While most of the issues were addressed, the indentation size effect persisted [83, 89, 109-111].

*Figure 2.20: Indentation size effect in single crystal and work hardened polycrystalline copper [89].*
W.D. Nix and H. Gao, demonstrated that the hardness increase with the decrease in the indentation load was tied to the geometrically necessary dislocations that form below the indenter and contribute to the strain hardening of the material [89]. The effect of the geometrically necessary dislocations, represented schematically in Figure 2.21, was shown to be less pronounced at higher indentation loads due to the increase in the indent/material interaction volume [89, 93].

![Figure 2.21: Geometrically necessary dislocations below the indenter [89].](image)

According to the strain gradient plasticity model proposed by W.D. Nix and H. Gao [89], the hardness of the material - \( H \) measured with nanoindentation technique is a function of indentation depth - \( h_c, h^* \) and \( H_o \) which is hardness that does not dependant of the indentation depth as represented by Eq.2.4 [89]. \( h^* \) represents the characteristic length scale that defines the depth dependence of hardness and the geometry of the indenter [89]. \( H_o \) (see Eq.2.5) is a function of the material shear modulus \( \mu \), burger vector \( b \), a constant \( \alpha \) which is 0.5 [89] and the statistically stored dislocation density - \( \rho_s \) present in the material prior to indentation. \( H_o \) also represents the true material hardness [89].

\[
H = H_o \sqrt{1 + \frac{h^*}{h_c}} \quad \text{Eq.2.4}
\]

\[
H_o = 3\sqrt{3}\alpha\mu b\sqrt{\rho_s} \quad \text{Eq.2.5}
\]

At microindentation loads surpassing 2 \( \mu m \) in indentation depth, the hardness is not affected by the geometrically necessary dislocations [89]. For that reason, the microindentation hardness is measured as a constant hardness or \( H_o \), unless the microindentation results are affected by the defects within the tested material or defects induced by the indentation process previously described [93]. In light of how different
parameters affect the hardness measurements at different length scales, the indentation testing carried out at one load risks missing important information on the mechanical behavior of the materials.

2.7 -Summary and Conclusions

The literature review revealed that complicated thermo-mechanical principles are involved in the deposition and bonding of the cold spray coatings. Depending on the deposition velocity and temperature conditions coatings with high or low cohesion strength can be obtained. The deposition of the coatings is achieved at a splat level, however limited research exists that investigates the effect of the deposition conditions on the adhesion strength of the splats. New testing techniques are therefore required for the testing of the bond strength of the individual cold spray splats. The particle bond strength was shown to affect the microindentation hardness measurement and tensile properties of the coatings however the research on this topic is sparse. At the same time, the mechanical properties of the cold spray coatings are also affected by the grain refinement and strain hardening of the cold sprayed materials. Nanoindentation mapping can be used for classification of the hardness distribution within the cold spray splats and coatings attributed to grain size. Furthermore, Nix and Gao strain gradient plasticity model can be applied to measure the true coating nanoindentation hardness independent of the indentation load or microscopic coating defects. The comparison between nanoindentation and microindentation hardness measurements can be then used to measure the extent to which the coating porosity and poor particle cohesion strength affect the microindentation hardness measurements in the coatings.
Chapter 3. Experiment Procedure

3.1 – Cold Spray Deposition

Cold Spray deposition was carried out at the McGill Aerospace Materials and Alloy Development Center (MAMADC) located at the Industrial Materials Institute (IMI) NRC-CNRC Boucherville with a Kinetic 4000 cold spray gun (CGT Technologies, Germany) shown in Figure 3.1a. Nitrogen or Helium gas was used as the propelling gas and was pressurized from 1 MPa to 4 MPa and preheated to temperatures ranging from 25˚C to 800˚C. The gas line carrying the preheated and pressurized gas is shown in Figure 3.1b.

![Figure 3.1: Cold Spray System (MAMADC lab, CNRC- IMI Boucherville, Quebec, Canada) showing: a) cold spray gun, b) gas line, c) powder feeder, d) MOC24 nozzle e) big robot arm and f) small robot arm.](image)

The powder was delivered into the cold spray gun from the powder feeder (shown in Figure 3.1c) at a rate of 1 to 20 g/min. The feedstock powder was accelerated with nitrogen gas through MOC24 nozzle (Figure 3.1d), reaching in-flight particle velocities between 580
and 850 m/s. Higher velocities, up to 1140 m/s, were obtained with helium gas when powder was accelerated through a VH70 (ASB Industries Inc., Barberton, USA) nozzle (not shown).

The feedstock powder was commercially pure titanium (Grade 1) or Ti6Al4V powder produced by plasma atomization (Raymore Industries, Inc.) (see Figure 3.2). The Ti and Ti6Al4V particles had a spherical morphology and an average particle diameter of 29 µm. The size distribution of the powder was measured with a laser scattering particle size distribution analyzer (HORIBA LA-920 ATS Scientific Inc., Burlington, Ontario) [112]. In chapter 7, some tests were also carried out using a commercially pure Ti powder with a non-spherical morphology. The powder had an average particle diameter of 63 µm previously reported by A. Rezaeian et al. [13] and was produced by HC Starck (HC Starck GmbH, Goslar, Germany).

![Figure 3.2: SEM images for the a) Ti Powder and b) Ti6Al4V Powder [113]](image)

The cold spray gun and the substrate were mounted onto the automated robotic arms (shown in Figure 3.1e and f), allowing a wide range of gun and substrate motions. Single splats and multilayer coatings were produced by changing the gun or substrate traverse speed and by changing the powder feeding rate.

3.1.1 – Cold spray splat deposition

In Chapters 4, 5 and 6, single cold spray splats were deposited by using a gun or a stage traverse speed of 1000 mm/s and at low powder feeding rate of 1 - 5 g/min. Multi-pass splats,
consisting of two splat layers, were produced by increasing the number of gun passes over the substrate surface. In Chapter 4, a mild steel substrate was used, in Chapters 5 and 6 Ti or Ti6Al4V splats were deposited on Ti or Ti6Al4V substrates. The substrates were left in as-received surface state, except for degreasing with acetone. In Chapter 5 and 6, the substrates were also preheated to 400°C on a hearing stage containing three heating elements. The substrate temperature was controlled with a thermocouple that mounted into the heating stage.

3.1.2 – Cold spray coatings deposition

For deposition of coatings, the powder feeding rate of 20 g/min and the gun or the stage traverse speed of 330 mm/s were used. Two types of coatings were produced and consisted of one pass coatings and multi-pass coatings. Single pass coatings were used in Chapter 4 and were deposited by moving the gun over the grit blasted steel substrate back and forth over the same pass (~1 cm in width) until a coating of 16 layers was produced.

Another type of coatings consisted of multi-pass coatings where the entire substrate surface was covered (1”- 3” in width) with 10 to 40 layers of coating with total of 6-12 gun passes. The coatings were deposited on steel in Chapter 4 and 7 and on Ti substrates in Chapter 8. The steel substrates were grit blasted with 24 grit alumina particles prior to the coating deposition and were then cleaned with pressurized air. Ti substrates were left in as received surface state and were only degreased with acetone.

3.1.3. – Deposition Conditions and Velocity Measurement

Splat and coatings were deposited with nitrogen or helium gas at increasing deposition velocities by changing the gas preheat temperature and pressure within the cold spray gun. The cold spray deposition conditions used are listed in Table 3.1. The conditions carry the number corresponding to the thesis chapters in which they were used.

The velocity of particles for each deposition condition listed in Table 3.1 was measured in free jet with a DPV2000 (Tecnar Automation, St. Bruno, QC, Canada). The DVP system consisted of a laser that was aligned perpendicular to the particle jet and towards an optical detector shown in Figure 3.3a.
Table 3.1: Gas conditions used for the deposition of Ti cold spray splats and coatings

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>Chapter</th>
<th>Helium</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Temperature (°C)</td>
<td>Gas Pressure (MPa)</td>
<td>#</td>
<td>Gas Temperature (°C)</td>
</tr>
<tr>
<td>300</td>
<td>2</td>
<td>4,6</td>
<td>25</td>
</tr>
<tr>
<td>300</td>
<td>3</td>
<td>4,6,7,8</td>
<td>25</td>
</tr>
<tr>
<td>300</td>
<td>4</td>
<td>4,6</td>
<td>50</td>
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<td>4,7,6,8</td>
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<td>500</td>
<td>4</td>
<td>4,5,6</td>
<td>350</td>
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<td>350</td>
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<td>4,6,7</td>
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<tr>
<td>800</td>
<td>4</td>
<td>4,5,6,7,8</td>
<td></td>
</tr>
</tbody>
</table>

The optical detector was equipped with a two slit photomask. As the particles traveled through the laser and in from of the optical detector, they scattered the light at different intervals between the two slits. The data was recorded as a function of signal intensity and time. The software measured the particle velocity by dividing the distance between the two slits by the time interval of the scattered light according to Eq. 3.1. In Eq.3.1, \( s \) stands for the distance between the two slits in the photomask, while \( TOF \) is the time of flight which is the time slot between the two signals as can be seen in Figure 3.3b [114].

![Figure 3.3](image_url)

*Figure 3.3: DPV 2000 System a) Optical Detector, b) Two peak signal with a two slit photomask [114].*
An average velocity of 1000 – 3000 particles for each deposition condition was measured at 4 cm distance from the gun nozzle with nitrogen gas and at 8 cm with helium gas. The same substrate distance away from the nozzle was used during cold spray deposition of splats and coatings. Some of the velocity measurements were carried by the author of the thesis while others were measured by the collaborators [14, 115]. In most cases, the velocity measurements were repeated prior to the sample preparation in order to take into account the changes made to the cold spray system over the years.

3.1.4 – Deposition Efficiency Measurement

The efficiency of the cold spray process was measured in terms of the deposition efficiency DE, by taking the ratio of the weight of the deposited powder \( W_d \) over the weight of the cold sprayed powder \( W_s \) according to Eq.3.2. The weight of the deposited powder, \( W_d \), was determined by subtracting the weight of the substrate from the weight of the cold sprayed sample according to Eq.3.3. The weight of the sprayed powder, \( W_s \), was calculated by multiplying the feeding rate of the sprayed powder \( \bar{m}_p \) by the distance traveled on the sample \( L_s \) and divided by the speed of the traveling gun \( v_{gun} \) according to Eq. 3.4.

\[
DE(\%) = \frac{W_d(g)}{W_s(g)} \times 100 
\]

Eq.3.2
\[
W_d(g) = W_{sample}(g) - W_{substrate}(g) 
\]

Eq.3.3
\[
W_s(g) = \frac{\bar{m}_p(\frac{g}{m_{\text{min}}})L_s(m)}{v_{gun}(\frac{m}{\text{min}}) \times 60(\frac{m}{\text{min}})} 
\]

Eq.3.4

3.2 – Polishing Procedure

The cold sprayed samples were cut in cross-section, and mounted into cold mount epoxy. In order to prevent sample charging during scanning electron microscopy, some samples were also mounted into the cold mount epoxy with conductive filler consisting of
nickel powder. The samples were then ground with 320 grit paper followed by 600, 800 and 1200 grit grinding papers. After the grinding steps, the samples were polished with 0.05 μm colloidal silica and 10% hydrogen peroxide solution for 20 - 40 min in order to remove any surface defects induced by the grinding steps. The samples were then etched with the Kroll reagent consisting of 2-3% HNO₃, 1% HF and distilled water. After etching, the samples were vibratory polished with 0.05 μm colloidal silica for 24 hours. The etching and vibratory polishing steps were repeated a couple of times.

3.3 – Light Optical Microscopy (LOM)

The images of splats were examined with light optical microscope (LOM) in Chapters 4 and 6. Image analysis software (Clemex Vision Professional 5.0, Clemex Technology Inc., Longueuil, QC, Canada) was used to measure the height and width of the cold spray splats from LOM images of splat cross-sections similar to the one shown in Figure 3.4. Splat width - w, to height - h, ratio was then used to calculate the splat flattening ratio. Flattening ratio is a measure of degree of splat deformation and is described in Eq. 3.5 [3, 116]. Typically, a flattening ratio of 5 - 30 splats was calculated and an average value was taken for each deposition condition. The standard deviation on the mean was used as the error bar.

Figure 3.4: Micrograph of the cross-section of a Ti splat obtained by LOM. The flattening ratio was measured from images such as these to examine the extent of deformation of Ti splats as a function of deposition velocity [112].
The flattening ratio was only measured for splats that were polished near the center of the splat. The definition of the splat center was made possible by the transparent nature of the cold mount epoxy. Furthermore, the geometry of the splats (deposited from the spherical powder) was self-similar in the vicinity on the splat center and the flattening ratio measurements were not affected by the slight offset of the splat cross-section from the actual position of the splat center.

LOM was also used to characterize the thickness of cold spray coatings. Each coating was imaged at x50 magnification and the coating thickness was measured with Clemex software from the coating cross-sections.

3.4 – Scanning Electron Microscopy (SEM)

A variable pressure scanning electron microscope (Hitachi VP-SEM, Japan) was used to characterize the interface between the Ti or Ti6Al4V splats and Ti or Ti6Al4V substrates at x1000x to x2000 magnification. The quality of the interface between the splats in the substrate was defined by lack of porosity within the bonded regions. In chapter 6, etched SEM images of splats were used to measure the flattening ratio of Ti splats deposited on Ti substrate according to Eq.3.5.

VP-SEM images of the coating cross-sectional collected in a backscattered mode were used to measure the coating porosity. For each coating, a total of ten micrographs were collected at x500 magnification with the exception of Chapter 4 where the porosity was measured at x200 magnification. The backscattered images were taken from coating cross-sections at a distance of a few millimetres away from the substrate interface and the coating surface. Average porosity was measured across the coating thickness with Clemex image analysis software. The porosity of a commercially pure Ti plate of 3 mm thickness (McMaster-Carr, Aurora, OH) was measured in the same manner as described above. In most cases, VP-SEM was operated at 5-10 keV voltage at 7-8 mm working distance in the scanning mode. 20 keV voltage and 15 mm working distance was used in the backscattered mode.
Channelling contrast images of the cold spray splats and coatings were obtained with Hitachi SU8000 Scanning Electron Microscope (Hitachi, Japan). SEM images of Ti splats and coatings were obtained at 5x - 30x magnifications in backscattered mode at 5 keV voltage. The channelling contrast and high resolution of the microscope was ideal for imaging of very fine, nano-sized grains and twins in splats and in the coatings. In Chapter 5, the SU8000 was used to measure the grain size and twin density within the splats. The grain size was measured manually by taking the average of two perpendicular diagonals in each grain. The average diameter of 30 – 100 grains was taken in different regions within the cold spray Ti splat with standard deviation used as an error bar. The twin density was measured by calculating the number of twins within a given area and according to the method used by Chichhili et al. [29].

3.5 – Electron backscatter diffraction (EBSD)

The electron backscatter diffraction was performed with Philips XL30 FEG-SEM equipped with TSL software. The accelerating voltage was set to 20 keV while the working distance was maintained at 15 mm. The step size was ranged between 50 nm and 200 nm and dictated the resolution of the images taken. The inverse pole figures were obtained with TSL software which color coded the grain orientation. Red color was assigned to grains orientation in [001] direction, blue for grain oriented in [101] direction and green was used for crystallographic [111] direction. The grain boundaries and grains below 50nm were not imaged and appeared as black data points in the EBSD map.

3.6 – Nanoindentation Testing

Two nanoindenter systems were used to measure the mechanical properties of cold spray coatings, a Hysitron Ubi 3 and a Hysitron Triboindenter. Hysitron Ubi 3 (Hysitron Incorporated, Minneapolis, MN, USA) can be seen in Figure 3.5. Both systems were equipped with a transducer, a Piezo Scanner and top down optics allowing image magnification of up to 20x on the Ubi 3 and up to 500x on the Triboindenter.
The transducer is the main component in the Hysitron system since it controls the load and displacement during indentation. The transducer consists of two electrodes (plates) with an AC current at 180° out of phase with each other. A third plate is placed between the anode plates and carries the indenter tip, Figure 3.6 [68]. The load is applied with a DC bias (up to 600 V) exerted onto the bottom plate which creates electrostatic attraction forces between the central and bottom plates.

The magnitude of the load applied is calculated according to the applied voltage. The tip interaction with the specimen induces a change in the voltage at the central plate. The change in the voltage has a linear relationship with the position of the central plate and is used to measure the tip displacement [68]. The applied load and tip displacement can be therefore measured during the indentation as load/unload curves similar to the one shown in Figure 3.7 [68].
In the present work, the hardness was calculated from load/unload curves by Oliver and Pharr method [104] and according to Eq. 3.6. In Eq.3.6, the hardness is a function of the peak load - $P_t$ (which was assigned), and the Berkovich indenter projected area - $A_p$, that is a function of the indentation contact depth - $h_c$, (see Eq.3.7). In Eq. 3.7, $C_o$, $C_1$, $C_2$ and $C_3$ are constants that are used to describe the area function of the tip, accounting for roughness and tip defects. For an ideal Berkovich tip, $C_o$ is 24.5. The tip area function for the Berkovich indenter, as per Eq. 3.7, and frame compliance of the instrument were calibrated on a fused quartz standard. These results were periodically checked prior to the nanoindentation testing.

\[
H = \frac{P_t (N)}{A_p (m^2)} \tag{Eq.3.6}
\]

\[
A_p = C_o h_c + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} \tag{Eq.3.7}
\]

In Eq. 3.7, indenter contact depth, $h_c$, was calculated from the load/unload curves according to Eq. 3.8. The contact depth is a function of the indenter penetration depth - $h_f$ and material stiffness - $S$ which is a slope of the unloading segment of the indentation load versus indentation depth described in Eq.3.9 [104]. The indenter shape geometry is taken into account by the geometry factor - $\varepsilon$. For a Berkovich indenter, geometry factor is 0.72 [104].
\[ h_c = h_f - \varepsilon \left( \frac{p_s}{S} \right) \quad \text{Eq.3.8} \]
\[ S = \frac{dP}{dh} = \frac{2Er\sqrt{Ap}}{\sqrt{\pi}} \quad \text{Eq.3.9} \]
\[ Er = \left[ \left( \frac{1-v_i^2}{E_i} \right) + \left( \frac{1-v_m^2}{E_m} \right) \right]^{-1} \quad \text{Eq.3.10} \]

The stiffness of the material can be also described as a function of the reduced elastic modulus of the material (see Eq.3.9). The reduced elastic modulus, \( Er \) consists of an inverse of the sum of Poisson ratios of the material - \( \nu_m \), and indenter - \( \nu_i \), divided by their respective elastic modulus \( E_m \) and \( E_i \). Eq.3.10 summarized this relationship [68].

### 3.6.1 – Profile Nanoindentation

Profile nanoindentation was performed in Chapter 4 with Hysitron Ubi3 at 1 mN load and 200 \( \mu \)N/s loading and unloading rate with 1 second hold time. 40 to 50 indents were indented at 20 to 40 \( \mu \)m indent spacing across the cold spray coating cross-section. The indentation was carried from the substrate and across the coating thickness. The diagram of profile indentation is shown in Figure 3.8.

![Figure 3.8: Diagram of profile indentation of the cold spray coating](image)

### 3.6.2 – Nanoindentation Mapping

Nanoindentation mapping was performed with Hysitron Triboindenter at 1mN load and 200 \( \mu \)m/s loading and unloading rate with 1 second hold time. A matrix of 200 to 400
indents spaced at 2.5 μm indent spacing was carried on individual cold spray splats and inside of the cold spray coatings. The top down optics were used to precisely position the indentation matrix at the center of the desired splat. The diagram of the matrix indentation on splats and coatings is shown in Figure 3.9a and b respectively.

![Figure 3.9: Diagram of nanoindentation matrix in a) cold spray splat and b) cold spray coating.](image)

The hardness and reduced modulus from the indentation test were plotted with graphing software (Origin 8.1, OriginLab Corp., Northampton, MA, USA) as a function of color and indent position in the matrix. The color scale was treated from blue, green, yellow and red with increase in the hardness and elastic modulus values. The black color was selected to represent the indents demonstrating low hardness and reduced modulus of epoxy and for indents affected by the coating porosity. The nanoindentation maps were performed on splats and coatings in Chapter 4 while only splat mapping was used in Chapter 5.

### 3.6.3 – Varied Load Indentation

Varied load indentation testing was performed with Hysitron Ubi3 in Chapters 7 and 8. Two matrix indentations of 2 by 4 indents and 2 by 5 indents were performed. For the first matrix, the indentation load was increased by the increments of 2.375 mN from 1 to 20 mN. For the second matrix, the load was increased by rate of 1.4461 from 500 nm to 20 mN. By using the rate increment, more indents can be obtained at lower loads. The segment times were kept at 5 second loading and unloading and 1 second hold time. The indent spacing for
both matrixes was kept 10 μm apart. Figure 3.9a and b demonstrates the two matrix diagrams. In Chapter 7, the varied load indentation was performed using the indentation matrix in Figure 3.10a while in Chapter 8 both indentation matrices were used. Ten matrices were placed randomly within the coating. The indentation results were analysed and the average hardness and elastic modulus were taken for each indentation load after data filtering. The standard deviation was used as an error bar.

Figure 3.10: Varied loading indentation matrix a) 2 by 4 with increment of 2.375 mN and b) 2 by 5 with increment rate of 1.4461.

3.6.4 – Data Filtering

During data analysis, the load unload curves were used for filtering of the indents affected by the sample porosity and particle de-bonding. The indentation into the pores or particle de-bonding resulted in a drastic increase in the indentation depth which affected the loading and unloading segment of the load/unload curve as shown in Figure 3.11. The change in the indentation depth and change in the unloading segment affected the measurements of hardness and reduced modulus. For that reason, the indentation curves demonstrating the behavior similar to indents 1, 2 and 3 were filtered out and were not included into the measurements of hardness and elastic modulus.
Figure 3.11: SEM image of 1-20 mN load nanoindentation indents in cold spray Ti coating and corresponding indentation load vs. indentation depth curves. A more pronounced decrease in the indentation depth was measured for the indents affected by the coating porosity (indent 1) and particle de-bonding (indents 2 and 3) [117].

3.7 – Microindentation Testing

In Chapters 4, 7, 8 the microindentation was performed with Clark Microhardness Tester CM-1000AT with a Vickers diamond indenter. In Chapter 4, the indentation was performed at 0.1 N load while in Chapters 7 and 8 the indentation loads of 0.1 – 5 N were used. Indent diagonals were measured by optical means at x500 magnification. The difference between the two diagonals was typically very small (0 – 7 % difference), but in cases where indents interacted strongly with coating defects (e.g. porosity) the difference was as large as 17 %. Vickers hardness, VH, was calculated by dividing the applied force (in kg) by the indent surface area in the standard manner [118]. However, for a comparison between the nanohardness, the Vickers hardness were converted to the units of GPa and a hardness, $H_{micro}$, based on a projected contact area of the Vickers indenter [66, 67, 118, 119]:

$$H_{micro}(GPa) = \frac{VH \times 9.8 \text{ m/s}^2}{1000 \times \sin 68^\circ}$$

Eq.3.11
Microindentation hardness values reported in Chapters 4, 7, 8 were calculated with Eq. 3.11 and are referred to as “microhardness”. Five indents, spaced at three indent spacing’s, were performed at a given load and the average hardness was reported with standard deviation as the error bar.

\[
h_{\text{micro}} = \sqrt{\frac{A_{\text{Vickers}}}{24.5}} = \sqrt{\frac{l_1l_2}{2\times24.5}} \quad \text{Eq. 3.12}
\]

In Chapters 7 and 8 the indentation depth - \( h_{\text{micro}} \) was measured according to Eq.3.12. In Eq.3.12 the indentation depth is a function of Vickers projected area - \( A_{\text{Vickers}} \), which is a function of the indenter diagonals \( l_1 \) and \( l_2 \) [66].

3.8 – Splat Adhesion Testing

Splat adhesion testing was performed using a Micro-Combi Scratch Tester (CSM Instruments, Inc., Needham, MA, USA) with a wedge shaped indenter [45]. The adhesion strength of splats was measured by applying a normal force, \( F_N \) of 30 or 300 mN onto the wedge shaped tip (100 µm in width) that was placed a distance of approximately 30 - 40 µm away from the splat. The substrate was then moved below the tip at 150 µm/min rate, as indicated schematically in Figure 3.12.

The adhesion strength of the splat was calculated as a function of tangential force, \( F_T \), exerted on the tip, the baseline force \( F_B \) and the splat area, according to Eq.3.13. The apparent splat area - \( A_s \), was measured prior to splat shearing according to Eq.3.14, where \( w \) is splat diameter measured with LOM on the scratch tester by taking the average width of the splat in x and y axis.

\[
\text{Adhesion Strength (MPa)} = \frac{F_T-F_B}{A_s} \quad \text{Eq.3.13}
\]

\[
\text{Area} = \pi \left(\frac{w}{2}\right)^2 \quad \text{Eq.3.14}
\]
Figure 3.12: A schematic diagrams of splat adhesion testing. On the left, a cross-sectional view and, on the upper-right, a top-down view of the test are provided. In the upper right, the cross-section area of the splat is noted, which is used in the calculation of the splat adhesion strength. In the lower-right, an example of the force-displacement curve obtained during the shearing of a splat[113].

For each deposition condition, 5-10 splats were tested. A narrow range of splat diameters, as observed with the microscope on the scratch tester, were chosen for each sample such that a similar pre-impact diameter was tested for all conditions. In Chapter 6, the particle pre-impact diameter - $D$, was calculated by assuming that upon the impact the splats deform from a spherical geometry into oblate spheroid geometry and according to Eq. 3.15:

\[
D \ (\mu m) = (w^2 h)^{\frac{1}{3}} = \left(\frac{w^3}{FR^3}\right)^{\frac{1}{3}} \tag{Eq.3.15}
\]

The height of the splat – $h$, was determined from the average splat flattening ratio – $FR$ where $h = w/FR$ (see Eq. 3.5). The average $FR$ was determined from splat cross-sections.
according to Eq.3.5 for all deposition conditions prior to splat adhesion testing. The average pre-impact diameter of the tested splats for all deposition conditions was calculated to be 34 ± 5 μm, and was close to the average size of the particles in the feed-stock powder (29 μm). The assumption of the oblate spheroid geometry has been used in the past in a method developed by Kim et al. [10] which uses an image analysis routine to measure the entire area of a splat cross-section. Method, using Eq. 3.15, is a simpler version that can be used to estimate the pre-impact diameters for splats that are tested by the splat adhesion technique.

3.9 - Profilometry

In Chapter 7, the surface roughness of the substrates was measured with a contact profilometer (Veeco Instruments, CA, USA). The average surface roughness (Ra) was determined from 6 line scans of 1 cm in length carried at 1.25 mm/s and 10 mg load on Ti and Ti6Al4V substrate. The scans were carried along and across the substrate length.

3.10 – Tensile Testing

In Chapter 8, tensile testing was performed with MTS tensile testing machine on as deposited and annealed titanium cold spray coatings. The coatings were electrical discharge machined (EDM) into the tensile bars with 2 mm by 2 mm gage width and thickness and 8mm gage length (see Figure 3.13a). The cold spray coatings were 5 - 7 mm thick and the tensile bars were cut perpendicular to the cold spray direction (see Figure 3.13b). The tensile bars were cut according to the dimensions proposed by F. Gartner et al. [21] and according to E8 ASTM standard.

The surface of the tensile bars was ground in steps of 320, 400 and 600 grit grinding papers and cleaned in the ultrasonic bath with acetone for 5 min. The tensile testing was performed by initially preloading the samples to 30 mN load in order to secure the grips. During the test, the strain rate stayed constant at 0.01s⁻¹. The tensile testing was then performed until the tensile fracture point.
3.11 – Annealing

In Chapter 8, annealing was performed in vacuum (4x10^{-5} torr) for 1 hour at 800°C with SBII Linberg furnace (Sola Basic Industries, Watertown, Wisc. USA). In order to reduce the oxygen pickup, Ti sponge was placed next to the samples during the heating stages. The samples were then air cooled to room temperature.
Chapter 4. Mechanical Property Mapping of Cold Sprayed Ti Splats and Coatings

The present chapter explores the effect of the cold spray deposition velocity on the deformation mechanisms and bonding of titanium splats and deposition efficiency of the coatings. Profile nanoindentation and nanoindentation mapping were used to investigate the mechanical properties of commercially pure cold spray Ti splats and coatings. Nanoindentation mapping was performed on splats and three regions in the cold spray Ti splats were identified: the splat impact region, the jetting region and the upper splat region. The hardness in the jetting region was measured to be low in comparison to the hardness directly at the splat impact site and was similar to the hardness in the upper splat region. In the coatings, an overall increase in the hardness, when compared to the feedstock powder, was measured. The coating hardness and elastic modulus did not change significantly with increase in the coating deposition velocity and the measurements remained constant across the coating thickness. A correlation between the mechanical properties and the presently known deposition temperature, stress and dislocation density models were made.

4.1 - Introduction

Cold Spray is an emerging coating deposition process [1] that is carried out at relatively low temperature condition [2, 3]. The deposition is achieved by powder acceleration to supersonic velocities. Upon the supersonic particle impact, the material undergoes plastic deformation which initially results in a conformal material adhesion [3]. At high enough deposition velocities, the particles undergo adiabatic shear instability where a localized fluctuation in the pressure and strain leads to a localized rise in the material temperature followed by the material jetting [4-8].

Much of the current understanding of the cold spray process has been garnered by experimentation and modeling of the deposition of Cu [5, 7-12]. Significant interest is placed on the temperature rise near the impact site and especially in the jetting region as this can have a profound effect on the final microstructure of cold spray coatings. For Cu, a temperature rise of up to 1200K was estimated for the particle impacting at the deposition velocity of 600m/s [4]. While the volume of research on Ti is less, similar studies revealed details of the interface phenomenon for this material [13-22]. S. H. Zahiri et al. [14] as well
as J. Vlcek et al. [27] reported a metallurgical material bonding that was observed in the jetting region in cold sprayed Ti. Also, S. H. Zahiri et al. [14] believed that high temperature fluctuations induced material softening and grain recrystallization with preferential grain orientation in Ti cold spray splats. Using transmission electron microscopy, K.H. Kim, et al. showed both regions of high dislocation density at the impact site of the splat with the substrate [23] and regions of recrystallization [24]. Thus, a complex and varied microstructure is observed in cold sprayed Ti that may also result in a variation in local mechanical properties.

In this study, the hardness mapping of cold sprayed Ti splats and coatings was used to investigate the presence or lack of thermal softening, which could be associated with material melting in the jetting region. The work carried out is based on a nanoindentation mapping of individual Ti cold sprayed particles deposited at various deposition velocity conditions. The variation in mechanical properties within individual cold spray splats and also within coatings was determined. Nanoindentation technique was used to provide a better understanding of the deposition mechanisms of cold spray Ti splats deposited at various deposition velocity conditions. The effect of the deposition velocity conditions on the mechanical properties of the coatings was investigated.

4.2 - Results and Discussion

4.2.1 – Microstructure of cold sprayed splats

The appearance of cold spray splats was found to vary as a function of deposition velocity, revealing features distinctive to the deposition mechanisms. Representative SEM images of splats deposited at velocities between 579 m/s and 825 m/s (see Figure 4.1) all showed material jetting, indicating the presence of adiabatic shear instability [4]. However, the jetting phenomenon increased with increase in the splat deposition velocity.

The increase in material deformation and material jetting with deposition velocity was further revealed by examination of splat cross-sections (see Figure 4.2(a), (b) and (c)). As deposition velocity increases, the flattening ratio increases (see Figure 4.2(d)). For a nondeformed powder particle the flattening ratio is 1. The flattening ratio of the splats deposited over a range of 570 m/s to 825 m/s increases from 1.8 to 4. The increase from 1 to
1.8 appears to be largely due to material deformation upon impact (minimal jetting at lower velocities), while the increase from 1.8 to 4 seems to be primarily associated with an increase in material jetting. Aside from material jetting other interesting features were observed that were due to the interaction of Ti particles.

![Micrographs of (SEM) of Cp Ti splats deposited at: a) 300°C, 2 MPa (580m/s), b) 300°C, 4 MPa (642m/s), c) 500°C, 2 MPa (636m/s), d) 500°C, 4 MPa (724m/s), e) 750°C, 3 MPa (770m/s) and f) 800°C, 4 MPa (825m/s) gas preheat temperature, gas pressure and particle velocity.](image)

*Figure 4.1: Micrographs of (SEM) of Cp Ti splats deposited at: a) 300°C, 2 MPa (580m/s), b) 300°C, 4 MPa (642m/s), c) 500°C, 2 MPa (636m/s), d) 500°C, 4 MPa (724m/s), e) 750°C, 3 MPa (770m/s) and f) 800°C, 4 MPa (825m/s) gas preheat temperature, gas pressure and particle velocity.*
Figure 4.2: Micrographs (LOM) of Ti splats cross-section deposited at a) 300°C, 4 MPa (642m/s), b) 500°C, 4 MPa (724m/s), c) 800°C, 4 MPa (825m/s) gas preheat temperature, gas pressure and particle velocity and d) the flattening ratio with standard deviation of Ti splats with respect to the splat deposition velocity.

At a deposition velocity of 636 m/s (see Figure 4.3), a crater formation can be seen at the impact site of the splat. The impact of the splats resulted in a plastic deformation in shape of the impacted body, typical of deformation contributing to a conformal splat adhesion mechanism. While there is also material jetting evident for this splat, the splat has pulled away and partially de-bonded. At higher deposition velocities, this de-bonding was not as pronounced.

Figure 4.3: Micrographs (SEM) of splats deposited at 500°C, 2 MPa (636 m/s) and demonstrating a conformal particle adhesion.
In Figure 4.4, a splat deposited at 770 m/s also appears to have partially pulled away. However, in this case, a region where the jetting region remains attached is observed. While impact angle and location of impact has an effect on these observations, the number of events resembling Figure 4.4 generally increased with deposition velocity and the number of events resembling Figure 4.3 generally decreased with deposition velocity. Thus, the increase in jetting with deposition velocity was a significant mechanism for bonding of particles in multi-pass splats.

At higher deposition velocity conditions, the jetting phenomenon becomes more pronounced and evidence of stronger splat adhesion is observed. Figure 4.4 shows a Ti splat deposited on a previously deposited Ti splat at the deposition velocity of 770 m/s. The close up of the splat shows a continuous bond between two splats in jetting region which could point to a formation of the metallurgical bond in that region [20].

![Figure 4.4: Micrographs (SEM) showing ductile fracture in the jetting region of CP Ti splat deposited at 750°C, 4MPa (770m/s).](image)

4.2.2 – Microstructure of cold sprayed Ti coatings

Figure 4.5 shows cross-sectional images of three Ti coatings that were produced at deposition velocities of 642 m/s, 724 m/s and 825 m/s. The coating thickness ranged from 0.9 mm to 1.4 mm. The coating porosity decreases with increase in the deposition velocity and dense coatings with porosity below 2% are produced at deposition velocity above 724 m/s. Figure 4.6(a) shows the effect of the deposition velocity on the Ti coating porosity. The deposition efficiency of the coatings increases with increase in the deposition velocity and
reaches 100% above the deposition velocity of 725 m/s. The transition coincides with the increase in the flattening ratio observed in Figure 4.2.

Figure 4.5: Micrograph (SEM) of cold spray Ti coating deposited at: a) 300°C, 4 MPa (642 m/s), b) 500°C, 4 MPa (724 m/s) and c) 800°C, 4 MPa (825 m/s).

The coatings discussed in this paper consist of single line coatings where the particle impact angle is different from standard multi-line coatings. Some differences in coating porosity measurements and deposition efficiency are expected between coatings produced here and those produced at similar conditions, but as multi-line coatings [22]. Single line coatings were chosen for this study because the particle jet center was easily connected to the center of the coating cross-section, avoiding any concerns over variation of velocity within the jet affecting the measurements [2].

Figure 4.6: Graphs of a) porosity with a standard deviation and b) deposition efficiency of cold spray Ti coatings versus powder deposition velocity.
4.2.3 – Nanoindentation mapping of cold sprayed splats and multi-pass splats

Mechanical property mapping was carried out on the cold spray Ti splats and feedstock Ti powder. Figure 4.7 depicts the distribution of hardness and modulus of feedstock Ti powder and cold spray splats deposited at 642 m/s, 724 m/s and 825 m/s.

![Image of hardness and modulus maps of Ti powder for Ti splat deposited at: 300°C, 3 MPa (642 m/s); at 500°C, 4 MPa (724 m/s) and at 800°C, 4 MPa (825 m/s). Micrographs (LOM) of the splats and powder are provided on the left-hand side. The hardness and reduced modulus color scale bars are provided on the right-hand side with black demonstrating lower end values and grey showing higher end values.](image)

The color notation is interpolated between the measurements from indented data points. The color scale has a gradient of 0.2 GPa for hardness and 10 GPa for elastic modulus. The upper and lower limits of the hardness and modulus color scale are annotated by grey and black while white indicates missing data points. In Figure 4.7, black regions represent the measurements made in the epoxy which has low hardness, below 2.2 GPa, and
modulus, below 80 GPa. The regions in grey can be found in the mild steel substrate that has a higher elastic modulus when compared to titanium. For comparison, the optical images of the indented cold spray splats are shown at the left-hand side of Figure 4.7.

Nanoindentation maps reveal that the hardness distribution inside of the cold spray splats or feedstock powder is not homogeneous (see Figure 4.7). In the feedstock powder, high hardness of 3.6 GPa to 3.8 GPa is measured at the powder outer surface layer. A martensitic microstructure was often observed in this region, possibly a result of surface tension during the powder production through a plasma atomization process. However, in splats, high hardness regions are mainly observed at the splat impact site with the substrate material. The hardness in these regions reaches 4.2 GPa and is color coded in red. Relatively lower hardness of 3.0 - 3.4 GPa is measured in the upper splat portion. In Table 4.1, the average hardness and modulus of the splats have been calculated. The average splat hardness does not increase significantly with increase in the deposition velocity. The splats hardness is, however, higher than that of the feedstock powder. The modulus of the single splats is similar to the modulus of the feedstock powder.

Table 4.1 Mechanical properties of cold spray Ti coatings and Ti splats

<table>
<thead>
<tr>
<th>Specimen/Conditions</th>
<th>Deposition Velocity (m/s)</th>
<th>Deposition Efficiency (%)</th>
<th>Coating Porosity (%)</th>
<th>Coating Hardness (GPa)</th>
<th>Coating Modulus (GPa)</th>
<th>Splat Flattening Ratio</th>
<th>Splat Hardness (GPa)</th>
<th>Splat Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti Powder/As-Polished</td>
<td>N/a</td>
<td>N/a</td>
<td>&lt;1</td>
<td>3.1±0.3</td>
<td>107±9</td>
<td>N/a</td>
<td>3.1±0.3</td>
<td>107±9</td>
</tr>
<tr>
<td>Ti/300°C, 2 MPa</td>
<td>580</td>
<td>19</td>
<td>18.0±10.1</td>
<td>3.2±0.3</td>
<td>99±11</td>
<td>1.8±0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti/300°C, 3 MPa</td>
<td>625</td>
<td>30</td>
<td>2.5±0.3</td>
<td>3.6±0.2</td>
<td>112±12</td>
<td>2.0±0.2</td>
<td>3.4±0.4</td>
<td>103±9</td>
</tr>
<tr>
<td>Ti/300°C, 4 MPa</td>
<td>642</td>
<td>49</td>
<td>5.9±1.5</td>
<td>3.7±0.2</td>
<td>116±13</td>
<td>2.2±0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti/500°C, 2 MPa</td>
<td>636</td>
<td>76</td>
<td>7.4±1.6</td>
<td>3.6±0.4</td>
<td>117±10</td>
<td>2.4±0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti/500°C, 3 MPa</td>
<td>694</td>
<td>83</td>
<td>1.4±0.6</td>
<td>3.7±0.3</td>
<td>120±11</td>
<td>2.5±0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti/500°C, 4 MPa</td>
<td>724</td>
<td>91</td>
<td>2.1±0.6</td>
<td>3.5±0.3</td>
<td>109±8</td>
<td>2.3±0.4</td>
<td>3.6±0.4</td>
<td>119±6</td>
</tr>
<tr>
<td>Ti/750°C, 3 MPa</td>
<td>770</td>
<td>100</td>
<td>0.7±0.1</td>
<td>3.7±0.4</td>
<td>120±7</td>
<td>3.0±0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti/800°C, 4 MPa</td>
<td>825</td>
<td>100</td>
<td>1.3±0.3</td>
<td>3.5±0.3</td>
<td>121±6</td>
<td>3.9±1.0</td>
<td>3.7±0.4</td>
<td>110±7</td>
</tr>
</tbody>
</table>

As opposed to the single pass splats, multi-pass splats showed an increase in the modulus. In Figure 4.8, modulus of 120 GPa and higher is measured in the splats deposited above 500°C gas preheat temperature. As the gas preheat temperature increases to 800°C, the modulus of the splats increases up to 130 GPa. In multi-pass splats, higher hardness is found both at the impact site between splats and near the steel substrate. In Figure 4.8, multi-pass titanium splats deposited at 642 m/s, 724 m/s and 825 m/s are shown along with hardness and
modulus maps. Regions of 3.7 - 4.2 GPa hardness were measured in the impact region between two splats as well as in the impact region of the splat on the steel substrate. However, in the jetting region, a lower hardness of 3.2 - 3.4 GPa was measured for the 825 m/s splat.

![Table and Image]

Figure 4.8: Hardness and reduced modulus of the multi-pass splat deposited at 300°C, 3 MPa (642 m/s); at 500°C, 4 MPa (724 m/s) and at 800°C, 4 MPa (825 m/s). Micrographs (LOM) of the splats and powder are provided on the left-hand side. The hardness and reduced modulus color scale bars are provided on the right-hand side with black demonstrating lower end values and grey showing higher end values.

4.2.4 – Nanoindentation of Cold sprayed Ti coatings

Profile nanoindentation across cold spray Ti coatings revealed that the mechanical properties of these cold spray coatings did not change with the coating thickness. A typical profile of hardness and modulus measured across coating thickness cross-section is shown in
Figure 4.9(a) for a coating deposited at 500°C gas preheat temperature, 4 MPa gas pressure and 724 m/s particle deposition velocity. Similar trends were observed for all coatings produced at all deposition velocity conditions. This result is contrary to previously published results for microindentation on cold sprayed titanium [11, 22] where the hardness was seen to increase near the substrate/coating interface due to a tamping effect. This difference is likely due to the effect porosity and particle de-bonding has on the hardness test. Nanoindentation is affected the least and represents mechanical properties of the cold sprayed material, while microindentation provides a measure of the overall mechanical response of the coating, including defects.

The average hardness and modulus from profile indentation is plotted against the deposition velocity in Figure 4.9(b), with the mechanical properties of the feedstock Ti powder plotted at 0 m/s. Higher hardness and modulus are measured in the cold spray coatings in comparison to the titanium feedstock powder. The hardness and modulus of the coatings deposited above 625 m/s was 3.7 ± 0.2 GPa and 125 ± 10 GPa respectively. The hardness and modulus of the initial feedstock powder was 3.2 ± 0.2 GPa and 110 ± 5 GPa. No significant change in the coating hardness with increase in the coating deposition velocity past 650 m/s range was observed.

![Figure 4.9: a) Nanoindentation profile hardness and reduced modulus of Ti coating deposited at 500°C 4 MPa (724m/s) away from the coating and the substrate interface plotted at 0 mm, b) Average profile nanoindentation hardness and reduced modulus with standard deviation of coatings plotted against their respective deposition velocities.](image)
Average hardness and modulus for all of the coatings are summarized in Table 4.1. It should be noted that mechanical property mapping was also conducted on coatings. Similar small scale variation in mechanical properties across particle boundaries was also observed. Thus, while the average properties of the cold sprayed coatings do not change over the length scale of the coating thickness, small variations similar to those observed in the splats do exist in the coatings at a similar length scale to the particles.

4.2.5 – Deposition Mechanisms, Mechanical Properties and Comparisons to Literature

Splat bonding mechanisms, extent of deformation, degree of jetting and mechanical properties were all observed to vary to greater or lesser degrees as a function of deposition velocity. The relationships between all of these phenomena are complex, but the results of this study along with those in the literature leads to the following discussion of the observable trends with deposition velocity.

When titanium was sprayed at velocities below 725 m/s, the deposition efficiency was below 100% and the flattening ratio of the splats was roughly constant between 1.8 and 2.5. While some material jetting was observed for these splats, it was somewhat minimal compared to those deposited at higher velocities (c.f. Figure 4.1 and Figure 4.7). Additionally, evidence of de-bonding of splats (c.f. Figure 4.3) indicated that the jetting was in some instances not providing a strong metallurgical bond. Above 725 m/s, the deposition efficiency was 100% and the flattening ratio rose to a value of 3 at 770 m/s and 3.9 at 825 m/s. In this regime, significant jetting occurred and evidence metallurgical bonding was also found (c.f. Figure 4.4). These observations, especially the increase in material jetting with particle velocity, are consistent with the current understanding of the mechanism of adiabatic shear instability as a deposition mechanism for cold spray [4, 6, 7]. The transition to 100% deposition efficiency at roughly 725 m/s matches very well the predicted critical velocity of ~700 m/s for 25 μm diameter titanium particles Schmidt, et al. [4]. In terms of mechanical properties, the cold spray splats and coatings are always on average harder than the feedstock Ti powder. However no significant increase in the coating or splat hardness was measured with the increase in particle velocity.
To explore this phenomenon further, we plot the hardness of cold spray splats near the interface and far from the interface as a function of deposition velocity (see Figure 4.10). Near interface hardness is generally significantly higher than the feedstock powder, indicating work hardening during the impact. This hardness remains relatively constant with particle velocity, seeming to indicate that the extent of work hardening has reached a maximum in this area even at the lowest velocity. However, as the velocity increases, the hardness far from the interface does increase gradually, perhaps due to some deformation and increased dislocation density in the upper splat regions. Lastly, the hardness of the jetting region is also plotted in Figure 4.10 for the splat with the highest deposition velocity of 825 m/s (c.f. Figure 4.8). In the jetting region, the hardness is similar to the feedstock powder. Thus, while the average mechanical properties remain constant with deposition velocity, the complex phenomenon of particle impact, deformation and jetting is also evident in the variation of hardness in the different regions of the splats. This discussion and the splat hardness maps correlate well with the dislocation density distribution in the TEM image of Ti splats taken by K. H. Kim et al. [24] and also the simulated stress distribution patterns proposed by H. Assadi et al. [7]. Thus, there appears to be a consistent picture of high dislocation density and hardness near the interface, minimal activity in the upper splat region, and the possibility of thermal softening in the jetting regions.

![Graph showing hardness distribution with respect to deposition velocity](image)

**Figure 4.10:** Hardness distribution with respect to the splat deposition velocity in Ti splat regions: near interface, in the jetting region and in the upper splat region.
According to R. Kapoor et al. [25], high strain rate deformation of Ti, such as that occurring in the jetting region, can be very efficient at converting deformation work into heat. The temperature rise in the jetting region was estimated to reach near melting point (<90% of Tm) for Ti splats deposited on a steel substrate with nitrogen gas at 950 m/s deposition velocity [20]. Higher temperatures have been estimated for Ti splats deposited on a Ti substrate [28]. The extent to which this heat affects the resulting microstructure and distribution of strain is difficult to predict. Others have shown that the temperature rise during impact of cold sprayed material is sufficient to induce a dynamic recrystallization in the cold spray deposited Ti splats [24]. In addition, there has been evidence that the recrystallization can result in preferential grain orientation of cold spray Ti coatings [14]. For all splats and coatings studied here, the modulus measured by indentation is within the normal range for Ti, which can vary from 100 to 145 GPa (c.f. Eq. 4.1). As it is not a pure uniaxial test, indentation is not very sensitive to changes variations due to crystallographic orientation [29, 30]. Thus, the small changes observed in the current data may or may not reflect some degree of preferred orientation in the sprayed material.

4.3 - Conclusions

The mechanical properties of cold sprayed Ti splats and coatings were studied by nanoindentation. When compared to the hardness of the feedstock powder, the distribution of hardness within individual Ti cold spray splats demonstrated three regions: 1) an impact site with an increase in hardness, 2) an upper splat region with similar hardness to feedstock material, and 3) a jetting regions where the hardness is similar to the feedstock material. At lower deposition velocities (< 650 m/s), the first two regions were more evident than the third, indicating primarily conformal adhesion. At higher deposition velocities (> 650 m/s), the third region, the jetting region, became more pronounced, indicating the formation adiabatic shear instability. The mechanical properties measured in these three regions are consistent with results in the literature that show increased dislocation density near the interface and dynamic recrystallization in the jetting region. Thus, at the highest deposition velocities, which are preferred due to low coating porosity and high deposition efficiency, there was sufficient heat in the jetting regions to promote dynamic recrystallization in Ti and
a reduction in hardness. However, there is retention of work hardening at the impact site away from the jetting region, where there is high strain, but insufficient strain rate to realize a significant temperature rise. Despite the significant differences in hardness in the different regions, the average hardness of cold sprayed Ti splats remained similar for all deposition velocities and was greater than the feedstock material. The same was observed for the cold spray coatings produced, where there were local variations in mechanical properties but the coating mechanical properties remained constant across the coating thickness cross-section.

4.4 - Acknowledgements

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Chapter 5. Microstructure and mechanical properties of Ti cold spray splats: determined by high resolution channelling contrast SEM imaging, EBSD and nanoindentation mapping techniques.

In the previous chapter, the cold spray process was shown to be a thermo-mechanical process where the deposition velocity affected the deformation, bonding and mechanical properties of the cold spray splats and coatings. The microstructural features obtained during cold spray deposition were too fine to be analysed using conventional microscopic techniques and the nanoindentation mapping technique was applied to infer different regions within the splats affected by strain hardening and thermal softening. In the present chapter, high resolution channelling contrast SEM imaging and EBSD mapping are used to correlate the mechanical properties obtained by nanoindentation mapping to the splat microstructure. The microstructure is then used to explore the deformation and bonding mechanisms of Ti splats to Ti substrate.

5.1 - Introduction

The cold spray is a process a metallic powder deposition is achieved through particle impact with the substrate materials at supersonic velocities. The powder is typically accelerated through a de-Laval type nozzle with preheated and pressurised helium or nitrogen gas. The velocity at which the material deposition is achieved is termed critical velocity [2, 3]. The critical velocity ranges for different materials and is often tied to the velocity required to onset the adiabatic shear in a given material [2, 49]. In metals, adiabatic shear occurs at high strain rates, $>10^3 \text{s}^{-1}$ for Ti [120], and is a temperature dependent phenomenon [2, 3, 5]. The critical velocity required to induce adiabatic shear and deposition of titanium is above 700 m/s [2, 13, 45, 113]. At impact velocities above the critical velocity of the material, 95% of the impact energy is converted to heat [2, 34, 42, 116, 121] which leads to a visco-elastic material flow or jetting away from the impact site [2, 8, 32, 37, 42]. While the localized rise in the temperature contributes to the thermal softening [6], the grain refinement and recrystallization induce strain hardening of the cold sprayed materials [33, 122-127].

Previous studies have shown that cold sprayed splats and coatings were harder when compared to the feedstock materials [112, 117], however the distribution of mechanical
properties within the cold sprayed splats and coatings was not homogenous [112]. The objective of the present study was to examine the effect of cold spray process on the microstructure and tie it to the mechanical properties in Ti splats. The microstructure of the cold sprayed material was compared to the microstructure of the feedstock powder using a high resolution scanning electron microscope - SU8000 (Hitachi, Japan). SU8000 microscope uses a photo-diode backscattered electron detector - PD-BSE which allows both channeling and composition contrast imaging [128, 129]. The SU8000 microscope is also equipped with a field emission gun which provides high resolution to the microscope making it ideal for imaging nanograin previously reported in cold spray Ti splats [8] and found in the adiabatic shear instability regions [5, 6, 120]. In addition to SU8000, electron backscatter diffraction - EBSD was used to characterize the texture within the splats. The hardness and elastic modulus was measured within the splats with nanoindentation mapping.

5.2 - Results

5.2.1- Microstructure and Mechanical Properties of Feedstock Powder

In Figure 5.1a, the SEM images of feedstock Ti powder particles are shown. The feedstock Ti powder demonstrated an acicular microstructure with lamellas ranging between 200 nm to 3μm in width and 1 - 20 μm in length. Very fine lamellas, were typically found at the edge of the powder particle. The formation of fine lamellas was attributed to the surface tension during powder production with plasma atomization process [14, 130]. The inverse pole figure of the Ti feedstock powder particle shown in Figure 5.1b and demonstrates the segregation of the lamella into 4 - 5 μm grain colonies, roughly 6 - 20 μm in size.

The hardness within the feedstock powder can be correlated to the microstructural features within the powder particles. In Figure 5.2a, hardness of 3.2 GPa was measured at the left-hand corner of the Ti powder particle, in the region where very fine lamella were observed (see Figure 5.1). The center of the powder particle had a hardness of 2.4 GPa and had very thick lamellas. The results in Figure 5.1 indicate that the hardness increased from 2.4 GPa to 3.2 GPa with decrease in the lamella thickness from 3 μm to 200 nm. The elastic modulus of the feedstock powder, shown in Figure 5.2b, was homogeneously distributed at ~90 GPa and was not affected by the lamella size or orientation.
Figure 5.1: a) SEM image in the backscattered mode and b) EBSD map of the feedstock Ti powder particle.

Figure 5.2: Nanoindentation a) hardness and b) elastic modulus maps of Ti feedstock powder. The units of hardness and elastic modulus are provided in GPa.

5.2.2: Effect of cold spray deposition at critical velocity

The cold spray deposition process induces significant deformation on the feedstock powder. As can be seen in Figure 5.3a, the feedstock powder deforms from spherical to oblate spheroid geometry. The acicular microstructure of the feedstock powder was retained even after the cold spray deposition at 724 m/s however, the lamellas aligned perpendicular to the impact direction as indicated by arrows in Figure 5.3b. A closer inspection of the splat impact site revealed the onset of grain refinement and recrystallization into equiaxed grains, ~200 nm in size, at the splat impact region shown by the upper arrow in Figure 5.3c. A formation of the metallurgical bonding was observed in the region of grain refinement and is shown by bottom arrow in Figure 5.3c.
The grains smaller than 200 nm could not be characterized using EBSD technique as and the regions of grain refinement were not indexed as can be seen at the left and right hand side edges of the splat as indicated by arrows in Figure 5.4. It is interesting to note that no significant grain refinement was observed in the substrate material and the deformation was predominately through twinning. A formation of twin was observed in the substrate at the splat impact site. The density of twins (or a number of twins for a given area [29]) was highest (~4.6x10⁶#/mm²) at the splat impact site and decreased away from the splat impact site. The twinning extended 30 μm into the substrate and contributed to strain hardening in that region (see Figure 5.5).

Figure 5.3: SEM images in backscattered mode of a) Ti splat deposited at 724 m/s on Ti substrate, b) splat/substrate interface taken at x5K magnification and c) splat/substrate interface taken at x30K magnification, demonstrating: a) twinning in the substrate, b) lamellar reorientation in the splat and c) bonding at the splat impact interface.

Figure 5.4: EBSD inverse pole figure of Ti splat deposited at 724 m/s with regions of grain refinement indicated by the arrows.
Figure 5.5: Nanoindentation a) hardness and b) reduced modulus of Ti splat deposited at 724 m/s. The units of hardness and elastic modulus are provided in GPa.

In Figure 5.5a and b, nanoindentation hardness and elastic modulus maps are shown. An increase in the hardness from 2.4 GPa to 4.0 GPa was measured at the splat impact site. High hardness regions correlated with the regions of high twin density within the substrate and location of grain refinement in the splat seen in Figure 5.3 and Figure 5.4.

5.2.3: Effect of cold spray deposition above critical velocity.

The splat, shown in Figure 5.6, was deposited at 825 m/s and above the critical deposition velocity of titanium. The degree of the splat deformation and jetting was more pronounced when compared to the splat deposited at 724 m/s. The splat demonstrated five regions with distinct microstructures. First region consisted of the original acicular microstructure found at the splat upper region (see Figure 5.6a and b). The second region consisted of a chain of small equiaxed grain (650 nm in size) in the middle of the splat which were encased between smaller grains (250 - 400 nm in size) shown in Figure 5.6c and d. The chain of equiaxed grains extended from one edge of the splat to another and increased in the size to 1μm in the jetting region (see Figure 5.6b).

In Figure 5.6 e and f, a conformal interface was observed between the splat and the substrate in the grain refinement region as indicated by arrows. The grain size was measured to be 95 ± 34 nm in the splat at the splat/substrate interface and increased to 150 ± 60 nm at 2 μm and to 230 ± 70 nm at 5 μm away from the interface. Within the splat the grain
refinement region was observed in roughly 50% of the splat cross-section. For each location within the splat, 30 to 100 grains were measured with the exception of the splat upper splat region where size of the grains limited to measurement to only 12 grains.

Some grain refinement was also observed in the substrate in Figure 5.6f and is indicated by arrows. The region of grain refinement in the substrate was very small, with overall thickness of ~ 250 nm. The deformation in the substrate was therefore predominately through twin formation. The region affected by twinning extended over a radius of 20 to 30 μm into the substrate (see Figure 5.6a and Figure 5.7). At the splat impact site, the density of the twins was 1.1 #/μm² and was twice the number observed in splat deposited at 724 m/s shown in Figure 5.3.

The hardness and elastic modulus maps of Ti splat deposited at 825 m/s are shown in Figure 5.8a and b. In Figure 5.8a, hardness of 3.6 - 4.0 GPa was measured at the splat impact site (in the region of very fine, 100 ± 30 nm grains). The hardness decreased towards the midsection of the splat reaching 3.0 GPa and correlated with the region of large recrystallized
grains (640 ± 240 nm in size) observed in Figure 5.6d. Just above the splat midsection, the hardness increased to 3.4 GPa, the hardness increase correlated with the decrease in the grain size seen in Figure 5.6d.

![Figure 5.7: Inverse pole figure of Ti splat deposited at 825 m/s.](image)

Figure 5.7: Inverse pole figure of Ti splat deposited at 825 m/s.

![Figure 5.8: Nanoindentation a) hardness map and b) reduced modulus map of Ti splat deposited at 724 m/s. The units of hardness and elastic modulus are provided in GPa.](image)

Figure 5.8: Nanoindentation a) hardness map and b) reduced modulus map of Ti splat deposited at 724 m/s. The units of hardness and elastic modulus are provided in GPa.

In the jetting region, the hardness was also measured to be 3.0 GPa. The decrease in the hardness correlated with the increase in the grain size to 1.0 ± 0.4 μm. Finally, the hardness dropped to 2.4 - 2.8 GPa towards the splat upper region where the original acicular microstructure was observed (see Figure 5.6b). In the substrate, the hardness also decreased from 4 GPa, at the splat impact site, to 2.4 GPa some distance (20 — 30 μm) from the impact site and correlated with the decrease in the twin density in these regions. The elastic modulus in the splat and in the substrate was measured to be 125 GPa in the substrate and in the splat.
When compared to the elastic modulus of the powder, the elastic modulus in the splat was higher by 30 GPa.

5.2.4 - Effect of substrate preheating on microstructure and mechanical properties of cold spray Ti splats.

In Figure 5.9, the cold spray splat deposited on a preheated Ti substrate is shown. The splat deposited on a preheated substrate demonstrated a lower degree of jetting (see Figure 5.9a) when compared to the splat deposited on the unheated substrate shown in Figure 5.6, however the substrate deformation was more pronounced. A metallurgically bonded interface was observed at the splat/substrate interface in Figure 5.9b. The bonded interface extended from one end of the splat to the midsection of the splat where a large pore formation was detected (see Figure 5.9c). Figure 5.9d demonstrates grain refinement at the splat/substrate interface (shown by white arrows) similar to the one observed for the splat deposited on the non-preheated substrate shown in Figure 5.6f but with significantly larger grain size of 240 ± 120 nm. Grain refinement was also observed in a very thin region (550 nm in thickness) in the substrate, just below the splat/substrate interface and is shown by the black arrows in Figure 5.9d. The size of the grains was smaller in the substrate than in splat and was measured to be 120 ± 40 nm. A chain of small pores were observed at the splat and substrate interface. The pores were located at the junction points between grains.

The inverse pole figure of the splat was shown in Figure 5.10 and revealed that the grain refinement occurred in 70% of the splat while the original acicular microstructure was retained in the upper splat region. The grain refinement region was larger for the splat deposited on the preheated substrate when compared to the splat deposited on the unheated substrate. Twinning was observed in the substrate and extended >30 µm into the substrate (see Figure 5.9a and Figure 5.10). The twin density at the impact site was measured to be 0.46 #/µm².
Figure 5.9: SEM images in the backscattered mode of a) Ti splats deposited at 825 m/s on preheated Ti substrate, b) the right hand side of Ti splat showing small jetting region and grain refinement at splat/substrate interface, c) the middle of the splat showing poor bonding, d) splat/substrate interface showing continuous, metallurgical bonding with white arrows point to the splat/substrate interface and white arrows point to grain refinement region within the substrate.

Figure 5.10: EBSD inverse pole figure of Ti splat deposited at 825 m/s on preheated substrate.
In Figure 5.11a), the hardness at the impact interface was between 3.6 - 4.0 GPa and decreased to 2.8 GPa away from the splat impact site. The decrease in hardness correlated with increase in the grain size in the splat and decrease in the twin density in the substrate. The elastic modulus of splat was 120 GPa and not significantly different from the elastic modulus of the substrate at 130 GPa as can be seen in Figure 5.11b.

![Figure 5.11: Nanoindentation a) hardness and b) reduced modulus maps of Ti splat deposited at 825 m/s on preheated substrate.](image)

In the single crystal HCP materials, the elastic modulus can vary by a magnitude as high as two and is affected by the indenter shape geometry, the indentation angle, the material texture and presence of surface oxides [131, 132]. In the present study, the elastic modulus was measured in the polycrystalline materials where the effect of material texture is less significant and the difference in the measurements made was too small for any meaningful correlations to be made.

5.3 - Discussion

At room temperature and at low strain rates, dislocation slip and twinning are predominant mechanisms of deformation in titanium [29, 36, 121, 133]. The dislocation and twin density contribute to material deformation through formation of new slip directions [134]. At very high strain rates, the shear localization results in the localized temperature rise also known as adiabatic shear [5, 29]. Finite element models of the adiabatic shear in cold sprayed Ti splats have shown that the temperature rise can reach the melting point of the
material [32, 41]. The combination of the high strain rate and high temperature favor the grain refinement and dynamic rotational recrystallization [5, 6, 29, 33, 120] which were reported in the cold sprayed materials [8, 32, 33].

Extensive twinning was observed in the substrate material. The twin affected region extended 30μm into the substrate where highest twin density was observed at the splat impact. The region with high twin density also corresponded to the region of high hardness. In Figure 5.12, the hardness was plotted as a function of the twin density a) and in terms of twin spacing b). Near the splat impact site, the twin spacing was smaller than the indent size measured to be 700 nm in size. The indentation into the twins contributed to the increase in the hardness measurements observed. According to previous studies, twins limit the dislocation mobility within the grains and serve as dislocation nucleation sites which contribute to an increase in the material hardness measurements [28, 121]. In Figure 5.12a, the hardness in the substrate was measured to reach up to 3.6 GPa at the splat impact site where the twin density was 1.2 twins/μm² at which point the hardness measurements plateaued. The plateau hardness indicates that no further strain hardening through twin formation in titanium is possible.

![Graphs showing the effect of twin density and spacing on hardness in Ti substrate impacted at 825 m/s.](image)

**Figure 5.12:** The effect of twin a) density and b) spacing on the hardness in Ti substrate impacted at 825 m/s.

Studies have shown that when the deformation in the material reaches an allowable limit of twin density and no further deformation through twinning can take place, the dislocation within the twins loop, form dislocations walls and induce grain refinement [5,
The thickness of the grain refinement region in the substrate varied with the splat impact velocity. Barely any grain refinement was observed in the substrate impacted at 723 m/s however with increase in the splat deposition velocity to 825 m/s, the thickness of the grain refinement region was measured to be 250 nm in the cold substrate (see Figure 5.6f) and 550 nm in the preheated substrate (see Figure 5.9d). The increase in the grain refinement region with temperature was previously reported and was attributed to the increase in the dislocation mobility within the material [5, 135].

The splats impact the substrate at a temperature above the room temperature, due to the particle interaction with the preheated gas [25]. For that reason, in the splats, the deformation through the grain refinement was favored. In splats, the grain refinement was initially observed in the splats deposited at 723 m/s (see Figure 5.3). The inverse pole figure of the splat (shown in Figure 5.4) revealed that ~10% of the splat cross-sectional area was affected by the grain refinement located in the splat jetting region. The degree of grain refinement increased with increase in the splat deposition velocity. In Figure 5.6, the splat deposited at 825 m/s demonstrated grain refinement within 50% of its cross-sectional area, with equiaxed grains size measured to be below 1μm. The size of the grains changed depending of the position in the splat. Very fine, 95 ± 34 nm grains were found at the splat/substrate interface. The size of grains increased away from the impact site and reached 640 ± 240 nm in the splat midsection (see Figure 5.6c). Larger, micron sized grains, where observed in the splat jetting region shown in Figure 5.6b. This distribution of grain size can be explained by the stress and temperature distribution in the cold spray splats. Previous thermo-mechanical simulations have shown that, the temperature was predicted to be highest in the splat jetting region as opposed to the center of the splat impact [2, 30, 41]. At the splat/substrate interface the temperature is expected to drop due to the heat conduction into the cold substrate [5] which would limit the grain growth in that region. The jetting region and the splat midsection, on the other hand, are less susceptible to heat loss through conduction which could contribute to the grain growth in these regions (see Figure 5.6b and d). Further evidence of the temperature effect on the grain size can be seen in Ti splat deposited on the preheating substrate and shown in Figure 5.9. Over 70% of the splat contained recrystallized grains. The grain size at the impact interface was 240 ± 120 nm as opposed to 95 ± 34 nm in the splat deposited on the unheated substrate. The distribution of
the grain size away from the impact site was homogeneous and did not demonstrate a formation of large grains in the splat midsection as was observed in the Ti splat deposited on the unheated substrate.

The variation in the grain size was reflected in the mechanical properties within the cold spray splats. High hardness was measured in the regions of high grain refinement at the splat/substrate interface while a decrease in hardness was measured away from the impact site. The hardness increase correlated with decrease in the grain size and can be explained by the grain boundary strengthening effect and the decrease in the dislocations mobility often observed in the grain refined materials [95, 97]. The equation used to describe this relationship is known as Hall-Petch (described in Eq.5.1) where the hardness is expressed as a function of the inverse square root of the grain size, \( d_g \), the initial material hardness \( H_\infty \) (which is hardness at infinitely large grain size) and a constant - \( k \). The constant \( k \) contains the effect of the grain boundary strengthening and the length of the dislocations produced per unit area of the grain boundary [95].

\[
H = H_\infty + k d_g^{-\frac{1}{2}}
\]  
Eq.5.1

In Figure 5.13 hardness measured in the Ti splat deposited at 825 m/s was plotted as a function of the grain size. The \( k \) value for titanium was calculated to be 0.56 and was close to the \( k \)-values measured for titanium in other studies [28, 98]. The hardness of the titanium at infinitely large grain size (intercept of the slope) was calculated to be 2.4 GPa. The value corresponded to the hardness measured in the bulk titanium plate with equiaxed 6.8 ± 4.5 μm grains plotted as an open square in the Figure 5.13. The intercept value was higher than previously reported [98], a phenomenon which could be explained by the indentation size effect [64, 89, 117, 136].

The indentation size effect is tied to the geometrically necessary dislocations that form below the indenter during indentation and contributed to an overall increase in the nanoindentation hardness measurements [64, 89, 117]. In the present study, nanoindentation testing was done at 1 mN load where indentation depth was typically 50 nm and indent size was 700 nm. The indent size was small enough to be subjected to the indentation size effect as was shown in another publication [117]. X. D. Hue et al. [136] investigated the effect of
the indentation size on the Hall-Petch relationship and demonstrated that while the indentation size did not affect the k values, at increase in the intercept - \( H_\infty \), similar to the one seen in this study, was observed.

![Graph](image)

**Figure 5.13:** Effect of grain size on nanoindentation hardness in different regions indicated by numbers within the splat deposited at 825 m/s.

In all cases, metallurgical bonding was only observed in the grain refinement region. The extent of the metallurgical bonding increased with increase in the grain refinement region in the splat and in the substrate, with increase in the substrate temperature and with increase in the conformity of the splat/substrate interface. High resolution SEM images of the splat/substrate interface demonstrated that metallurgical bonding occurred though the grain recrystallization and the formation of new grain boundaries between the splat and substrate nanograins. The definition of the splat/substrate interface was only made possible due to a chain of very small pores located in the junction points seen in Figure 5.9d. The metallurgical bonding can be therefore attributed to the microstructural intermixing as was previously proposed [8]. The interfacial grain recrystallization and growth may have contributed to the metallurgical bonding even though a number of researchers make contrary statements [10, 42].

**5.4 - Conclusion**

The deposition velocity of the cold spray process affects the degree of adiabatic shearing and grain refinement in the cold sprayed material. In cold spray splats 100 nm
grains formed at the impact interface. The grain size varied within the splat and was higher in the splat jetting region and midsection when compared to the impact interface attributing to inhomogeneous temperature distribution with the splat. The variation in the grain size affected the hardness measurements within the cold spray splats. The cold spray process induced deformation in the substrate where a formation of high density twins increased the substrate hardness. Preheating of the substrate was shown to contribute to an increase in the substrate deformation, grain refinement and a formation of very conformal interface between the splat and the substrate. A strong metallurgical bonding between the splat and the substrate was tied to the grain refinement, recrystallization and microstructural intermixing on nano-scale level. The interfacial grain growth cannot be ruled out and may have contributed to the metallurgical bonding.

5.5 - Acknowledgement

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Chapter 6. The effect of deposition conditions on adhesion strength of Ti and Ti6Al4V cold spray splats.

Cold spray is a complex process where many parameters have to be considered in order to achieve optimized material deposition and properties. In the cold spray process, deposition velocity influences the degree of material deformation and material adhesion. While most materials can be easily deposited at relatively low deposition velocity (< 700 m/s), this is not the case for high yield strength materials like Ti and its alloys. In the present study, the effects of deposition velocity, powder size, particle position in the gas jet, gas temperature, and substrate temperature on the adhesion strength of cold sprayed Ti and Ti6Al4V splats was evaluated. A micromechanical test technique, developed for this project, was used to shear individual splats of Ti or Ti6Al4V and measure their adhesion strength. The splats were deposited onto Ti or Ti6Al4V substrates over a range of deposition conditions with either nitrogen or helium as the propelling gas. The splat adhesion testing coupled with microstructural characterization was used to define the strength, the type and the continuity of the bonded interface between splat and substrate material. The results demonstrated that optimization of spray conditions makes it possible to obtain splats with continuous bonding along the splat/substrate interface and measured adhesion strengths approaching the shear strength of bulk material. The parameters shown to improve the splat adhesion included the increase of the splat deposition velocity well above the critical deposition velocity of the tested material, increase in the temperature of both powder and the substrate material, decrease in the powder size, and optimization of the flow dynamics for the cold spray gun nozzle. The adhesion strength of Ti splats measured with the splat adhesion technique was compared to the literature cohesion strength of Ti coatings deposited under similar conditions and measured with tubular coating tensile (TCT) test.

6.1 - Introduction

The cold spray process is based on numerous principles of gas flow, material deformation and thermodynamics [40]. The coating deposition is achieved with a de-Laval type nozzle, where pressurized and preheated nitrogen or helium gas undergoes compression and expansion, imparting supersonic velocities to the feed stock powders [15]. The particle
velocity at which deposition takes place is known as critical velocity, which is a function of
the material yield strength and temperature, and is material-dependent [49]. For Ti and Ti
alloys the critical velocity can be as high as 700 to 900 m/s [2, 49]. At the critical velocity,
the leading theory for the mechanism of cold spray deposition in metals is that the high strain
rate in the material leads to plastic deformation and the formation of, what is reported to be, a
region of adiabatic shear instability [4, 27, 37, 41, 49]. In the adiabatic shear instability
region, temperature can approach and even reach the melting point of material thus leading to
viscoelastic material flow, formation of a conformal interface, and metallurgical bonding [3,
4, 37].

The cold sprayed particles that undergo deformation and adhere to the substrate
material are often referred to as splats. The deposition mechanisms of splats vary depending
of the in-flight particle velocity, henceforth “deposition velocity”, and typically follow three
generally accepted deposition mechanisms [2, 15, 30, 34, 37, 39, 41, 45, 49, 112]. At the
deposition velocity below but approaching the critical velocity, the material undergoes plastic
deformation that is measured as a function of splat width divided by the splat height and
referred to as splat flattening ratio or FR [23, 112]. At velocity below the critical velocity, the
transition to the adiabatic shear instability is limited and results in limited metallurgical
bonding [2, 37, 49]. For that reason, the bonding between the splat and the substrate is mostly
through a weak conformal adhesion from mechanical interlocking of asperities. Figure 6.1a
illustrates this deposition mode.

As the deposition velocity surpasses the critical velocity, Figure 6.1b, the formation
of the adiabatic shear instability becomes more pronounced leading to a viscoelastic material
flow. During splat deformation, the material flows in an outward direction from the impact
region, resulting in material jetting. The jetting contributes to an increase in the length of the
interface between the splat and the substrate and increase in the splat flattening ratio. The
formation of adiabatic shear instability and increase in the length of the splat-substrate
interface leads to a greater fraction of metallurgical bonding and a stronger splat adhesion
[37, 45].

Another type of the deposition behaviour is often observed for splats deposited at
velocities significantly higher than the critical velocity. The deformation takes place not only
in the cold sprayed materials but also in the substrate material. The intimate contact between
the splat and the substrate contributes to a more continuous, void or oxide free, bond between two interfaces and even stronger splat adhesion as can be seen in Figure 6.1c [30, 34].

![Figure 6.1: General appearance of cold sprayed splats as a function of particle velocity with respect to the critical velocity. When the particle velocity is low (a), deformation takes place, but very little adiabatic shear. At medium particle velocities (b), there is significant deformation of the splat and formation of adiabatic shear and metallurgical bonding in these local regions. However, the substrate remains undeformed. At the highest particle velocities (c), both the splat and substrate deform extensively and a combined adiabatic shear process leads to an increase in the length of the conformal interface and an increase in the density of regions that have become metallurgically bonded.](image-url)
Figure 6.1 illustrates three commonly known deposition mechanisms in cold spray splats. However, not all the splats in the jet undergo deposition. When the particle velocity is lower than the critical velocity, some particles do not deposit and instead rebound from the substrate [2, 15, 137]. The rebound phenomenon is attributed to the elastic strain energy stored in the material which counteracts the impact forces. Similarly, at very high deposition velocity, the elastic strain energy can surpass the bonding energy and can lead to splat erosion [38, 40]. The elastic strain energy is typically highest at the center of the impact and contributes to the particle de-bonding and void formation in that region [38, 40]. Void formation may occur in the rebound region, as indicated by the dotted lines at the center of the splat in Figure 6.1b and c.

A number of particle impact simulations have been used to understand the deposition mechanisms of metals like copper and aluminum onto copper or aluminum substrates, as well as titanium and its alloys onto steel and titanium substrates [2, 3, 30, 34, 37, 49, 138, 139]. The deposition velocity was shown to have a significant effect on the particle deformation [112] and adhesion [30, 45] but was also predicted to affect the temperature rise in the adiabatic shear instability region [2, 30, 37]. Recent studies indicate that other parameters such as particle impact temperature [38] and substrate temperature [115] may also affect the cold spray deposition process [15, 45]. Higher impact temperature of the splats or substrate lowers the critical velocity required for the cold spray deposition [2] and was shown to contribute to a better splat adhesion to a substrate material as well as to the particle cohesion strength in the coating [45, 50]. Particle and substrate temperature were also shown to vary with gas preheat temperature [49, 50, 140]. Other parameters expected to affect the cold spray deposition process include the powder size [2, 141], particle position in the gas jet [25] and particle impact angle [50].

Because the bonding process for cold spray takes place at the “splat level,” a measurement of the adhesion of a single splat to a substrate provides a fundamental measurement of the bonding, and can, in some circumstances, be a good indicator of the cohesive strength in a coating [117]. To date, there are only a few reports in the literature of methods for measuring the adhesion of the cold sprayed splats. A micromechanical test technique that measures the splat adhesion strength was therefore developed [45], where, in the previous report, the technique was termed a “modified ball bond shear test” due to its
similarity to ball bond shear testing of solder bumps [142]. Since the original report, Dickinson, et al. [46] developed a similar method for testing of TiO₂ ceramic cold sprayed particles on stainless steel substrates. Other groups have developed a method using a laser shock adhesion test (LASAT) that measures the bonding strength for splats present over a roughly 1 cm² area [30].

The present study expands significantly on a previous report using the splat adhesion test on Ti splats on Ti substrates [45], which focused primarily on the effect of spray conditions for Ti splats sprayed with nitrogen gas. In the present study, the effect of spray conditions on splat adhesion strength are explored again, but now for both Ti and Ti6Al4V splats sprayed with both helium and nitrogen gases onto substrates held at room temperature or pre-heated to 400°C. Also, testing was performed on varied splat sizes and on splats at varied position across a single deposition pass in order to test the effect of the particle size and the particle position in the gas jet on the splat adhesion strength. Light optical microscopy (LOM) and scanning electron microscopy (SEM) were used for the evaluation of the splat deformation mechanisms and characterization of the splat substrate bonding interface. Three splat shearing regimes were identified by observation of residual shear tracks on the substrate surface and the features in the force-displacement curves, which were recorded during the shearing of the splats. The present study explores a wide range of deposition conditions for Ti and Ti6Al4V and uses the splat adhesion test and other characterization methods to determine those conditions leading to high adhesion strength. Results for adhesion at the splat level are compared to bond strength and cohesion strength measurements for Ti reported in the literature.

6.2 – Results

6.2.1 – Mechanical property characterization

In Table 6.1 the hardness and reduced elastic modulus of the feedstock Ti and Ti6Al4V powder as well as Ti and Ti6Al4V substrates are summarized. The average hardness of the commercially pure Ti powder and Ti substrates were the same at 3.1 GPa with reduced modulus of each material very close to the Young’s modulus of Ti. The
hardness of the Ti6Al4V powder and substrate was higher than that of the pure Ti at 4.8 GPa and 5.8 GPa respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (GPa)</th>
<th>Reduced Elastic Modulus (GPa)</th>
<th>Surface Roughness Ra (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti powder</td>
<td>3.1 ± 0.4</td>
<td>114 ± 10</td>
<td>-</td>
</tr>
<tr>
<td>Ti substrate</td>
<td>3.1 ± 0.3</td>
<td>125 ± 6</td>
<td>0.60 ± 0.12</td>
</tr>
<tr>
<td>Ti6Al4V powder</td>
<td>4.8 ± 0.3</td>
<td>104 ± 5</td>
<td>-</td>
</tr>
<tr>
<td>Ti6Al4V substrate</td>
<td>5.8 ± 1.1</td>
<td>123 ± 11</td>
<td>0.52 ± 0.14</td>
</tr>
</tbody>
</table>

Table 6.1: Properties of Ti and Ti6Al4V powder and substrates

In Table 6.1, the average surface roughness of as received Ti and Ti6Al4V substrates is also listed. Both substrates demonstrate comparable Ra values that fall within the standard deviation on each measurement.

6.2.2 – The effect of the gas temperature and pressure on the deposition velocity

Ti or Ti6Al4V powder was deposited onto Ti or Ti6Al4V substrate at velocities ranging from 580 to 1140 m/s, which were obtained by varying the nitrogen or helium gas temperature from 25°C to 800°C and by changing the gas inlet pressure from 1 – 4 MPa. The average deposition velocity increased with increase in the gas temperature but also increased with increase in the inlet gas pressure. At similar gas preheat temperature and pressure, higher velocities were obtained with helium gas when compared to nitrogen gas. The deposition conditions and the corresponding average deposition velocities are listed in Table 6.2.

In Table 6.2 some of the samples were produced at different time frame, within a period of 1 year from when most of the splats were produced, and the deposition velocity for a given gas preheat temperature and pressure condition was re-measured prior to sample preparation. The measurements made at a later time frame are indicated by a star. The difference in the particle velocities can be attributed to the changes made in the cold spray system over time including the replacement of the gun nozzle. Some of the particle velocity measurements, listed in the Table 6.1, were previously published [45, 117].
Table 6.2: Splat Deposition Conditions

<table>
<thead>
<tr>
<th>Gas</th>
<th>Ti Powder on Ti</th>
<th>Ti6Al4V Powder on Ti6Al4V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(at RT and at 400°C)</td>
<td>(at RT and at 400°C)</td>
</tr>
<tr>
<td>Gas Temperature (°C)</td>
<td>Gas Pressure (MPa)</td>
<td>Deposition Velocity (m/s)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>4</td>
</tr>
<tr>
<td>Helium</td>
<td>Ti on Ti (at RT)</td>
<td>Ti6Al4V on Ti6Al4V (at RT)</td>
</tr>
<tr>
<td>Gas Temperature (°C)</td>
<td>Gas Pressure (MPa)</td>
<td>Deposition Velocity (m/s)</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>616</td>
</tr>
<tr>
<td>50</td>
<td>2</td>
<td>787</td>
</tr>
<tr>
<td>50</td>
<td>3</td>
<td>877</td>
</tr>
<tr>
<td>350</td>
<td>2</td>
<td>877</td>
</tr>
<tr>
<td>350</td>
<td>3</td>
<td>950</td>
</tr>
<tr>
<td>350</td>
<td>4</td>
<td>1140</td>
</tr>
</tbody>
</table>

*Particle velocity measured at a different time frame

While the gas temperature and pressure are the main parameters affecting particle velocity, other parameters such as the particle position in the gas jet [25] and the size of the powder particles [2] can also have an effect on the particle velocity. The particles located at the edge of the jet travel at a lower speed when compared to particles propelled at the center of the jet [25]. At the same time, smaller particles travel at a faster speed than larger particles [2]. Due to these facts, the actual velocity for each deposition condition follows a Gaussian distribution as shown in Figure 6.2.

In Figure 6.2, three particle velocity distributions for low, intermediate and high deposition velocity conditions are shown. At low deposition conditions, although the average velocity is 625 m/s, a small portion of particles reach the minimum critical velocity for Ti ranging between 700 and 900 m/s [2]. Similarly, at high deposition condition where most of the particles travel at an average deposition velocity of 770 m/s some of the particles travel below the minimum critical velocity.
To circumvent some of the uncertainty in the particle velocity measurements, mainly the splats at the center of the deposition pass were examined. This position corresponds to particles near the center of the gas jet, where the velocity is the highest. Furthermore, measurements were carried out on particles close to the average feedstock powder diameter of 29 µm, removing some of the variation in velocity associated with particle size. Additionally, these particles are the most populous within the velocity distributions, such as those in Figure 6.2. Thus, it is expected that particles tested in this manner arrived at the average velocity for the given spray condition. Other testing was carried out as a function of splat position across the deposition pass or as a function of splat size along the center of the deposition pass. In these cases the variation in properties measured is a function of velocity, due to its variation across the gas jet and with splat size.

6.2.3 – Effect of particle velocity and preheat temperature on splat deposition

In Figure 6.3, representative SEM images of the etched Ti (a-c) and Ti6Al4V (d-f) splats deposited at increasing deposition velocities are shown. Ti splats deposited on Ti
substrate as well as Ti6Al4V splats deposited on Ti6Al4V substrate showed three different deposition regimes. As can be seen in Figure 6.3a and d, at deposition velocity approaching the critical velocity (~700m/s), the splat deformation was not extensive and material jetting region was limited. Bonding took place mainly through conformal adhesion between the splat and the substrate. As the deposition velocity increased, the splats became more deformed and extensive material jetting took place, as can be seen in Figure 6.3b and e. Regions of continuous bonding was observed in the splat at 45 degree angle from the splat impact site while a void formation was observed at the center of the splat/substrate interface.

As the deposition velocity increased even further, substrate deformation became more pronounced (see Figure 6.3c). The substrate deformation contributed to the formation of an intimate, possibly metallurgical, contact between the Ti splat and substrate. Under the same deposition conditions, Ti6Al4V splats deposited on Ti6Al4V showed a lower degree of substrate deformation and bonding when compared to Ti splats deposited on Ti (see Figure 6.3e). The bonding interface between the Ti6Al4V splat and substrate was not continuous, as can be seen in Figure 6.3f.

Figure 6.3: Etched SEM cross-sectional micrographs of Ti splats deposited on Ti at a) 724m/s (N₂ at 500°C 4MPa) b) 825m/s (N₂ at 800°C 4MPa) c) 1140m/s (He at 350°C 4MPa) and Ti6Al4V splats deposited on Ti6Al4V substrate at d) 741m/s (N₂ at 500°C 4MPa) e) 834m/s (N₂ at 800°C 4MPa) f) 1115m/s (He at 350°C 4MPa). The dark regions between the splat and the substrate indicate regions of poor bonding and void formation.
The splat deformation was measured in terms of flattening ratio, from the etched images of splats similar to the ones shown in Figure 6.3 and according to Eq. 3.5. The flattening ratio was plotted as a function of particle deposition velocity (see Figure 6.4). As can be seen in Figure 6.4a, the Ti splat flattening ratio increased with increase in the deposition velocity up to 850 m/s but then stabilized and slightly decreased at 1140 m/s. Similar splat deformation behavior was observed in etched splat cross-sections shown in Figure 6.4a-c. The splat deposited at 825 m/s was more deformed than the splat deposited at 724 m/s however the splat deposited at 1140 m/s had a lower flattening ratio. At 1140 m/s a significant increase in the substrate deformation was observed. Average Ti substrate deformation depth was calculated from SEM images of 10 - 30 etched splat cross-sections and was measured to be 2.1 ± 2.2 μm at 825 m/s and 8.1 ± 4.3 μm at 1140 m/s which is approximately 10% and 40% of the splat height.

Figure 6.4: Flattening ratio versus deposition velocity for a) Ti splats and b) Ti6Al4V splats deposited with nitrogen and helium gases at varied gas preheat temperatures. No Ti6Al4V splats, deposited with nitrogen gas, were found below 650 m/s.

The flattening ratio of Ti6Al4V splats, shown in Figure 6.4b, increased from roughly 2.0 at 650 m/s to 3.0 at deposition velocity of 850 m/s. The splat flattening ratio did not increase at higher deposition velocities obtained with helium gas. The cross-sectional SEM image of the splat deposited at 1115 m/s (see Figure 6.3f) had very limited substrate deformation compared to the Ti substrate seen in Figure 6.3c. Deformation depth for Ti6Al4V substrates increased from 0.5 ± 1.3 μm at 834 m/s (which is similar to the roughness of the substrate) to 4.6 ± 1.6 μm at 1115 m/s.
A steady increase in the splat adhesion strength was observed with increase in the splat deposition velocity, as seen in Figure 6.5. For Ti splats deposited on Ti substrates at velocities greater than 800 m/s, the splat adhesion strength approached the shear strength of Ti at 380MPa [143]. The results correlated well with the SEM image shown in Figure 6.5 that showed an increase in the splat/substrate bonded interface with increase in the splat deposition velocity.

![Figure 6.5: Adhesion strength versus deposition velocity for a) Ti splats deposited on Ti substrate and b) Ti6Al4V splats deposited on Ti6Al4V substrate with nitrogen and helium gases at varied gas preheat temperatures. No Ti6Al4V splats, deposited with nitrogen gas, were found below 650 m/s.](image)

The adhesion strength of Ti6Al4V splats deposited on Ti6Al4V substrate was lower than that of Ti splats deposited on Ti substrate and was significantly lower than the shear strength of Ti6Al4V at 550MPa [143]. The adhesion strength for the Ti6Al4V splats was mostly constant at 100MPa but reached ~320MPa at the highest deposition velocity of 1115m/s. Ti6Al4V has higher shear strength when compared to pure Ti and higher impact velocities are required to induce adiabatic shear.

### 6.2.4 – Splat shearing behaviors

During the adhesion testing, three types of splat shearing regimes were observed and are shown in Figure 6.6. In the first shearing regime, a rapid increase in the tangential forces with respect to the stylus displacement was observed and was followed by a rapid drop in the
tangential forces. The total stylus displacement associated with the shearing event was smaller than the width of the splat. Also, the very small rise in the tangential forces (~15 mN) with tip displacement indicates poor splat adhesion strength (12 MPa). The sheared region showed a presence of the crater in place of the sheared splat with no visible shear tracks (see Figure 6.6 regime 1b)) indicating that the splat adhesion occurred was mainly through a weak conformal bonding. First shearing regime was typically observed for splats deposited below the critical velocity (700 m/s for Ti).

In second shearing regime, the rise in the tangential forces occurred over a wider displacement range than in regime 1. In Figure 6.6, the peak tangential force reached 300 mN and was followed by a rapid drop in the tangential force half way into the splat. Splats demonstrating regime 2 shearing behavior also had higher adhesion strength (239 MPa) compared to those in regime 1. Regime 2 shearing behavior was observed in Ti splats deposited on Ti substrate at 825 m/s and in Ti6Al4V splats deposited on Ti6Al4V substrate at 1115 m/s. Examination of the sheared region on the substrate revealed shear tracks that formed a ring around the impact crater. The ring formation had the outline of the sheared splat that correlated with the region of continuously bonded interface observed from the splats cross-sections in Figure 6.3b and f.

Finally, the third shearing regime was defined by a smooth rise and drop in the tangential forces during the shearing of the splat. As compared to regimes 1 or 2, regime 3 had no drastic drop in the tangential forces at the end of the shearing event and the width of the tangential force peak was roughly the width of the sheared splat. For the third shearing regime, the shear tracks formed a full circle with no crater formation. The splats demonstrating this type of shearing behaviour had adhesion strength approaching the theoretical shear strength. The third shearing regime was observed for Ti splats deposited at 1140 m/s. The average adhesion strength of the splats deposited at this velocity was measured to be 294MPa, below the shear strength of Ti. The cross-sectional image of a splat deposited at this velocity is shown in Figure 6.3c, where it is seen that not all of jetting region participated in the splat bonding. Thus, the actual splat contact area calculated according to Eq. 3.14 was slightly overestimated and may explain why splats shearing according to regime 3 do not have adhesion strength closer to the actual shear strength of Ti. Ti6Al4V
splats deposited on Ti6Al4V substrate did not demonstrate regime 3 shearing behaviour and sheared according to regime 2 at 1115 m/s.

Figure 6.6: Three regimes of splat shearing behavior are shown with corresponding top view LOM images of splats a) before shearing and b) after shearing, c) with respective tangential force vs. displacement curves.

In Figure 6.7, SEM images of a sheared region on a Ti substrate are shown for a condition that exhibited regime 2 behavior. Three features of splat shearing behavior are observed and include the crater formation which is surrounded by a ring of the shear tracks and finally the shear tracks themselves. The shear tracks (shown in Figure 6.7a) formed a ring in the shape of the sheared splat. The inside of wall of the shear track ring contained fine dimples (see in Figure 6.7b) that were produced as the splat was de-bonded from the substrate. The dimples are indicative of a ductile fracture in Ti and Ti6Al4V [56, 144-146] and point to a metallurgical bonding in that region. At the center of the ring, a crater
formation was observed. The center of the crater had a smooth, dimple-free surface which shows that no metallurgical bonding took place in that region. Regime 2 shearing behavior was typically observed for splats deposited above 800 m/s. The observations of where bonding took place in the sheared region correlated well with the regions of continuously bonded interface seen from SEM images of the splat deposited at 825 m/s and shown in Figure 6.3b.

![Figure 6.7: SEM image of the regime 2 sheared region at low a) and at high b) magnification. The shear band rings surrounding the crater are shown with dimpled ductile fracture at the inside rim of the crater.](image)

6.2.5 Effect of powder particle size and position in the gas jet.

In the previous sections, the adhesion strength was measured for splats with similar pre-impact particle diameter of ~ 34 μm as calculated according to Eq. 3.15. In industrial applications, powder size distribution will vary and a better understanding of the effect of the particle size on the adhesion strength of splats is required. In Figure 6.8, the effect of the particle size on the splat adhesion strength was evaluated. As can be seen in Figure 6.8, the adhesion strength of smaller splats was higher when compared to larger splats. The splats, with an estimated particle pre-impact diameter between 10 and 20 μm, had adhesion strength in the range of 250 to 300 MPa, while 40 to 60 μm splats have particle adhesion strength ranging between 150 and 250 MPa. The results correlated well with the general understanding of the particle flight dynamics where particles of smaller size were shown to
have a higher in-flight velocity when compared to particles of larger size [49, 147] and consequently had a better adhesion strength.

Figure 6.8: The adhesion strength of Ti splats deposited at 852m/s (N₂ 800°C and 4MPa) with respect to the particle size calculated according to Eq.314. Splat adhesion was measured at the center of the deposition track. A decrease in the particle adhesion strength was observed with increase in the particle size.

The powder particle position in the gas jet can have an effect on the particle velocity. A particle in the center of the gas jet travels at a higher velocity than the splats at the edges of the jet [25]. The particle deformation and bonding strength can be therefore affected. In Figure 6.9, the splat adhesion strength was measured across the width of a deposition pass (i.e. perpendicular to the gun traverse direction). The adhesion strength of splats with roughly same particle diameter (~ 34 μm) was measured. The splat adhesion strength was highest (~250 MPa) in the 4 - 8 mm which corresponded to the center of the pass width. Lower adhesion strength, ranging from 0 - 100 MPa, was measured for the splats located at the edge of the pass at 0-4 and 8-12 mm.
6.2.6 - Substrate temperature effect

The splats presented in the previous sections were deposited as a single pass at high gas traverse speed and on the substrate at room temperature. Previous studies have shown that the temperature of the substrate material increases due to heat transfer from the impingement of the pre-heated gas jet [26, 115]. As a result of splat impact with the substrate and adiabatic shear, the temperature of the substrate will rise as well [15, 26, 41, 140]. In order to “simulate” the substrate temperature rise due to the gas jet and successive impacts, substrates were preheated to 400°C prior to splat deposition. Measurements of the adhesion strength from these splats may mimic more closely the bonding that takes place in a full coating.

As can be seen in Figure 6.10a and b, Ti splats deposited on preheated Ti substrate showed a more extensive bonded interface when compared to Ti splats deposited on Ti substrate at ambient temperature under same deposition conditions, as shown in Figure 6.3a and 6b. Furthermore, Ti splats deposited at 825 m/s (see Figure 6.10b) showed similar substrate deformation and bonding as one obtained at much higher deposition velocity with
ambient substrate conditions (see Figure 6.3c). The average depth of the preheated Ti substrate deformation was measured to be $4.2 \pm 2.8 \, \mu m$ and was higher than for the non-preheated substrate at $2.1 \pm 2.2 \, \mu m$ measured for 825 m/s deposition condition. Ti6Al4V splats deposited on preheated Ti6Al4V substrate are shown in Figure 6.10c and d, where no significant substrate deformation, even after substrate preheating, was observed. The Ti6Al4V preheated substrate deformation depth was measured to be $0.8 \pm 1.3 \, \mu m$ and was very similar to the deformation depth of the non-preheated substrate at $0.5 \pm 1.3 \, \mu m$ at 834 m/s deposition condition. Ti6Al4V retains its specific strength up to 500°C [148] and higher substrate preheat temperatures are needed to induce substrate deformation.

Figure 6.10: Etched cross-sectional micrographs obtained with SEM for a) Ti splats deposited at 724 m/s ($N_2$ at 500°C 4MPa) on Ti substrate preheated to 400°C, b) Ti splats deposited at 825 m/s ($N_2$ at 800°C 4MPa) on Ti substrate preheated to 400°C, c) Ti6Al4V splat deposited at 741 m/s ($N_2$ at 500°C 4 MPa) on Ti6Al4V substrate preheated to 400°C and d) Ti6Al4V substrate deposited at 832 m/s ($N_2$ at 800°C 4 MPa) on Ti6Al4V substrate preheated to 400°C.
The flattening ratio for Ti and Ti6Al4V splats deposited on preheated substrates is shown in Figure 6.11a and b. The splat flattening ratio for Ti splats on preheated Ti substrate demonstrated a slight decrease when compared to the same splats deposited on unheated substrates. This behavior can be explained by the substrate deformation observed in Figure 6.11b. On the other hand, the flattening ratio of Ti6Al4V splats deposited on preheated substrates was similar to that of Ti6Al4V splats on unheated substrates as shown in Figure 6.11c. The results correlate well with the SEM images shown in Figure 6.10c and d where no substrate deformation was observed.

Unlike the similarity for flattening ratios from preheated and unheated substrates, a dramatic increase in the splat adhesion strength was measured for Ti and Ti6Al4V splats deposited on preheated substrates. In Figure 6.12a, the adhesion strength of Ti splats reached ~250 MPa at a deposition velocity of 700 m/s, a significant improvement from 100 - 120 MPa measured for the same velocity splats on unheated substrates. A similar increase in the adhesion strength was measured for Ti6Al4V splats deposited at slightly higher deposition velocity of 700 m/s in Figure 6.12b.

For Ti splats deposited on preheated substrates, the regime 3 behavior was observed for deposition velocities at or above 825 m/s. For non-preheated substrates, this occurred at a

---

**Figure 6.11:** Flattening ratio of a) Ti splats deposited on Ti substrate at 25°C and preheated to 400°C and b) Ti6Al4V splats deposited on Ti6Al4 substrate at 25°C and preheated to 400°C. The flattening ratio decreases for Ti splats deposited on preheated substrate. No change in the flattening ratio was measured for Ti64 splats deposited on Ti64 substrate at 25°C or at 400°C.
much higher velocity of 1140 m/s. For Ti6Al4V splats deposited on preheated substrates, splats deposited at or above 834 m/s exhibited regime 2 behavior, much lower than the 1115 m/s observed in splats deposited on the unheated substrates.

Figure 6.12: Splat adhesion strength as a function of deposition velocity for a) Ti splats deposited on Ti substrate at 25°C and preheated to 400°C b) Ti6Al4V splats deposited on Ti6Al4 substrate at 25°C and preheated to 400°C. The adhesion strength is higher for splats deposited on preheated substrate.

6.3 - Discussion

The most widely accepted mechanism for metallurgical bonding in cold sprayed metals is the formation of adiabatic shear instability [2, 3, 15, 149]. The ability of a cold sprayed particle to undergo plastic deformation and adiabatic shear is a function of material properties, such as yield strength and melting point as well as process conditions, such as deposition temperature, particle velocity and particle size [2, 3, 112, 150]. When a particle arrives at the substrate at its critical velocity, adiabatic shear takes place, which then contributes to a formation of a metallurgical bonding [37, 39]. However, even when a coating is created with average in-flight particle velocity well above the critical velocity, incomplete bonding is often observed [40, 41, 45]. This is especially true for materials with high melting point and high yield strength, like Ti and its alloys [2].

The cold spray process is somewhat complex and the effects of particle or substrate characteristics, temperature, gas flow and the nozzle design on the quality of cold spray
deposits are not easy to evaluate using experimental methods. Many studies instead make use of computational simulations [2, 25, 37, 49]. The technique used here measures bond strength at the splat level, which is the level where the basic mechanism of adiabatic shear instability takes place. Identification of the effect of processing parameters on the underlying mechanism of adiabatic shear instability and the extent to which bonding occurs at the splat level is one viable way to gather information useful to optimizing the cold spray process. The splat adhesion test [45] can directly address the effect of the process conditions on bonding of cold spray splats. Thus, process parameters for cold spray can be explored without spraying large quantities of material to identify the best conditions leading to sufficient adiabatic shear for a formation of a continuous and strong bonding.

One important processing consideration is the effect of non-uniform distribution of velocity across the gas jet. Many simulations have indicated that particle velocity is not continuous and varies depending on the particle position in the gas jet [25, 51, 52]. Zahiri et al. [25, 52] demonstrated that the particles traveling at the center of the gas jet had a higher particle velocity when compared to the particles traveling at the edge of the gas jet. As was seen in Figure 6.9, the adhesion of splats deposited at the edges of the gas jet had lower adhesion (~ 20 – 100 MPa) compared to those arriving in near the center of the jet (~ 200 MPa). This effect was likely due to the drop-off in the velocity away from the center of the jet. The poor adhesion strength of particles at the edges of the gas jet can affect the mechanical integrity of the cold spray coatings. To optimize the deposition of hard to deposit materials, such as Ti and Ti6Al4V, a better design of the nozzle may be required [15, 51, 151]. One work suggested, the use of a rectangular nozzle provided a more homogenous velocity distribution across the gas jet when compared to the circular nozzle [152]. If in the future, high quality cold sprayed coatings of high melting point, high strength materials [2] are to be realized, nozzle design and optimization of the gas flow will be significant contributions leading to success in this endeavour.

Feedstock particle size is another important processing parameter as different particle sizes lead to different velocities [2, 49, 147]. Assuming one has already chosen an optimum range of particle sizes, within this size range, small particles travel at higher velocities than larger particles. At the same time the ability of smaller particle to undergo adiabatic shear is reduced and higher velocities are often required in order to deposit smaller particles when
compared to particles of larger size [2, 49]. The results from splat adhesion test showed that for Ti, the adhesion strength for smaller particles was higher when compared to larger particles. Particles with diameters of 15 µm or less had adhesion of roughly 300 MPa, while those with diameter surpassing 40 µm had adhesion on the order of 200 MPa. The ratio of the deposition velocity vs. critical velocity of smaller particles was, therefore, higher than for the larger particles. For these tests where we examined particle size, their size ranged from 10 to 60 µm and they were located at the center of the deposition pass. For these conditions, the effect of the particle size may not have played a substantial role on the adiabatic shear. Also the bow shock effect [15], where small particles deviate from the deposition trajectory, was not taken into account. Furthermore, the particles were deposited directly on the annealed substrate material. The effect of particle size on the particle bonding mechanisms in a coating subjected to high stress may be different [2, 14]. Additional studies on the particle size effect on the deposition efficiency and structural integrity of Ti and Ti6Al4V cold spray coating may provide additional insight on the effect of particle size beyond what has been shown here.

The material composition had a significant effect on cold spray deposition. The adhesion strength of Ti splats deposited on Ti was consistently higher than the adhesion strength of Ti6Al4V splats deposited on Ti6Al4V substrate. This behavior can be explained by a significantly higher yield strength of Ti6Al4V at 1200 MPa when compared to that of pure Ti at 700 MPa [27]. The yield strength of the material affects the critical velocity required to induce adiabatic shear and therefore the ability of the material to form a strong, metallurgical bond [2, 3].

For cold spray, increasing temperature has the beneficial effect of reducing the yield strength of the sprayed material [153]. The gas interaction with the feedstock powder and substrate as well as the particle impact with the substrate will all increase the temperature both locally and globally [15, 26, 37, 49]. According to Schmidt et al. [49], using calculations done for copper particles, the particle temperature can reach up to 200°C in the gas preheated to 600 °C. With increase in the temperature, the shear strength of Ti6Al4V subjected to high strain rates decreases [153] an effect that will lead to an earlier onset of adiabatic shear instability and better material bonding. For Ti6Al4V splats deposited on Ti6Al4V substrate at 650 and 850 m/s, the use of nitrogen gas, preheated to higher
temperatures than helium, resulted in a slight increase in the adhesion strength (~50 MPa) (see Figure 6.5b). For Ti, where the shear stress is considerably lower than that of the alloy, the effect of the gas preheat temperature on particle adhesion was more subtle but still noticeable. For deposition velocity between 600 and 650 m/s, the adhesion strength of splats can be ranked with gas temperature. The highest adhesion strength was for splats deposited with nitrogen at 500°C followed by those with nitrogen at 300°C and lastly by those with helium at 50°C. However, at higher deposition velocities, which clearly exceed the critical velocity for Ti, there was no difference due to gas temperature. For example, at a deposition velocity of roughly 800 m/s, the adhesion strength was nearly identical for splats deposited with nitrogen at 800°C and those deposited with helium at 50°C.

Particles sprayed with higher gas pre-heat temperatures are expected to retain some thermal energy and arrive at the substrate at a higher temperature than those with lower gas pre-heat temperatures. The gas pre-heat temperature via the gas jet can also affect the substrate; however, the deposition of the splats was carried out with a single pass at a high transverse velocity. Thus, the gas interaction with the substrate material was limited. In terms of cold spray coatings, it is important to note that the gas temperature will increase the substrate temperature given enough time [15]. J.-G. Legoux et al. [26], using an infrared camera, measured temperatures upwards of 330°C in regions of a substrate subjected to a stationary impact with nitrogen gas preheated to 500°C and passed through a cold spray nozzle. Such increase in the temperature can reduce the shear stress of Ti6Al4V and can affect the deformation and adhesion mechanisms of the material [153, 154]. To evaluate the effect of the substrate temperature on the deposition of the cold spray splats, Ti and Ti6Al4V splats were deposited on Ti or Ti6Al4V substrates preheated to 400°C. An increase of over 100 MPa in adhesion strength was measured in both cases. Furthermore, near ideal shearing behavior, regime 3 behavior, was observed for Ti splats deposited at 825 m/s on preheated Ti substrate as opposed to 1140 m/s in case of an unheated substrate. Ti6Al4V splats also demonstrated an improvement in the splat adhesion behaviour. Ti6Al4V splats deposited at 834 m/s on preheated Ti6Al4V substrate sheared according to the regime 2, whereas same splats deposited on unheated substrate sheared according to regime 1. In regime 2 shearing behaviour material demonstrates regions with a ductile fracture, shown in Figure 6.7, which
is indicative of a partial metallurgical bonding, whereas in regime 1, the particles adhered mainly through a weaker conformal adhesion.

The flattening ratio did not reflect the drastic increase in the splat adhesion strength seen in Ti splats deposited with helium gas in Figure 6.5a and on preheated substrates in Figure 6.11. The current results indicate that the splat flattening ratio, while a good indicator of the extent of plastic deformation, and to some extent adiabatic shear (e.g. jetting), is not necessarily a good indicator for bonding and splat adhesion strength. Thus, to fully explicate the splat bonding and the portion of the adiabatic shear process that leads to bonding, other parameters must be considered, such as: strain rate, stress localization, temperature, and the conformity of the interface between the adiabatic shear instability region and the substrate material which is enhanced through substrate deformation.

Splat adhesion testing can be used to measure the adhesion strength and identify bonding mechanisms for the individual cold spray splats based on the appearance of the load-displacement curves (i.e. the regime assignments made here). The height, the width, and the shape of the load-displacement curves were used to define the strength, the type, and the continuity of the bonded interface between splat and substrate material at any location in the deposition pass. S. Guetta et al. [30] also measured the adhesion strength of splats with a laser shock adhesion test (LASAT). LASAT measures the tensile stress required to de-bond splats over a 1cm region in the substrate and is, therefore, less sensitive to the adhesion strength of individual splats and their position in the substrate [30]. LASAT was, however, used to measure the adhesion strength of splats imbedded in the substrate and the adhesion strength of cold spray coatings [30, 155].

Most adhesion testing techniques are designed for the bond strength of coating to substrate, similar to the standard, ASTM C-633-99. All of these suffer from issues with epoxy strength that limits that maximum strength that may be measured. For example, in a hydraulic adhesion/tensile test, the coating is typically glued to two circular elements with a heat cured epoxy and then pulled apart [37, 47]. The hydraulic adhesion/tensile test was used by T. S. Price et al. [47] to measure the bond strength of Ti coating deposited on as-received and grit blasted Ti6Al4V substrate. The coatings were deposited at 500 m/s and the bond strength was measured to be 32 - 37 MPa [47]. Using similar methods, Morrocco et al. [48] measured the bond strength Ti coatings on polished, grit blasted or ground Ti6Al4V
substrates. The bond strength was found to be between 5 and 25 MPa. G. Bae et al. [37], measured the bond strength of Ti coatings deposited at 650 m/s on steel substrates. The bond strength was measured to be between 49 and 69 MPa. In most cases, the failure occurred in the epoxy, failing at 85 MPa, and the bond strength of the coatings deposited at higher deposition velocities could only be reported as greater than 85 MPa [37, 47].

The cohesive strength between particles within coatings is also of particular interest and can be measured by a recently developed technique called the tubular coating tensile (TCT) test. The method was first developed by Schmidt et al. [49] for the measurement of the cohesive strength of copper cold spray particles in the coating deposited on the aluminum substrate. More recently, Binder et al. [50] used TCT test to measure the cohesive strength of cold sprayed Ti particles in coatings deposited with nitrogen gas at pre-heat temperatures from 600°C to 1000°C. The coatings were deposited with a Kinetics 8000 Cold Spray Gun and spherical Ti powder with 33.5 µm average diameter. The deposition velocities were not measured but were calculated to range between 650 and 800 m/s for 25 µm particles [50].

Interesting correlations were found between the cohesive strength in Ti coating sprayed by Binder et al. [21] and the adhesion strength of Ti splats sprayed for this study (see Figure 6.13). In general, particle cohesion strength for Ti correlated well with the adhesion strength of Ti splats. For deposition velocities below 700 m/s, the magnitude of the cohesive strength matches the splat adhesion strength on unheated substrates very well and a similar trend with velocity was seen in both datasets. However, at higher velocities (> 700 m/s) that are only achievable with high gas pre-heat temperatures, the cohesive strength was higher than the splat adhesion strength. This is likely an effect of the gas jet heating the substrate and coating during deposition, leading to an enhancement to the metallurgical bonding. This hypothesis is further supported by a comparison between the cohesive strength and the data for splat adhesion strength on heated substrates. At velocities below 700 m/s, the splat adhesion strength on heated substrates is higher than the cohesive strength. At these velocities, the gas preheat temperature used for a coating is lower and temperature effects are reduced. Thus, a splat on pre-heated substrate at these velocities should have a stronger bond. For higher deposition velocities (> 700 m/s), where gas jet heating is more significant, the cohesive strength and splat adhesion strength on heated substrates agree very well. In a previous study, a similar correlation between cohesive strength and splat adhesion strength
was observed [117], but the comparison made here between Binder, et al. [50] and measurements of splat adhesion strength is the first time that both the effect of velocity and temperature have been correlated in this way for the coating and splat levels.

Figure 6.13: A plot of splat adhesion strength (measured here) and cohesive strength [50] versus deposition velocity. All data presented is for Ti sprayed with nitrogen as the propelling gas.

The splat adhesion test was shown to reveal trends for adhesion strength versus deposition velocity or temperature that are relevant to the bonding for a full coating, both between coating and substrate and cohesive strength within the coating. Also, the small scale precision of the method was useful for tracking the effects of particle size and position in the gas jet on the adhesion strength of splats. These are two variables that are known to have an effect, but are nearly impossible to measure experimentally with conventional techniques. There are, however, a few limitations for the current technique that merit mentioning. First, the adhesion testing cannot be carried on the splats deposited on top of very rough substrates. The roughness of the substrate will contribute to the noise in the measurements and if the roughness is high enough it would completely prevent a splat from being tested. Also, splats that are embedded in the substrate cannot be tested. Splats tested here, had at most 40% of their height below the substrate and were easily tested. However, as the extent of embedding
increases, not only will the error on the measurement increase but the splat will eventually become untestable. Despite these small drawbacks to the technique, it is applicable to most materials being cold sprayed and provides valuable information on the connection between adhesion strength and process conditions at the splat level, which does not require a significant investment in quantity of sprayed material. However, like any micromechanical test, a better understanding of the splat adhesion test would be gained by a thorough finite element analysis (FEA). For example, the ball-bond shear test for solder joints was recently reviewed and examined with FEA to explore small variations in test conditions and their effect on the experimental results [156]. For the splat adhesion test, questions about splat embedding, splat shape, defects at the splat/substrate interface and their relationship with fracture modes and failure mechanisms should be addressed in a similar manner.

6.4 - Conclusion

A splat adhesion technique, also called the modified ball-bond shear test, was used to examine the effect of the deposition velocity, gas temperature, substrate temperature and particle size on the adhesion strength of Ti and Ti6Al4V splats deposited on Ti or Ti6Al4V substrates. Strong adhesion strength approaching the bulk shear strength was measured for Ti splats deposited on Ti substrates at velocities significantly higher (e.g. 1140 m/s) than the critical velocity. Ti6Al4V splats deposited on Ti6Al4V substrate demonstrated poor particle adhesion and a bonded interface that was not fully continuous, with only traces of metallurgical bonding, even at deposition velocities of 1115 m/s.

An increase in the adhesion strength of splats was measured with preheating of the Ti and Ti6Al4V substrates to 400°C. A nearly ideal shearing behavior with fully bonded splat/substrate interface and adhesion strength of 284 MPa was observed for Ti deposited at 825 m/s on preheated substrates. Preheating of Ti6Al4V substrates also had a significant effect on the splat adhesion strength for Ti6Al4V splats, raising the splat adhesion strength from 100 MPa to 250 MPa. A combination of high velocities, preheating of the powder and substrate may be a key to the deposition of Ti6Al4V with adhesion strength that approaches the strength found in Ti6Al4V made by traditional methods.
The adhesion strength of splats was found to vary with particle size and particle position in the deposition pass. Particle deposited at the center of the deposition pass and of smaller particle diameter showed superior adhesion strength when compared to the large particles or particles at the edge of the deposition pass.

The extent of particle deformation measured in terms of splat flattening ratio, did not reflect well the degree of splat adhesion. The deformation of the substrate, on the other hand, was found to have a beneficial effect on the particle adhesion attributed to a confinement of the adiabatic shear region within the splat/substrate interface leading to a more successful metallurgical bonding.

6.5 - Acknowledgement

The cold spray equipment was provided by CFI project No. 8246, McGill University. The authors acknowledge the technical assistance of Bernard Harvey, Mario Lamontagne, Jean-Francois Alarie and Frederic Belval. The authors would also like to thank Jolanta Klemberg-Sapieha at École Polytechnique for access to the instrument used for splat adhesion testing.
Chapter 7, Mechanical Behavior of Ti Cold Spray Coatings Determined by a Multi-Scale Indentation Method

In Chapters 4 and 5, the hardness of the cold spray coatings was shown to be affected by the grain refinement, thermals softening, coating porosity and poor particle cohesion strength. The effect of these parameters varied depending of the indentation load used. The indentation testing at the single load was therefore insufficient for the comparison of the mechanical properties of the cold spray coatings to the properties of the bulk materials. In the present study, the effect of the indentation load on the hardness measurements on cold spray Ti coatings was evaluated. Varied load indentation was carried out with nanoindentation at loads between 1 and 20 mN and with microindentation at loads between 0.1 and 5 N. Nanoindentation measurements showed an indentation size effect and were fit to the Nix-Gao model for strain gradient plasticity. The microindentation measurements depended on the indentation size in a manner different from the Nix-Gao model and were strongly affected by the material porosity and cohesive strength between cold sprayed particles. By comparing results from the two indentation techniques, a hardness loss parameter was formulated that helped explain the mechanical behavior at all length scales and its relation to the various defects within the coating. Comparisons of the hardness loss parameter between cold spray coatings and a bulk Ti plate showed that this new parameter provided a good measure of when the mechanical behavior of the cold spray coatings approached that of a traditionally manufactured material. Evaluation of the hardness loss parameter of coatings and the bulk material, combined with microstructural characterization before and after indentation, was used to examine the relationships between processing conditions, coating microstructure and mechanical behavior for coatings fabricated with spherical and non-spherical Ti powders.

7.1 – Introduction

For well over a hundred years, hardness testing has provided scientists and engineers with a quick measure of the mechanical properties of a material or coating [157]. However, the technique has also been fraught with potential artifacts, many of which are related to a phenomenon known as the “indentation size effect” [81, 84, 89, 90, 118, 158-162]. This typically refers to the simple observation that the hardness measured by an indentation test is
often not constant, but instead changes with applied load. The explanation of this effect has changed over the years as sample preparation, indenter manufacture and testing apparatus have become more sophisticated. Initially, the size effect was most often tied to sample problems (e.g. roughness, work hardening, contamination), indenter problems (e.g. bluntness, roughness or simply poorly characterized geometry), or testing problems (e.g. poor calibration) [92, 163]. With modern hardness testing most, if not all, of these problems have been addressed and there is now the opportunity to explore and use the indentation size effect as a means to characterize the mechanical properties of materials [83, 89, 109, 110].

Modern versions of indentation size effect generally result from the fact that as the indent size changes, its interaction with defects within the material changes. For metals and alloys tested at very low indentation loads, there is generally a hardness increase with decreasing indent size. This version of the indentation size effect has been shown to take place due to an increase in strain gradients tied to the geometrically necessary dislocations that form below the indenter. A strain gradient plasticity model, commonly called the Nix-Gao model [89], has been used extensively in the literature, where the model allows one to determine a true material hardness independent of load or indent size. For ceramics and other brittle materials, such as intermetallic compounds, there is an indentation size effect due to the extent of fracture of the material [67, 83, 84, 110]. Depending on what one wishes to learn about the material, low load indentations can be used to explore the yield strength [67] or the high load limit can be applied to examine a hardness under conditions of extreme fracture [83, 84, 110].

The examples in the previous paragraph for useful versions of the indentation size effect are for engineering materials manufactured by traditional methods that have a relatively constant and homogenous distribution of defects. The problem presented here is for a material manufactured by cold spray [1-3], a young material processing technology that consolidates metallic powders by propelling them to supersonic velocities. The powders impact onto a substrate and build up a coating. Many complex phenomena take place during deposition, including: work hardening, formation of adiabatic shear instabilities and recrystallization [8, 35, 112, 164]. The plastic deformation and formation of the adiabatic shear instability are believed to contribute to the bonding [37, 41, 45, 49] for both particle to substrate (i.e. coating adhesion) and particle to particle (i.e. coating cohesion). Also, cold
sprayed coatings demonstrate regions of high dislocation density and grain refinement [8] and have varying amounts of large scale defects such as porosity and particle boundaries [64, 65]. The extent and character of the defects within cold sprayed materials is very dependent on the processing conditions and will not necessarily be constant within a given coating. Thus, this is a challenging material for hardness testing where analysis of the indentation size effect is necessary and was shown to reveal significant additional information compared to a single load analysis for the hardness [64].

In this paper, nanoindentation and microindentation techniques were used for varied load indentation on Ti cold spray coatings and bulk Ti plate (see Figure 7.1a) with the same acicular microstructure of the feedstock titanium powder used for coating deposition (see Figure 7.1b). The mechanical response of the coatings and the bulk Ti plate to the indentation load was evaluated by a measure of the hardness but also by post-examination of indents. The coating hardness at varied indentation loads was explained through the formulation of a hardness loss parameter that was correlated to coating porosity, cohesive strength and work hardening.

![Etched images (LOM) of (a) bulk Ti plate and (b) feedstock Ti powder. Acicular Ti microstructure was observed in feedstock powder and in the bulk Ti plate.](image)

**Figure 7.1:** Etched images (LOM) of (a) bulk Ti plate and (b) feedstock Ti powder. Acicular Ti microstructure was observed in feedstock powder and in the bulk Ti plate.
7.2 - Results and Discussion

7.2.1 – Cold Spray Deposition and Coating Characterization

The cold spray coatings were deposited from spherical and non-spherical powders at increasing deposition velocity. By changing process conditions, changes in the in-flight velocity of cold sprayed particles were realized. Figure 7.2 is a plot of measured particle velocity versus gas pre-heat temperature, with gas pressure also noted as labels on the graph. Average deposition velocities ranging from 608 to 805 m/s were obtained for spherical coatings and from 652 to 859 m/s for non-spherical coatings. The higher average velocity obtained for non-spherical powder compared to spherical powder is typically explained by the higher drag forces experienced by the irregular powder [14, 62]. For one coating sprayed with He and spherical powder, the deposition velocity reached 1173 m/s.

![Graph showing deposition velocity vs. gas preheat temperature and pressure](image)

**Figure 7.2:** Effect of the carrier gas preheat temperature and pressure on the spherical and non-spherical particle deposition velocity. The deposition velocity increased with gas preheat temperature and with gas pressure. Higher deposition velocities were measured with helium gas as opposed to nitrogen gas.

The results in Figure 7.2 were all measured within the same time frame of spraying the coatings studied here and were reported in previous publications by W. Wong et al.[14, 115]. Splats were sprayed some time after the coatings were prepared with identical temperature and pressure conditions. In all instances, a 6 -10 % increase in the average velocity was
measured for identical process conditions. The increase in velocity was attributed to small changes in the cold spray system that resulted in a more stable gas flow. Comparisons between material properties for splats sprayed at different conditions are expected to still be useful in comparison to the coatings as the velocity increase was a systematic change for all spray conditions. The extent of individual splat deformation (see Figure 7.3) and quality of the cold sprayed coatings (see Figure 7.4) changed as a function of deposition velocity.

![Figure 7.3: SEM images of top view and etched cross-section of cold spray splats deposited at a-b) 625 m/s (N₂ at 300°C 3 MPa) c-d) 825 m/s (N₂ at 800°C 4 MPa) and e-f) 1173 m/s (He at 350°C 4 MPa) particle velocity, gas preheat temperature and pressure conditions. A more pronounced bonding was observed at the splat and the substrate interface for splats deposited at a higher deposition velocity.](image)

Top view and cross-sectional micrographs of splats are shown in Figure 7.3. The etched cross-section of splats deposited at low deposition velocity showed non-continuous bonding between the splat and Ti substrate. The appearance of the splat-substrate interface became more continuous with increase in deposition velocity. Along with this indication of increased bonding, the splats became more deformed and pan-caked. While these observations are for Ti onto Ti, similar observations have been made for Ti deposited on mild steel [45]. As deposition velocity increased, coating microstructure was also modified for spraying with either the spherical [c.f. Figure 7.4(a-c)] or non-spherical powders [c.f. Figure 7.4(d-f)]. In both cases, an increase in deposition velocity translated into a more fully dense coating. This
effect was even more pronounced when spraying with He. Figure 7.5 shows a coating cross-section for the one specimen of spherical powder sprayed with He. This coating showed no obvious porosity at this magnification.

![Micrographs acquired by SEM for spherical (a-c) and non-spherical (d-f) Ti coatings deposited with nitrogen gas with a deposition velocity and gas conditions of: a) 608 m/s (N₂ at 300°C 3 MPa), b) 648 m/s (N₂ at 500°C 3 MPa), c) 805 m/s (N₂ at 800°C 4 MPa), d) 652 m/s (N₂ at 300°C 3 MPa), e) 725 m/s (N₂ at 500°C 3 MPa) and f) 859 m/s (N₂ at 800°C 4 MPa).](image1)

*Figure 7.4: Micrographs acquired by SEM for spherical (a-c) and non-spherical (d-f) Ti coatings deposited with nitrogen gas with a deposition velocity and gas conditions of: a) 608 m/s (N₂ at 300°C 3 MPa), b) 648 m/s (N₂ at 500°C 3 MPa), c) 805 m/s (N₂ at 800°C 4 MPa), d) 652 m/s (N₂ at 300°C 3 MPa), e) 725 m/s (N₂ at 500°C 3 MPa) and f) 859 m/s (N₂ at 800°C 4 MPa).*

![Micrograph acquired by SEM for a spherical Ti coating deposited at deposition velocity of 1173 m/s (He at 350°C 4 MPa).](image2)

*Figure 7.5: Micrograph acquired by SEM for a spherical Ti coating deposited at deposition velocity of 1173 m/s (He at 350°C 4 MPa).*

Porosity measurements are plotted versus deposition velocity in Figure 7.6. The coatings deposited with non-spherical powder showed a higher porosity than coatings
deposited with spherical powder. For both powders, an increase in the deposition velocity led to a decrease in coating porosity.

Figure 7.6: Coating porosity with respect to deposition velocity. The spherical coatings deposited with nitrogen are plotted as closed circles while the spherical coating deposited with helium gas is plotted as an open circle.

For spherical powders, the coating porosity approached that of the bulk Ti plate for deposition velocities above 750 m/s. For non-spherical powders, the highest deposition condition, with a velocity of 859 m/s, led to low porosity of about 2%. One other condition, with a velocity of 762 m/s, led to a low porosity. It was not clear why this spray condition led to a more favorable porosity while others with higher velocities did not.

7.2.2 – Splat Adhesion Strength

Changes in the deposition velocity also resulted in changes in the splat adhesion strength. In Figure 7.7, the splat adhesion strength is plotted as a function of deposition velocity for Ti splats deposited from spherical Ti powder onto a CP Ti plate. As deposition velocity increases, the splat bond strength increases and approaches the bulk shear strength of Ti. For most splats deposited with nitrogen, the splat de-bonded at the splat-substrate interface. For the splats deposited with He, most were partially embedded in the substrate and failed within the particle itself. Thus, the splat adhesion strength for splats with He are expected to be a lower limit for the strength of the bonded interface. As particles impact,
deformation and the formation of an adiabatic shear instability are the main mechanisms for metallurgical bonding of cold sprayed material [2, 3, 37], measurements of splat adhesion strength may provide useful comparisons to the indentation load response of coatings, which is reflective of cohesion strength between sprayed particles.

![Shear Strength of Bulk Ti](image)

**Figure 7.7**: Splat adhesion strength for Ti splats on a commercially pure Ti plate. The data points in black represent the adhesion strength of splats deposited with nitrogen gas. The data point in open circle represents the adhesion strength of splat deposited with helium gas. The adhesion strength of splats increased with increase in the deposition velocity. The horizontal line is the shear strength of grade 2 bulk Ti and is provided as a reference [165].

### 7.2.3- Nanohardness and Microhardness Results and Comparison

Results from nanoindentation testing (at a constant peak load of 1 mN and indents across the coating) are presented in Figure 7.8(a) as average nanohardness versus deposition velocity. No significant variation in nanohardness was observed as a function of position within the coatings. This trend has been observed previously [33, 112], where nanoindentation provided hardness associated with material with minimal influence of porosity and other macroscopic defects. The nanohardness of the coatings was higher compared to the bulk material and the starting powders (all plotted at 0 m/s in Figure 7.8a). Also, coatings prepared with non-spherical powders were marginally harder than those
prepared with spherical powders. Lastly, at this indentation load, the starting powders and bulk Ti plate all had similar hardness.

In Figure 7.8(b), microhardness of spherical and non-spherical coatings is plotted with respect the deposition velocity. The hardness of the feedstock powder was not measured using a microindentation technique because, even for low loads, the indent size approached the size of the particles. The microhardness values for spherical and non-spherical coatings were similar to each other for all spray conditions and not significantly higher or lower than the hardness of the bulk Ti plate.

![Image](image_url)

**Figure 7.8:** Cold spray coatings a) nanohardness at 1mN load and b) microhardness at 0.1 N load. Higher nanohardness was measured for the cold spray coatings when compared to the nanohardness of the feedstock powder and bulk Ti plate. The nanohardness was higher for the non-spherical coatings and lower for the spherical cold spray coatings. On the other hand, no difference between the microhardness of the cold sprayed coatings and microhardness of the bulk Ti plate was measured.

From examination of Figure 7.8, different conclusions can be made about the relative hardness of the coatings, powders and substrate, depending on whether nanohardness results (c.f. Figure 7.8a) or microhardness results (c.f. Figure 7.8b) are used. A number of parameters affect the hardness measurements in the nanoindentation and in the microindentation regimes. Reduction in grain size or increase in material work hardening and dislocation density are often associated with the increase in the hardness [92]. On the other hand, a decrease in the hardness can be tied to material defects such as porosity and in the case of coatings to the particle de-bonding [65, 92, 166]. The degrees to which these
parameters affect the hardness measurements depend on the indentation load and size. Thus, for materials such as cold sprayed coatings, which have different amounts of work hardening, porosity and particle bonding strength, it becomes critical to explore the indentation size effect in detail to determine a best method that explains the hardness response of all materials consistently.

7.2.4-Nanoindentation Size Effect on Hardness.

Matrix nanoindentation with indents at varying load was performed in random locations in the coatings. An example of a matrix of indents imaged in the SEM is shown in Figure 7.9. As can be seen in Figure 7.9a, the indent #1, which encountered porosity, demonstrated an uncharacteristic increase in the indentation depth (c.f. Figure 7.9b) compared to other indents that did not encounter porosity. In some instances, indentation in a coating with poor cohesive strength could result in particle de-bonding similar to one observed with indent #3 and possibly indent #2 in Figure 7.9a.

![Figure 7.9: a) SEM image of 1-20 mN load nanoindentation indents in spherical coating deposited at 608 m/s (N_2 at 300°C 3 MPa) and b) corresponding indentation load vs. indentation depth curves. A more pronounced decrease in the indentation depth is measured for the indents affected by the coating porosity – indent 1 and particle de-bonding - indents 2 and 3.](a)

Like the porosity interaction, particle de-bonding induced an uncharacteristic increase in the indentation depth for a given indentation load as can be seen in Figure 7.9b. Other
Indents for this matrix were acceptably similar to one another within typical experimental error encountered for nanoindentation. These indents also were found to be far away from porosity and particle boundaries (c.f. Figure 7.9a). By the examination of the indentation load-depth curves coupled with topographical imaging of residual indents, a systematic data filtering was carried out on each indent to limit the effect of the coating porosity and particle de-bonding on the nanohardness measurements. Indents that appeared to be affected by defects, from significant deviations in the load-displacement data, observation of defect interaction in AFM images or both, were discarded and not included in the final results reported here.

The average nanohardness at eight different loads ranging from 1 to 20 mN is plotted in Figure 7.10 as a function of the contact depth for the bulk Ti plate and all of the coatings. For every dataset, the qualitative trend is the same: with increasing indentation depth the nanohardness decreases. Due to the nature of the method used, where larger scale defects were avoided, the variation in hardness seen in Figure 7.10 is likely due to the version of the indentation size effect due to geometrically necessary dislocations, often referred to as the Nix-Gao model [89]. This model, using the law of strain gradient plasticity and dislocation density distribution, is governed by Eq.7.1,

$$H = H_o \sqrt{1 + \frac{h^*}{h_c}}$$  \hspace{1cm} \text{Eq. 7.1}$$

where $H$ is the nanohardness, $h_c$ is the indentation depth, $H_o$ is a material hardness at infinite indentation depth, and $h^*$ is a characteristic length scale.

The nanohardness measurements presented in Figure 7.10 were fit to Eq. 7.1 and the results of the fits are summarized in Table 7.1. The best fit curves are also included in Figure 7.10. In general the Nix-Gao model provided a confident fit to the nanohardness measurements. However, the most confident fit was obtained for the bulk Ti plate. Fits to the data for cold spray coatings were in some cases not as confident and generally occurred for cases where the coating had high porosity. Thus, despite the data filtering to remove suspect indents, there may be some small influence of porosity and particle de-bonding on the nanohardness results that leads to a small departure from the Nix-Gao model.
Figure 7.10: Nanohardness data and the result from fitting to Eq.7.1 for a) spherical cold spray coatings, b) non spherical cold spray coatings and the bulk Ti plate (shown in both (a) and (b)).

Table 7.1: Strain gradient plasticity fit parameters for spherical and non-spherical coatings

<table>
<thead>
<tr>
<th>Spherical Coatings</th>
<th>h* (nm)</th>
<th>H_o (GPa)</th>
<th>Non-spherical Coatings</th>
<th>h* (nm)</th>
<th>H_o (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>608 m/s (N_2 at 300ºC 3 MPa)</td>
<td>39±15</td>
<td>2.92±0.12</td>
<td>652 m/s (N_2 at 300ºC 3 MPa)</td>
<td>34±14</td>
<td>3.36±0.14</td>
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<tr>
<td>648 m/s (N_2 at 500ºC 3 MPa)</td>
<td>64±20</td>
<td>2.86±0.13</td>
<td>725 m/s (N_2 at 500ºC 3 MPa)</td>
<td>27±13</td>
<td>3.62±0.14</td>
</tr>
<tr>
<td>688 m/s (N_2 at 600ºC 3 MPa)</td>
<td>37±9</td>
<td>3.06±0.07</td>
<td>762 m/s (N_2 at 600ºC 3 MPa)</td>
<td>63±9</td>
<td>3.16±0.07</td>
</tr>
<tr>
<td>785 m/s (N_2 at 750ºC 4 MPa)</td>
<td>85±31</td>
<td>3.15±0.20</td>
<td>844 m/s (N_2 at 750ºC 4 MPa)</td>
<td>54±13</td>
<td>3.23±0.11</td>
</tr>
<tr>
<td>805 m/s (N_2 at 800ºC 4 MPa)</td>
<td>36±12</td>
<td>2.98±0.10</td>
<td>859 m/s (N_2 at 800ºC 4 MPa)</td>
<td>80±25</td>
<td>2.86±0.16</td>
</tr>
<tr>
<td>1173 m/s (He at 350ºC 4 MPa)</td>
<td>144±20</td>
<td>2.60±0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk Ti</td>
<td>84±11</td>
<td>2.19±0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The parameter $H_o$ in Eq.7.1 is an indication of a “true” material hardness at a condition where only statistically stored dislocations influence the hardness (independent of load or depth) and there is no effect from larger scale defects. In Figure 7.11, $H_o$, is plotted as a function of deposition velocity. The spherical and non-spherical cold spray coatings demonstrate higher hardness when compared to the bulk Ti plate, plotted at 0 m/s. While no direct comparison for $H_o$ can be made for the feedstock powders, the comparison to the Ti plate, which had similar hardness to the powders at a load of 1 mN, provides evidence that...
the cold sprayed particles become harder upon impact. Higher hardness measurements in the cold spray coatings is likely a result of high impact stresses and strain induced by the cold spray deposition process, but perhaps also grain refinement as previously reported by K. Kim et al. [8, 33].

![Figure 7.11: True hardness, $H_o$, of the bulk Ti, spherical and non-spherical cold spray coatings vs. deposition velocity. The spherical coating deposited with helium gas is plotted in an open circle.](image)

Trends for the true hardness, $H_o$, versus deposition velocity for both the spherical and non-spherical coatings were found to be rather weak. For spherical coatings, the true hardness stayed constant within the error on the measurements. For non-spherical coatings, there was a slight decrease in hardness with increasing velocity. Ti has a hexagonal closed packed structure and plastic deformation in the material is limited. It is possible that after the initial plastic deformation, the remainder of the impact stress is converted to heat and no further work hardening takes place [27, 35, 116, 121, 133]. For both spherical and non-spherical coatings, the true hardness was nearly constant over all deposition conditions with the averages being $H_o = 2.85\pm0.23$ GPa for spherical coatings and $H_o = 3.25\pm0.28$ GPa for non-spherical coatings. The difference in the true hardness between coatings prepared with the different powders may be due to differences in the starting powders and the way they deform upon impact. A higher oxygen content in the non-spherical powder [14] compared to the spherical powder may explain some of the increase in hardness. Another consideration is
the size of the particles. For the smaller, spherical particles, it was previously shown that the impact site has an increase in hardness while regions that undergo jetting can have thermal softening [112]. One may consider that only a small portion of the larger, non-spherical particles undergo jetting, while the rest of the particle is free to work harden upon impact and due to impact from other particles.

7.2.5- Microindentation Size Effect on Hardness.

Microindentation measurements also revealed a size effect, but in a different manner than nanoindentation measurements. For coatings prepared with spherical powder, two types of general behavior of microhardness versus indentation depth were observed (see Figure 7.12a). For the two spherical coatings, prepared at low deposition conditions (i.e. deposition velocities of 608 and 648 m/s), the microhardness decreased with indentation depth up to approximately 5 μm and then became constant. All other spherical coatings, with higher deposition conditions, revealed a relatively constant and stable microhardness, the same trend observed for the bulk Ti plate.

![Figure 7.12: Microindentation hardness as a function of the indentation depth for a) spherical and b) non-spherical cold spray coating. The microhardness decreased with increase in the indentation depth for coatings deposited at low deposition velocity. A plateau hardness for all coatings was eventually reached.](image)

Coatings prepared with non-spherical powder had a similar demarcation between high and low deposition conditions, but also slightly different trends (see Figure 7.12b). For the
two non-spherical coatings prepared at low deposition conditions (same conditions as for spherical but with velocities of 652 and 725 m/s), the hardness was relatively constant at depths up to 5 – 7 µm and then dropped above these depths. For non-spherical coatings prepared with higher deposition velocity, the hardness was stable (i.e. no rising or falling), but was also somewhat scattered. All of the observations on microindentation trends of hardness with depth are summarized in Table 7.2.

Table 7.2: Summary of plateau hardness and behavior of hardness versus indentation depth for microindentation results. For comparison, porosity and adhesion strength measurements are presented as well.

<table>
<thead>
<tr>
<th>Spherical Powders</th>
<th>Coating Porosity (%)</th>
<th>Splat Adhesion Strength</th>
<th>General Behavior of H vs. h</th>
<th>$H_{\text{plateau}}$ (GPa)</th>
<th>Non-spherical Powders</th>
<th>Coating Porosity (%)</th>
<th>General Behavior of H vs. h</th>
<th>$H_{\text{plateau}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$ at 300ºC 3 MPa</td>
<td>High</td>
<td>32±52</td>
<td>1</td>
<td>1.14±0.03</td>
<td>$N_2$ at 300ºC 3 MPa</td>
<td>High</td>
<td>3</td>
<td>1.01±0.36</td>
</tr>
<tr>
<td>$N_2$ at 500ºC 3 MPa</td>
<td>Low</td>
<td>92±51</td>
<td>1</td>
<td>1.32±0.09</td>
<td>$N_2$ at 500ºC 3 MPa</td>
<td>High</td>
<td>3</td>
<td>1.41±0.23</td>
</tr>
<tr>
<td>$N_2$ at 600ºC 3 MPa</td>
<td>Low</td>
<td>128±86</td>
<td>2</td>
<td>1.85±0.04</td>
<td>$N_2$ at 600ºC 3 MPa</td>
<td>Low</td>
<td>4</td>
<td>1.83±0.20</td>
</tr>
<tr>
<td>$N_2$ at 750ºC 4 MPa</td>
<td>Low</td>
<td>152±16</td>
<td>2</td>
<td>2.21±0.08</td>
<td>$N_2$ at 750ºC 4 MPa</td>
<td>High</td>
<td>4</td>
<td>2.30±0.29</td>
</tr>
<tr>
<td>$N_2$ at 800ºC 4 MPa</td>
<td>Low</td>
<td>238±33</td>
<td>2</td>
<td>2.15±0.35</td>
<td>$N_2$ at 800ºC 4 MPa</td>
<td>Low</td>
<td>4</td>
<td>2.41±0.26</td>
</tr>
<tr>
<td>He at 350ºC 4 MPa</td>
<td>Low</td>
<td>25±21</td>
<td>2</td>
<td>2.57±0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti plate</td>
<td>Low</td>
<td>-</td>
<td>2</td>
<td>1.97±0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* A porosity of less than 3% was marked as low while greater than 5% was marked as high.

1 – hardness drops “early,” plateaus above 5 µm
2 – no hardness drop, stable
3 – hardness drops “late,” above 7.5 µm
4 – no drop, hardness is stable but scattered

Differences between the spherical and non-spherical coatings for their trends of microhardness versus indentation depth are likely due to the significant difference in particle size. At low loads, diagonals of Vickers indentations were on the order of 10 µm, large enough to interact strongly with particle boundaries for the spherical coatings, but not necessarily for the non-spherical coatings with larger powder size. At higher loads, the
diagonals for the Vickers indents reach 60 – 100 μm, a size that certainly provides interactions with particle boundaries for both spherical and non-spherical coatings.

For higher deposition velocity, spherical coatings had a very stable and constant microhardness, while the non-spherical coatings had a stable but scattered microhardness. This trend may also be due to the differences in average particle sizes, but could be also due to differences in deposition velocity and the fact that the non-spherical coating had, on average, more porosity. Another consideration is that the non-spherical powders have an irregular shape. Upon arrival, a metallurgical bond is developed at the impact site but if a significant portion of the particle does not participate strongly to the impact event, the bonding strength may be reduced. Thus, one would expect a higher degree of variability of the cohesive strength when using irregular powders. Despite differences in the general behavior of microhardness versus depth, all of the coatings exhibited a constant microhardness at the highest loads where there is the most significant interaction with defects such as particle boundaries and porosity. Thus, to provide a simple characterization of the microhardness for comparison between coatings, the values for the highest three loads were averaged. These results are presented in Table 7.2 as “plateau hardness”.

Trends in microhardness identified in Figure 7.12 and summarized in Table 7.2 were correlated with features observed in optical micrographs of residual indents. Figure 7.13 is a collection of optical micrographs for the bulk Ti plate (c.f. Figure 7.13a and b), coatings sprayed with nitrogen with velocities of 608 m/s (c.f. Figure 7.13 c-d) and 805 m/s (c.f. Figure 7.13e and f), and the coating sprayed with helium (c.f. Figure 7.13 g and h). In each case, an image is provided for a residual indent at the lowest load (0.1 N) and the highest load (5 N). For the residual indents on the Ti plate, a deviation from a perfect diamond shape was observed (see Figure 7.13b). This is due to plastic anisotropy that has been previously observed for CP Ti [167]. Otherwise, the indents were well behaved with no obvious interaction with defects.
Figure 7.13: Optical images of 0.1 N and 5 N indents in a-b) bulk Ti plate, spherical Ti coatings deposited at c-d) 608 m/s ($N_2$ at 300°C 3 MPa), e-f) 805 m/s ($N_2$ at 800°C 4 MPa) and g-h) 1173 m/s (He at 350°C 4 MPa) particle deposition velocity, gas preheat temperature and gas pressure. Indenter interaction with coating porosity and particle debonding in the indentation site were observed.
In contrast, the indents on the coatings deposited at low deposition velocity of 608 m/s exhibited evidence of particle de-bonding and interaction with porosity. Comparing the plateau hardness of the Ti plate to this coating (c.f. Table 7.2), these defects led to a distinct reduction in the hardness. The two coatings prepared at higher velocity conditions with nitrogen (c.f. Figure 7.13e and f) and helium (c.f. Figure 7.13 g and h), showed residual indents that were much similar to those on the bulk Ti plate. Some particle de-bonding and interaction with porosity was observed, but not nearly as much as for the lower deposition velocity conditions. These observations are consistent with trends identified in Table 7.2 where the high deposition velocity condition coatings have the same trend of microhardness with depth as the bulk Ti and have plateau hardness as high or higher than the bulk Ti plate.

Figure 7.14: Optical images of 98 mN and 4900 mN indents: in non-spherical deposited at a-b) 652 m/s (N₂ at 300°C 3 MPa) and at c-d) 859 m/s (N₂ at 800°C 4 MPa) particle deposition velocity, gas preheat temperature and gas pressure.

Optical micrographs of residual indents in non-spherical coatings provided similar information. For a coating with lower deposition velocity of 652 m/s, there is evidence of extensive defect interaction (c.f. Figure 7.14a and b), while for high deposition velocity of
859 m/s, there is not nearly as much defect interaction (c.f. Figure 7.14c and d). These differences in defect interaction with the indenter were reflected in differences in the plateau hardness for the two non-spherical coatings (c.f. Table 7.2). Observation of residual indents for the other spherical and non-spherical coatings, while not shown here, showed information consistent with data in Table 7.2 and the observations discussed here.

7.2.6- Formulation of a Hardness Loss Parameter

As discussed in section 7.2.3, indentation at only one load, whether it be with nanoindentation or microindentation, provides an incomplete and potentially incorrect comparisons for the mechanical properties of cold sprayed materials. An exploration of two distinctly different versions of an indentation size effect for nanoindentation (c.f. section 7.2.4) and microindentation (c.f. section 7.2.5) provided valuable information on the mechanisms for changes in the measured hardness. As can be seen in Figure 7.10, in the nanoindentation regime, the hardness drops with indentation load following the strain gradient plasticity model of Nix and Gao [89]. Thus, with nanoindentation performed in regions least affected by porosity and particle boundaries, the dominant mechanism for the hardness changes (i.e. indentation size effect) in Figure 7.10 must be variation in the density of geometrically necessary dislocations beneath the indenter. This version of the indentation size effect becomes less pronounced at higher indentation loads and the nanohardness eventually converged to a constant hardness value, $H_o$, which is independent of the indentation depth. This parameter, $H_o$, is the “true” material hardness, which is dependent on the statistically stored dislocation density in the material and could be also tied to the material grain size, work hardening and recrystallization linked to cold spray deposition process [8, 33, 38, 65, 112]. In a fully dense material, $H_o$ should correlate well with indentation at higher loads and greater indentation depth (e.g. the microhardness measured here).

In the cold spray process, there is significant evidence that near fully dense materials can be fabricated [1]. However, very little research has been done to quantify the extent to which a coating with very low porosity will behave mechanically in the same manner as the material prepared by traditional bulk manufacturing methods. Other factors besides porosity
come into play, such as the cohesion between cold sprayed particles. In this study, these additional defects caused the coating microhardness to drop and, in cases where there was significant indenter-defect interaction, to vary with indentation depth (see Figure 7.12). The plateau hardness, taken from the highest three loads, is representative of a microhardness that has significant interaction with porosity and particle boundaries near the indentation site.

With these two important hardness parameters defined and tied to specific types of defects in the coatings: “true” material hardness, $H_o$, tied to dislocations, and the plateau hardness, $H_{plateau}$, tied to porosity and particle boundaries, we now formulate the concept of a “hardness loss.” The microhardness measurements were consistently lower than $H_o$, which can be seen by comparing Figure 7.10 and Figure 7.12, or values of $H_o$ and $H_{plateau}$ in Table 7.1 and Table 7.2. Also, Figure 7.15 provides an example dataset of both nanohardness and microhardness for one of the spherical cold spray coatings.

![Figure 7.15: Indentation size effect on nanohardness and microhardness measurements in spherical cold spray coating deposited at 608 m/s ($N_2$ at 300°C 3 MPa). The difference between true hardness - $H_o$ and plateau hardness – $H_{plateau}$ is measured in terms of “hardness loss”.

The difference between $H_o$ and $H_{plateau}$ is the “hardness loss” related to the presence of porosity and incomplete particle bonding within the coating. As the “true” hardness of the materials studied here also varies slightly from coating to coating due to differences in initial
dislocation density and small variations in microstructure due to recrystallization, the hardness loss was best taken as a percent difference by the following equation:

\[
\text{Hardness Loss (\%)} = \frac{H_o(GPa) - H_{\text{plateau}}(GPa)}{H_o(GPa)}
\]

Eq.7.2

The hardness loss was calculated for all the cold spray coatings and bulk Ti with Eq.7.2 and the \(H_o\) and \(H_{\text{plateau}}\) values from Table 7.1 and Table 7.2. A decrease in the hardness loss was observed with increase in the deposition velocity, as shown in Figure 7.16. A hardness loss reaching 0% was measured for the coating deposited with He gas at 1173m/s. Interestingly, the hardness loss in the bulk material was not zero (~10%) and was likely due to the asymmetric nature of some of the indents, as seen in Figure 7.13b. Other defects may have led to hardness loss for the bulk material such as porosity, or grain boundary sliding or microcracking. Some part of the hardness loss may also be related to the small differences between the Berkovich and Vickers indenters [118, 119].

![Figure 7.16: Percent hardness loss in a) spherical and b) non-spherical cold spray coatings plotted as a function of deposition velocity. A linear regression fit for the hardness loss of spherical and non spherical cold spray coatings is shown. The spherical coating deposited with helium gas is plotted in an open circle.](image)

The dependence of the hardness loss parameter on porosity revealed a direct relationship for both spherical (see Figure 7.17a) and non-spherical coatings (see Figure
7.17b). However, as noted in Table 7.2, the coatings fit into two groups of low porosity (<3%) and high porosity (>5%). For spherical coatings with low porosity, there were significant differences in hardness loss despite similar porosity. Similarly, for high or low porosity non-spherical coatings, there are significant differences in hardness loss within each group. Thus, the apparent direct relationship seen in both Figure 7.17a and b is somewhat deceptive. Other mechanisms for hardness loss must be at play.

![Figure 7.17: Percent hardness loss vs. a) spherical and b) non-spherical coating porosity. An increase in the hardness loss is measured with increase in the coating porosity for spherical and non-spherical Ti coatings. The spherical coating deposited with helium gas is plotted in an open circle.](image)

Other than porosity, the other mechanism for hardness loss, seen in Figure 7.13 and Figure 7.14, was particle de-bonding. This mechanism is somewhat complex and is a function of the inter-splat bonding strength (i.e. cohesive strength). The cohesive strength of a cold spray coating depends on the formation of the adiabatic shear instability, which is believed to become significant above the critical velocity for a given material. For Ti, the critical velocity has been found to be anywhere from 700 m/s to 900 m/s [2]. For the spherical particles of similar size to those sprayed here, the critical velocity is expected to be between 700 and 750 m/s [2, 14, 33]. For the non-spherical Ti powder, the critical velocity has been measured previously to be 690 - 880 m/s [13]. The extent of metallurgical bonding will still vary as a function of particle velocity, particle impact angle, the in-flight particle temperature, heat input from the particle impact and a corresponding temperature rise of the coating during deposition. Many of these phenomena are difficult to measure experimentally,
especially the in-flight particle temperature. Computer simulations can successfully predict the heat input from the gas and particle impact with the substrate [26, 37].

As a first step in understanding the relationship between the hardness loss parameter and cohesive strength, we consider the correspondence between hardness loss and the splat adhesion strength (see Figure 7.18). Despite the complexity associated with cohesive strength as discussed in the previous paragraph, the relationship between Ti splat adhesion strength and hardness loss parameter was good. Thus, the basic mechanism of splat impact leading to adiabatic shear instability and metallurgical bonding seems to translate quite well to hardness loss due to particle cohesive strength.

![Figure 7.18: Percent hardness loss of spherical coatings as a function of cold spray splat adhesion strength on a bulk Ti plate. A decrease in hardness loss was measured with increase in the splat adhesion strength. Shear strength of a grade 2 Ti [165] was used when plotting data for the bulk Ti plate.](image)

Comparisons between the hardness loss of the cold spray coatings and the bulk Ti can provide a new understanding for optimization of the cold spray process to obtain a near fully dense material with similar mechanical response to materials fabricated by more traditional methods. The fits provided in Figure 7.16 are linear regressions to the data for both the spherical and non-spherical coatings prepared with nitrogen. The intercept at 0% hardness loss is indicative of the material behaving in an ideal bulk-like manner with no particle de-
bonding and porosity and with no other significant mechanisms for indentation size effect other than the geometrically necessary dislocations of the Nix-Gao model. Such behavior was only observed for the coating deposited with He at deposition velocity of 1173 m/s. Coatings deposited with nitrogen all had deposition velocities below 850 m/s and also exhibited particle de-bonding at least to some small extent. Thus, considering these observations and using the intercepts at zero hardness loss from Figure 7.16, the minimum recommended deposition velocities in order to achieve ‘bulk like’ properties for the spherical and non-spherical Ti powders deposited with nitrogen gas are 910 m/s and 950 m/s, respectively. However, to define zero hardness loss as the necessary condition for a quality coating is perhaps too strict. The hardness loss for the Ti plate was roughly 10%, and considering the error bars, coatings with a hardness loss on the order of 15% behaved in a similar manner. One would need to fully explore the effect of variation in cohesive strength in these coatings on the bulk behavior, perhaps in a tensile testing configuration [54].

It is important to note that higher gas temperature, when compared to Helium coating, is used to deposit nitrogen coatings. The gas temperature has been previously shown to have an effect on particle adhesion and can affect the hardness loss parameter [45]. Separate study is required to define the intercept velocity for coatings deposited with He. It would also be interesting to explore the effect of other process conditions, such as feed stock power temperature and the substrate temperature, on the hardness loss parameter and whether these changes can provide a significant reduction in the intercept velocity from Figure 7.16.

The hardness loss technique explored here has implications for hardness testing in general, but especially for materials fabricated by powder consolidation. To simply measure hardness at one load, whether it is large or small will not provide a complete picture of the mechanical response of the material. The technique developed and reviewed here, with combined nanohardness and microhardness and development of the hardness loss parameter, provides a relatively simple alternative that will give a more complete picture of the mechanical integrity of a material made by cold spray or other powder consolidation techniques.
7.3 - Conclusions

The mechanical behavior of Ti cold spray coatings, prepared with both spherical and non-spherical powders, was examined by indentation methods. Single load indentation testing was found to be insufficient and led to potentially erroneous comparisons among the coatings fabricated. Instead, a method using many indentation loads was used to explore the indentation size effect in both the nanoindentation and microindentation regimes. In combination with observation of the residual indents, a hardness loss parameter was formulated that uses both data from nanoindentation, which was representative of dislocation based indentation size effect (i.e. the Nix-Gao model), and from microindentation, which was representative of indentation size effect related to porosity and poor particle adhesion. Using the multiple load indentation method developed here and a number of other experimental techniques, the following conclusions were made:

1) Based on the hardness measurements and the true hardness calculated from the Nix-Gao fits to nanoindentation data, the cold spray Ti coatings were harder than the starting powders and harder than the annealed bulk Ti specimen, likely due to work hardening that takes place upon particle impact.

2) All of the cold spray coatings prepared with nitrogen as the propelling gas exhibited a microhardness, $H_{\text{plateau}}$, that was lower than the true hardness, $H_o$, obtained from the Nix-Gao fits to nanoindentation data. This hardness loss was due to interaction of the indenter with particle boundaries and porosity.

3) A hardness loss parameter was developed that described the extent to which porosity and poor cohesion strength affect the mechanical behavior of the cold spray coatings. The hardness loss decreased as deposition velocity increased. For the lowest spray condition, the hardness loss was 61% for spherical coatings and 70% for non-spherical coatings. For the highest spray condition with nitrogen propelling gas, the hardness loss was 28% for spherical coatings and 16% for non-spherical coatings.

4) Adhesion strength was measured between Ti splats on a bulk Ti plate. The adhesion strength increased as a function of deposition velocity. Also, as the adhesion strength increased, the hardness loss decreased, indicating the measurements of splat adhesion can
provide some indication of cohesive strength within a coating sprayed with the same conditions.

5) Based on trends of hardness loss with porosity and adhesion strength and examination of images of residual indents, the main mechanism for hardness loss was found to be particle de-bonding (i.e. poor cohesive strength). While porosity did influence the hardness loss, the effect of particle de-bonding was more obvious as a range of cohesive strength was realized in the coatings studied here while only a narrow range of porosity was observed.

6) For the coating prepared with helium as the propelling gas, the hardness loss was close to zero (1%). At the same time, the splat adhesion strength was high and no evidence of particle de-bonding in residual indents was observed.

7) The hardness loss parameter was used to compare cold sprayed material to a bulk Ti plate prepared by traditional manufacturing methods. This led to a recommended minimum deposition velocity for fully dense Ti coatings with “bulk-like” behavior (i.e. no particle de-bonding or significant porosity effects). For the powders sprayed here, the minimum velocity was 910 m/s for spherical powders and 950 m/s for non-spherical powders.

8) The technique of multiple load indentation and use of the hardness loss parameter was found to adequately explain the mechanical behavior in cold spray coatings that have a wide range of defects. In comparison to single load indentation methods, the new technique provided a more complete description of the mechanical behavior and the ability to make meaningful comparisons between coatings.

7.4 - Acknowledgements

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Engineering Laboratory (FCSEL) at École Polytechnique de Montreal for providing access to the instrument used for splat adhesion testing.
Chapter 8. Tensile Testing of As Deposited and Annealed Titanium Cold Spray Coatings.

In the previous chapters, the mechanical property testing was investigated under shear with a modified ball bond shear techniques and under compression with multi-scale indentation technique. In the present chapter, the mechanical properties of cold spray coatings were investigated in tension with a micro-flat tensile coating - MTC technique. The effect of the grain refinement, coating porosity and particle cohesion strength on the ultimate tensile strength and ductility was evaluated for as deposited and annealed titanium cold spray coatings. The three techniques were used to determine the deposition conditions at which the cold spray titanium demonstrated mechanical properties of commercially manufactured titanium.

8.1. Introduction

Over past decade, extensive research was carried in the cold spray process for deposition of high strength, high melting point materials like titanium and its alloys for potential applications in aerospace industries [14, 15, 19, 35, 37, 115, 168]. During cold spray deposition, thick, dense coatings are produced from metallic powder. Coatings with diverse shapes can be deposited at high deposition rate onto various substrates, making cold spray ideal for near net shape production technology and part repair [15]. The potential applications for the cold spray process are promising but the properties of the coatings are not fully explored [19]. Up to date, research was carried with goal of determining the mechanical and microstructural properties of titanium the cold spray coatings. Titanium coatings were shown to have low oxide content [15, 17, 35, 148] but were shown to exhibit extensive grain refinement [8, 10], work hardening [14, 37, 64, 112, 117] and poor particle adhesion and cohesion strength [50, 113, 117]. The tensile properties of the titanium cold spray coatings were measured to be below average and demonstrated only a marginal improvement after annealing [15, 35]. In most studies, the mechanical and microstructural property testing was performed on the titanium coatings with existing defects that were not fully explored [15, 35].
In the previous work described in Chapters 4-7, a strong correlation was found between the deposition conditions, microstructure, microstructural defects, such as porosity and particle cohesion strength, and mechanical properties [112, 113, 117]. In the present chapter, mechanical and microstructural properties of titanium cold spray coatings were investigated at wide-range of deposition velocity and gas temperature conditions. The cold spray deposition conditions were optimized to produce coatings with low defect content. The microstructure of the coatings was analyzed with channeling contrast imaging while the mechanical properties were measured with nanoindentation and microindentation techniques described in the previous chapter [117]. The ultimate tensile strength and the ductility of as deposited and annealed cold spray coatings was measured with micro flat coating tensile test [54]. The failure mechanisms within the cold spray coatings were correlated with coating microstructure, strain hardening and the particle adhesion/cohesion strength that was measured with modified ball bond shear technique [45, 113]. The coatings demonstrating mechanical properties approaching those of commercially manufactured titanium were determined and two methods for the optimization of the cold spray deposition method were proposed.

8.2. Results

8.2.1 - Microstructure

The cold spray coatings, 5 mm in thickness, were deposited at increasing deposition velocity with spherical, commercially pure Ti powder. The coatings were deposited at five different deposition conditions with helium and nitrogen gas. The velocity for each deposition condition was measured prior to the sample preparation and is listed in Table 8.1. The deposition velocity measurements were higher than the velocity reported in the previous publications [112, 113, 117] attributing to the replacement of the nozzle and improvement in the systems that were made over time.

The cross-section of as deposited and annealed cold spray coatings produced according to the conditions listed in Table 8.1 are shown in Figure 8.1. Denser coatings were obtained at higher deposition velocity. The annealing did not contribute to a significant
coating densification. The average porosity of the coatings was measured from the ten SEM images similar to the ones shown in Figure 8.1.

### Table 8.1: Cold Spray coating deposition condition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>Gas preheat Temperature (ºC)</th>
<th>Gas Pressure (MPa)</th>
<th>Deposition Velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti 300 ºC 3 MPa</td>
<td>Nitrogen</td>
<td>300</td>
<td>3</td>
<td>648</td>
</tr>
<tr>
<td>Ti 500 ºC 3 MPa</td>
<td>Nitrogen</td>
<td>500</td>
<td>3</td>
<td>723</td>
</tr>
<tr>
<td>Ti 800 ºC 4 MPa</td>
<td>Nitrogen</td>
<td>800</td>
<td>4</td>
<td>852</td>
</tr>
<tr>
<td>Ti 350 ºC 2 MPa</td>
<td>Helium</td>
<td>350</td>
<td>2</td>
<td>877</td>
</tr>
<tr>
<td>Ti 350 ºC 4 MPa</td>
<td>Helium</td>
<td>350</td>
<td>4</td>
<td>1140</td>
</tr>
</tbody>
</table>

![SEM images](image.png)

**Figure 8.1:** SEM images in backscattered of a) - e) as deposited and f) – j) annealed cold spray coatings deposited at increasing deposition velocity with nitrogen gas and with helium gas.

The coating porosity was plotted in Figure 8.2 as a function of the coating deposition velocity. A gradual decrease in the coating porosity was observed with increase in the coating deposition velocity. The porosity of the coatings was slightly lower in the annealed coatings; however whether the drop was attributed to the annealing or simple difference in the coatings is unclear. The porosity of the coatings varied within the sample, from sample to sample and depended on the thickness of the deposited coatings [14, 112, 117]. In the present study, the thickness of the coatings was 5-7 mm and demonstrated higher porosity when compared to the coatings reported in the previous study that were ~ 0.5 mm thick [117].
The coatings were produced from the spherical Ti powder that contained the acicular microstructure shown in channeling contrast images in Figure 8.3a. The powder particles were cold sprayed onto the bulk Ti plate, shown in Figure 8.3b. The microstructure of the powder was different from the microstructure of the bulk Ti plate that contained large equiaxed grains measured to be 20 ± 8 μm in size.

The annealing of the cold spray coatings at 800°C for one hour resulted in substantial grain growth shown in Figure 8.4k-o. The microstructure of annealed cold spray coatings consisted of equiaxed grains, similar in size to the one observed in the bulk Ti plate and
shown in Figure 8.3b. After annealing, the coalescence of the particle within the coating was observed. The particles formed new grain boundaries with the neighboring particles and in some cases, the grain growth extended across the particles interfaces. In most coatings, the pores segregated into larger pores and were the last remainder of the particle interfaces.

Figure 8.4: Channeling contrast images of: a) - e) as deposited taken at x1K magnification; f) - j) as deposited cold spray coatings at x10K magnification and k) – o) annealed cold spray coatings deposited at increasing deposition velocity with nitrogen and helium gases at x10k magnification.
### 8.2.2 - Multi-Scale Indentation Hardness

The hardness of as deposited and annealed cold spray coatings was measured with nanoindentation and microindentation techniques described in the previous publication [117]. The data from varied load nanoindentation was fit to the Gao and Nix strain gradient plasticity model [89, 117]. The true material hardness, determined from the fit, was then plotted in Figure 8.5 as a function of the coating deposition velocity. The plateau hardness obtained from varied load microindentation testing was plotted in the same graph.

![Figure 8.5: Hardness of a) as deposited and b) annealed cold spray coatings deposited with helium and nitrogen gas at increasing deposition velocity, determined with nanoindentation and microindentation techniques.](image)

The as deposited coatings were significantly harder (>3 GPa) than the bulk Ti plate (2.2 GPa). The nanoindentation hardness of the coatings did not increase significantly (difference between 3.0 and 3.6 GPa) with the increase in the coating deposition velocity. It is, however, important to note, that lower hardness was measured in the coatings deposited with nitrogen at higher gas preheat temperature when compared to the coatings deposited with helium at lower gas preheat temperature but similar deposition velocity.

After annealing of the coating, the nanoindentation hardness decreased to the level of the bulk Ti plate at 2.2 GPa. Slightly higher hardness was measured in the coatings deposited with helium coating and can be attributed to the residual stresses observed in Figure 8.4n and o.
The microindentation hardness measurements in as deposited and annealed cold spray coatings differed from the nanoindentation results and demonstrated a significant increase in the hardness (from 1 GPa to 1.9 GPa) with coating deposition velocity. It is also interesting to note that after annealing, the microindentation hardness of the coatings was also lower than the hardness of the bulk Ti plate. In the previous studies, coatings porosity and poor particle cohesion strength were shown to affect the microindentation hardness [117]. Similar observations were made in the present study.

The extent to which the coating defects affected the hardness was measured in terms of percent hardness loss by taking the percent difference between the nanoindentation and microindentation hardness measurements [117]. In Figure 8.6, the hardness loss was plotted as a function of the coating deposition velocity. The hardness loss was 60% in coatings deposited at 648 m/s and decreased to 18% for coatings deposited at 1140 m/s approaching the hardness loss of bulk Ti at 11%. The annealed coatings demonstrated a similar hardness loss than as deposited coatings.

In the previous publication, the hardness loss of 1 ± 6% was measured for the coating deposition at 1173 m/s [117]. The variation in the results could be attributed to the
differences in the deposition velocity, smaller coating thickness and lower porosity of previously reported coating.

8.2.3 – Tensile Properties

The cold spray coatings were machined into micro flat tensile bars perpendicular to the coating deposition direction according to the dimensions used by Gartner et al. [54]. The tensile bars produced are shown in Figure 8.7a and had 8 mm gage length with 2 by 2 cm gage width and thickness. The bars were pulled to the point of fracture and an example of stress strain curves obtained is shown in Figure 8.7b. The strain rate remained constant at 0.01 s⁻¹. The ultimate tensile strength and the strain to failure were measured from the curves similar to the ones shown in Figure 8.7b for all cold spray coatings and average of three data points was reported in Figure 8.8 with standard deviation used as an error bar.

![Diagram of tensile bars](image)

Figure 8.7: a) Dimensions of the tensile bars machined from the cold spray coatings and b) stress vs. strain curves for as deposited and annealed coating deposited at 1140 m/s.

In Figure 8.8a and b, the ultimate tensile strength and percent strain of as deposited and annealed cold spray coatings was plotted as a function of coating deposition velocity. Most of the coatings failed in a brittle manner and demonstrated low ultimate tensile strength and ductility. Only coating deposited at 1140 m/s demonstrated ultimate tensile strength that
was higher than the tensile strength of the commercially manufactured titanium and typical of strain hardened material [60, 61].

![Graph](image)

*Figure 8.8: a) ultimate tensile strength and b) engineering strain and of as deposited and annealed cold spray Ti coatings compared to the ultimate tensile strength and strain of coarse grained cp. titanium tested at 10^{-3} strain rate [60].*

After annealing, a small increase in the cold spray coating ductility was observed. It is important to note that annealing did not contribute to the decrease in the ultimate tensile strength but actually increased it. Only the coating deposited at 1140 m/s demonstrated a decrease in the ultimate tensile strength and demonstrated tensile properties approaching that of a commercially manufactured, coarse grained titanium [35, 60, 61].

The SEM of the fracture surface shown in Figure 8.9a-f revealed that coatings deposited below 1140 m/s had regions with undeformed, spherical particles with only limited degree of bonding (see Figure 8.4a and b). This phenomenon was more pronounced in the coatings deposited at low deposition velocity. The coatings deposited at 1140 m/s demonstrated regions with very fine, cleaved fracture surfaces indicating that while the fracture was brittle, but it occurred within the particles and not along the particle interfaces.

In the annealed coating deposited at 648 m/s and 852 m/s (shown in Figure 8.9d and e), the fracture was observed across the particle interfaces with fractured regions demonstrated some degree of ductile failure. Very fine, dimple formation was observed in the annealed coating deposited at 1140 m/s, shown in Figure 8.9f. The dimples were...
significantly smaller than the particle or grain size and indicate that the ductile failure within
the coatings deposited at 1140 m/s occurred across the particles.

![Figure 8.9: SEM images of fracture surface of the a) – c) as deposited and d) – f) annealed cold spray coatings.](image)

The mechanism of the failure within the coatings was investigated from the cross-
sectional SEM images of the gage length of the tensile samples shown in Figure 8.10a-f. Most as deposited coatings, with the exception of 1140 m/s coating, failed across the particle interfaces (see Figure 8.10a and b) confirming previous observations that the poor cohesion strength of the particles was the main cause of premature coating failure.

After annealing, the coatings deposited below 852 m/s still failed across the particle interfaces. However some instances of failure through the particles were observed, pointing to better particle cohesion strength. Better particle cohesion strength in the annealed coatings therefore explains the increase in the ultimate tensile strength and ductility observed in Figure 8.8a. The increase in the particle cohesion after annealing was, however, small and only the coating deposited at 1140 m/s demonstrated tensile properties similar to the commercially manufactured material.
8.3 – Discussion

The cold spray coatings contained a complex microstructure where grain refinement, porosity and poor particle cohesion strength affected the mechanical properties of the coatings. The hardness of coatings was measured to be higher than in the feed stock powder due to grain refinement but was also shown to decrease due to the coating porosity and poor particle cohesion strength. The tensile properties of the coatings were affected by the strain hardening and microscopic defects, and, in most cases, failed in a brittle manner along the particle interfaces. Even after annealing, the coating failure occurred along particle interfaces, indicating that annealing contributed only to a small increase in the particle cohesion strength.

In the previous work, the cohesion strength of the particles was shown to correlate with the splat adhesion strength measured with ball bond shear testing technique [45, 113, 117]. The main contributor to the splat adhesion/cohesion strength was the ability of the material to form metallurgical bonding with the substrate material weather it’s a Ti plate or a pre-deposited particle [45, 113]. The coatings deposited at higher deposition velocity were
previously shown to have better particle adhesion/cohesion strength and lower porosity [113, 117]; these coatings were also shown to have better tensile properties. In Figure 8.11a, the ultimate tensile strength of the coatings was compared to the splat adhesion strength measured with modified ball bond shear techniques previously described [45, 113] and plotted as a function of the splat deposition velocity. The adhesion strength was tested for splats deposited on titanium substrate under same deposition conditions and within same time frame as the tensile coatings. In Figure 8.11a, the ultimate tensile strength of the coatings was shown to have similar magnitude as the splat adhesion strength (with the exception of 1140 m/s coating). The similarity in the splat adhesion strength and ultimate tensile strength serves as a further confirmation of previously made observation that the failure in the coatings occurred due to poor particle cohesion. In the coating deposited at 1140 m/s, the failure was shown to occur across the particles and for that reason, the coating ultimate tensile strength was higher than the splat adhesion strength. A good correlation was also found between the tensile properties and hardness loss parameter plotted in Figure 8.11b. As with tensile results, the percent hardness loss was previously shown to depend on the particle cohesion strength and coating porosity [117]. The coatings demonstrating good tensile properties are shown to have low percent hardness loss while the coatings demonstrating high percent hardness are shown to have low tensile properties.

![Figure 8.11: The correlation between a) the ultimate tensile strength in as deposited coatings and splat adhesion strength and b) ultimate tensile strength and percent hardness loss in as deposited and annealed cold spray coatings.](image-url)
It is interesting to note that both methods indicate the mechanical properties of the coatings are not only dependent of the coating deposition velocity but are also dependent of the gas preheat temperature. The coatings deposited at 877 m/s with helium gas preheated to 350°C demonstrate higher percent hardness loss and lower ultimate tensile strength when compared to the coatings deposited at 852 m/s but with nitrogen gas preheated to 800°C. The mechanical properties of the coating deposited at 1140 m/s and tested with indentation and tensile testing, were similar to the mechanical properties measured in the commercially manufactured coarse grained titanium [35, 60, 61].

In the present chapter, the mechanical properties of the coatings were explored under shear, compression and tension. A correlation was found between the splat adhesion/cohesion, hardness loss parameter and tensile properties. The results demonstrated that through analysis of the splat adhesion it is possible to determine the deposition conditions under which the cold spray titanium would demonstrate the properties of commercially manufactured material. The optimization of the cold spray deposition process is also possible through multi-scale indentation testing that not only measures the material strain hardening but can also be used to quantify coating defects. Three micromechanical testing methods described in this study provide a comprehensive approach to the optimization of the cold spray process for deposition and heat treatment of titanium cold spray coatings with mechanical properties for any application.

8.4 – Conclusions

The cold spray titanium coatings demonstrate superior ultimate tensile strength but low ductility when compared to the coarse grained commercially manufactured titanium. Low coating ductility is a result of the grain refinement and strain hardening. The annealing of the cold spray coatings is required in order to reduce strain hardening and increase coating ductility. The microscopic defects within the coatings affect mechanical properties of the coatings. In order to obtain the properties of commercially manufactured material, the coatings have to be deposited at optimal deposition conditions with near theoretic particle cohesion strength and low coating porosity. Modified ball bond shear and/or multi-scale
indentation techniques provide new methods for determination of the optimal cold spray deposition conditions.

8.5 – Acknowledgement

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Chapter 9. Conclusion and Future work

9.1 - Conclusions

New micromechanical testing techniques such as nanoindentation mapping, splat adhesion and varied load indentation testing were explored for characterization of the mechanical properties of cold spray titanium splats and coatings. The effect of the cold spray deposition parameters including: gas temperature, pressure, powder size and morphology as well as deposition velocity on the microstructure, hardness and bond strength of the coatings were investigated.

The nanoindentation mapping was used to define the effect of grain refinement and strain hardening on the hardness distribution within titanium cold spray splats and coatings. The magnitude of the strain hardening was greater at the particle interface and decreased towards the splat midsection and splat jetting region.

The splat deformation, grain refinement and recrystallization were shown to contribute to the formation of a conformal interface and metallurgical bonding at the splat/substrate interface. A new adhesion testing technique was developed to measure the adhesion strength of Ti and Ti6Al4V splats on the Ti or Ti6Al4V substrates. The adhesion strength of splats increased with the splat deposition velocity, the gas preheat temperature and the substrate temperature. Near theoretical adhesion strength (320MPa) with fully bonded splat/substrate interface was measured for titanium splats deposited at 1140 m/s. With preheating of the substrate to 400°C, fully bonded titanium splats were obtained at the deposition velocity of 825 m/s. Ti6Al4V splats did not demonstrate fully bonded splat interface even at 1115 m/s or at 854 m/s with substrate preheating to 400°C. Nevertheless, under same deposition velocity, better splat adhesion strength was measured for splats deposited at higher gas preheat temperature. The particle size and position in the gas jet were also contributing factors to the splat adhesion. Higher splat adhesion was measured for the titanium powder particles between 10 and 20 μm in diameter and for particles located in the center of the gas jet.

A good correlation was found between the splat adhesion strength and particle cohesion strength in the coatings. The deposition conditions under which the splats
demonstrated high adhesion strength were also condition under which cold spray coatings had low coating porosity and low particle debonding during indentation testing. A multi-scale indentation method was developed where nanohardness, determined with Gao and Nix strain gradient plasticity model, was compared to the plateau hardness measured with microindentation technique. The difference between the two measurements was used to determine the hardness loss parameter attributed to the poor particle cohesion strength and coating porosity. The hardness loss parameter was used to define the deposition conditions for which the coatings demonstrated mechanical properties of fully dense material.

The material strain hardening, coating porosity and poor particle cohesion strength affected the tensile properties of the coatings. Titanium coatings deposited below 1140 m/s failed in the brittle manner with crack propagation that occurred along the particle interfaces. The ultimate tensile strength of the coating was similar in magnitude to the adhesion strength of the splats attributed to coating failure through particle de-bonding in the coatings. Only the coatings deposited at 1140 m/s, a deposition condition that demonstrated near theoretical splat adhesion strength, failed across the particles and demonstrated mechanical properties (ultimate tensile strength of 600 MPa and engineering strain of 15 %) comparable to the ultra-fine grained commercially manufactured material.

Annealing of titanium cold spray coatings at 800°C for 1 hour, contributed to the grain growth and reduction in the material strain hardening but did not contribute to a significant particle sintering or decrease in the coating porosity. Most coatings demonstrated a marginal increase in the ductility and ultimate tensile strength and continued failing along the particle interfaces. Coating deposited at 1140 m/s demonstrated the tensile properties of commercially manufactured coarse grained titanium with 30 % engineering strain and 300 MPa ultimate tensile strength.

A good correlation was found between the splat adhesion/cohesion, hardness loss parameter and tensile properties. The results demonstrated that through analysis of the splat adhesion it is possible to determine the deposition conditions under which the cold spray titanium coatings would demonstrate the properties of commercially manufactured material. The optimization of the cold spray deposition process is also possible through multi-scale indentation testing that not only measures the material strain hardening but can also be used to quantify the effect of coating defects on the mechanical properties of the coatings. Three
micromechanical testing methods described provide new approaches to the optimization of the cold spray process for deposition and heat treatment of titanium cold spray coatings with mechanical properties for any application.

9.2 – Future Work

The present work was based on investigating of new techniques for mechanical property characterization of the titanium splats and coatings produced by cold spray process. The splat adhesion testing method was used to measure the shear strength of titanium splats, however, some degree of splat deformation under tension was also observed. Furthermore, the effect of the splat imbedding on the measurements of the splat adhesion strength was not investigated. Further studies with finite element modeling of the splat adhesion testing can provide a better understand the effect of the splat embedding, splat shape, defects at the splat/substrate interface on the splat adhesion and their relationship with fracture modes and failure mechanisms.

For the multi-scale indentation testing, a marginal increase in the hardness loss parameter was measured after annealed of the cold spray coatings. Whether the increase was attributed to the experimental error or changes in the material deformation mechanisms with applied load have to be determined.

The splat adhesion testing and multi-scale indentation methods, described in the study can also be used for characterization of the mechanical properties of materials produced by other powder consolidation techniques. Future work on this topic would prove beneficial for the future development of comprehensive mechanical characterization techniques for powder consolidated coatings.

In the present work, the effect of the cold spray deposition and annealing on the oxide content was not explored and requires further investigations. Further studies on the residual stresses and fatigue failure testing have to be, also, undertaken.

Other avenues for research include incorporation of the hot isostatic pressing as a post processing method after cold spray deposition. The hot isostatic pressing technique can potentially reduce the porosity content in the coatings and will contributed to a better particle consolidation.
Original Contributions to Knowledge

1. Nanoindentation mapping was applied for the first time to define the hardness distribution within the individual titanium cold spray splats. The hardness distribution was correlated to the regions of strain hardening and thermal softening resulting from grain refinement and recrystallization within the cold spray titanium splats.

2. A new modified ball bond shear technique was implemented for measurement of the adhesion strength of individual cold spray splats. The technique was sensitive enough to measure the effects of the gas preheat temperature, particle size and particle position in the gas jet on the splat adhesion strength.

3. For the first time, a multi-scale indention method was used to measure the difference between the nanoindentation and microindentation hardness to quantify the effect of microscopic defects on the microindentation results defined as hardness loss parameter.

4. The hardness loss parameter provides a novel method where the mechanical properties of the cold spray coatings can be compared to the fully dense, bulk materials regardless of the degree of material strain hardening.

5. The present work is first to combine and compare mechanical testing conducted over a range of length scales on cold sprayed splats and coatings. On the splat level, the effect of the deposition conditions on strain hardening and adhesion of individual splats, determined by nanoindentation mapping and splat adhesion testing, was correlated with cohesion strength and the hardness loss observed during multi-scale indentation testing of coatings. The information collected on the mechanical properties of cold spray titanium on the splat and coating levels helped identify failure mechanisms in the coatings subjected to micro-tensile testing.
6. The current work demonstrates new ways of mechanical property characterization at all length scales that are not only applicable on coatings produced by the cold spray process but can be potentially used on coatings produced by other powder consolidation techniques.
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