MICROSTRUCTURAL STUDIES OF COLD SPRAYED PURE NICKEL, COPPER AND ALUMINUM COATINGS

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Abstract

Cold spray is a relatively new coating technology in which coatings are produced by spraying metal powders at high velocity, generating bonding through severe plastic deformation at temperatures well below the melting point of the powders. In the present study, pure face centered cubic metals (i.e. nickel, copper and aluminum) coatings were produced by cold spray. Electron backscatter diffraction and transmission electron microscopy were used to investigate the microstructural changes of these powder particles during cold spraying. The effect of gas temperature on the microstructure of copper coatings and the role of post-cold spray heat treatment in the nickel coatings are also studied. Of particular interest are grain refinement, recrystallization and particle/particle bonding mechanisms of the cold sprayed powders.
Résumé

La projection dynamique par gaz froid, ou «cold spray», est une technologie relativement nouvelle avec laquelle des revêtements sont produits en projetant des poudres métalliques à grande vitesse, créant ainsi des liaisons particule/particule par déformation plastique intense à des températures bien inférieures aux points de fusions des poudres. Dans la présente étude des revêtements de métaux purs à cristallographie cubique faces centrées (i.e. nickel, cuivre et aluminium) ont été produits par projection dynamique par gaz froid. La microscopie électronique en transmission (MET) et la diffraction des électrons rétrodiffusés, ou EBSD (Electron Back Scattered Diffraction), ont été utilisées pour étudier les modifications de microstructures des particules de poudres durant la projection dynamique par gaz froid. L’effet de la température du gaz sur la microstructure des revêtements de cuivre ainsi que le rôle d’un traitement thermique post-déposition pour les revêtements de nickel sont aussi étudiés. Un intérêt particulier a été porté sur l’affinement de la taille de grain, la recrystallization et les mécanismes de liaison particule/particule des poudres projetées.
Acknowledgements

First, I must thank my supervisors, Professor Jerzy A. Szpunar and Professor Stephen Yue, for their key insights and encouragement. They have introduced me to the fascinating field of cold spray, given me a lot of freedom in research, and offered invaluable advice leading to the completion of this research project. This thesis would not have been possible without their trust and support.

This project was supported by CFI NO. 8246. I will give my warm thanks to all my colleagues in the cold spray project at MAMADC. Dr. Eric Irissou and Dr. Jean-Gabriel Legoux at NRC-IMI, for the production of the cold sprayed samples; Prof. Richard Chromik, for accessing the nanoindentation facility in his group; Dr. Ahmad Rezaeian, for his work on heat treatment and micro-hardness tests; Dina Goldbaum, for her nanoindentation tests; Wilson Wong and David Levasseur, for their helpful discussions.

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Finally, my parents, Chunhua Wu and Zhaowu Zou, deserve more applause than I can express here. Their love and support have been the driving force for me to move forward, and given me the opportunity to explore what I can become.
Preface

This thesis contains nine chapters. Five of them (Chapter 4 to Chapter 8) have already been published or been submitted for publication in peer-reviewed journals or conferences. It should be clearly stated that due to the manuscript-based format, i.e., whole chapters to be copies of papers. Some minor duplication has inevitably occurred.

This thesis, entitled “Microstructural Studies of Cold Sprayed Pure Nickel, Copper and Aluminum Coatings”, is organized into the following chapters: Chapter 2 presents a literature review on the fundamental and applied aspects of cold spray technology and research objectives. Chapter 3 describes the materials and experimental methods used in this study. Chapters 4, 5 and 6 present the microstructural evolutions of nickel, copper and aluminum powder particles processed by cold spray, respectively. The effect of gas temperature on the microstructure and properties of cold sprayed copper coatings is studied in Chapter 7, while Chapter 8 presents the role of annealing on the microstructure and properties cold sprayed nickel coatings. Finally, Chapter 9 gives a conclusion of the current work and makes suggestions for future work.

Contributions of Authors

The author of this thesis is the primary author in all papers included in this thesis. Prof. Jerzy A. Szpunar and Prof. Stephen Yue are supervisors of the author’s Master of Engineering program and are included as co-authors. Dr. Eric Iriessou and Dr. Jean-Gabriel Legoux at NRC-IMI are included as co-authors, in recognition of their work of producing cold spray samples. For the papers in Chapters 4 and 7, Dr. Wen Qin is included as a co-author, in recognition of his help in revising manuscript and enlightened discussions. For the papers in Chapters 7 and 8, Dr. Ahmad Rezaeian is one of the co-authors, in recognition of his help in the sample preparation. For the paper in Chapter 5, Dina Goldbaum is included as a co-author, in recognition of her contribution in the nanoindentation tests.

The papers that form Chapter 4 to Chapter 8 in this thesis are as follow:


Chapter 6: Y. Zou, E. Irissou, J. Legoux, J. A. Szpunar, S. Yue, “The role of high-velocity impact in the bonding formation and microstructural transformation in cold sprayed Al coating” submitted to Applied Surface Science


# Table of Contents

Abstract.................................................................................................................................................. i

Résumé .................................................................................................................................................... ii

Acknowledgements ................................................................................................................................... iii

Preface...................................................................................................................................................... iv

Chapter 1 Introduction ............................................................................................................................. 1

Chapter 2 Literature Review ...................................................................................................................... 3

2.1 Cold Spray Technology and Its Applications .................................................................................. 3

2.1.1 Overview of cold spray.................................................................................................................. 3

2.1.2 The advantages and disadvantages of cold spray .......................................................................... 6

2.1.3 The applications of cold spray ...................................................................................................... 8

2.2 Bonding Mechanism and Powder Consolidation due to Cold Spraying ....................................... 11

2.2.1 Bonding mechanism .................................................................................................................... 11

2.2.2 Powder consolidation and coating formation ............................................................................... 13

2.3 Microstructural Evolution of Cold Sprayed Coatings .................................................................. 16

2.3.1 Thermo-mechanical processing mechanisms .............................................................................. 16

2.3.2 Microstructure characteristics of cold sprayed coatings ............................................................ 16

2.3.3 Effect of gas temperature ............................................................................................................ 18

2.3.4 The role of post processing heat treatments in mechanical properties and microstructure .......... 20

Chapter 3 Materials and Experimental Methods .................................................................................... 23

3.1 Materials ........................................................................................................................................... 23
3.2 Cold Spray Process ............................................................................................................. 24

3.3 Sample Preparation and Microstructural Characterization .............................................. 25
  3.3.1 Scanning electron microscopy ...................................................................................... 25
  3.3.2 Electron backscattered diffraction ............................................................................. 25
  3.3.3 Transmission electron microscopy ............................................................................. 26

Chapter 4 Microstructural Evolution of Nickel Powder Particles Processed by Cold Spray ........................................................................................................................................ 27
  4.1 Introduction ....................................................................................................................... 27
  4.2 Experimental ................................................................................................................... 28
  4.3 Results and Discussion .................................................................................................... 28
  4.4 Conclusions .................................................................................................................... 33

Chapter 5 Microstructure and Nanohardness of Cold Sprayed Nickel and Copper Coatings ........................................................................................................................................ 34
  5.1 Introduction ....................................................................................................................... 34
  5.2 Experimental ................................................................................................................... 35
  5.3 Results and Discussion .................................................................................................... 36
  5.4 Conclusions .................................................................................................................... 41

Chapter 6 Microstructural Evolution and Bonding Formation of Cold Sprayed Aluminum Coating ........................................................................................................................................ 42
  6.1 Introduction ....................................................................................................................... 42
  6.2 Experimental ................................................................................................................... 43
  6.3 Results and Discussion .................................................................................................... 43
  6.4 Conclusions .................................................................................................................... 51
Chapter 7 Effect of Gas Temperature on the Microstructure and Properties of Cold Sprayed Copper Coatings ................................................................. 52
7.1 Introduction ................................................................................................. 52
7.2 Experimental .............................................................................................. 53
7.3 Results and Discussion ............................................................................ 55
7.4 Conclusions ............................................................................................... 61
7.5 Appendix ................................................................................................... 62

Chapter 8 The Role of Annealing in the Microstructural Transformation and Mechanical Properties of Cold Sprayed Nickel Coatings ........................................ 65
8.1 Introduction ................................................................................................. 65
8.2 Experimental .............................................................................................. 66
8.3 Results and Discussion ............................................................................ 67
8.4 Conclusions ............................................................................................... 70

Chapter 9 Conclusions and Future Work ...................................................... 71
9.1 Conclusions ............................................................................................... 71
9.2 Future Work .............................................................................................. 72

Bibliography .................................................................................................... 73
Chapter 1 Introduction

Cold spray (or fully cold gas-dynamic spray) is an evolving technology for the production of coatings and bulk forms. In the cold spray process, powder particles are accelerated to very high speeds (500-1200 m/s) by high-pressure compressed gas at a temperature that is always lower than the melting point of the deposited material, forming coatings from particles in the solid state [1-6]. Due to the low-temperature deposition process, cold sprayed coatings are essentially free of thermally induced deleterious defects commonly observed in traditional thermal spray coatings, such as oxidation, evaporation, gas release, shrinkage porosity and thermal residual stresses [4, 5]. These offer significant advantages and attract considerable interest of manufacturing industries.

Although various types of coatings, e.g. pure metals, alloys, polymers, composites and metallic glasses, have been obtained using cold spray, the actual mechanism by which the solid metal particles deform and bond in the cold spray process are not precisely known. A prevalent opinion based on finite element analysis (FEA) indicates that the bonding of particles depends on the occurrence of adiabatic shear instability (ASI) at impact during high strain-rate deformation at interfaces with the substrate and other particles [2, 7, 8]. The FEA studies [2, 7-10] show that the powder particles experience very high strain (up to 10) and very high strain rate (up to \(10^9/s\)) during cold spraying. However, detailed microstructural investigations showing corresponding experimental evidence in the particle/particle interfacial region are still lacking.

Cold spraying strongly affects the microstructures of the subsequent coating (including porosity and coating morphology) [11, 12]. So far, Optical Microscope (OM), Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM) have been used tools to characterize the microstructure of cold sprayed samples. For example, Borchers and his co-workers [13, 14] employed SEM to observe the morphology of the particles in as-sprayed coatings, and used TEM to investigate the substructures of as-deformed particles. In cold sprayed nickel and copper coatings, they found very non-uniform appearance, with grain sizes ranging from a few microns to a few hundred nanometers, elongated and equiaxed grains and subgrains. Despite the increasing prevalence of these characterizations, however, due to limited resolution of
OM, lack of quantitative data of SEM and small examined area of TEM, the relationship between these new grains/subgrains and the original grains is still not precisely understood. Moreover, how these local changes of microstructure influence the mechanical properties is also not clear. In addition, cold spray is essentially a thermo-mechanical process, but so far, few studies have presented a systematic comparison between cold-spray deformed microstructures and microstructures produced by other thermo-mechanical processes, such as hot and cold rolling and equal channel angle pressing (ECAP) [15].

The characterization of as-sprayed microstructures is very important in developing an understanding of the thermo-mechanical evolution of microstructure during cold spraying, and will give insights on particle bonding and reduction of porosity due to cold spraying. In the present study, Electron Backscattered Diffraction (EBSD) in conjunction with Field Emission Gun SEM (FEG-SEM) was used for microstructural analysis of cold sprayed coatings. EBSD can examine very large areas of samples and provide statistically significant data of crystal orientations, boundary misorientations, image quality, etc [16-18]. It is very suitable for the microstructural investigation of samples after non-uniform deformation, compared to TEM. Nevertheless, TEM will give much higher resolutions. Therefore, FEG-SEM and TEM is a very powerful combination of experimental techniques to help elucidate the bonding mechanisms and the complex thermo-mechanical history of metal powder particles during cold spraying.

Pure face centered cubic metals such as nickel, copper and aluminum, were deposited and investigated, since their crystal structures are simple and there is a relatively large body of information of these metals in the cold spray literature.

In this thesis, the microstructural evolutions of nickel, copper and aluminum powder particles processed by cold spray are investigated. In addition, the effects of gas temperature on the cold sprayed copper coatings and post processing heat treatment on the nickel coatings are studied, respectively.
Chapter 2 Literature Review

2.1 Cold Spray Technology and Its Applications

Cold spray was originally developed in the mid-1980s at the Institute of Theoretical and Applied Mechanics of the Russian Academy of Sciences in Novosibirsk by Dr. Anatolii Papyrin and his co-workers [6]. They successfully deposited a wide range of pure metals, metallic alloys, polymers and composites onto a variety of substrate materials, and they demonstrated that high density coating and deposition rates can be obtained using the cold spray process. At present, a wide spectrum of research on cold spray is being conducted at institutions and companies around the world.

2.1.1 Overview of cold spray

The cold spray system accelerates powder particles, making them impact, deform and bond to create a dense layer of material on the substrate. A critical velocity needs to be attained before bonding takes place. As shown in Figure 2.1 (a), if the particle velocity \( V_p \) is low, the particle simply bounces off the surface of the substrate. When \( V_p \) exceeds the critical value \( V_{cr} \), the process of particle adhesion to the substrate begins and forms an overlay deposit, analogous to thermal spray coatings [2, 4-6]. A critical velocity is defined as the particle velocity that causes the adhesion of the particle to the substrate. An example of the data used to obtain the critical velocities for different materials is shown in Figure 2.1 (b), where the effect of particle velocity on deposition efficiency is plotted for various metals [5]. The measured deposition efficiency \( k_d \) is calculated as:

\[
k_d = \frac{\Delta m_s}{M_p}
\]

(2.1)

where \( \Delta m_s \) is the change of weight of a substrate and \( M_p \) is the weight of all particles impinging on the substrate. This \( V_{cr} \) is in the range of 500-900 m/s and depends on various characteristics of the particle and substrate materials [3, 19, 20]. The literature
regarding the mechanisms of bonding and porosity reduction during cold spraying will be reviewed in Section 2.2.

Assadi et al. [2] used FEA simulation to work out the effect of various material properties on the critical velocity in the cold spray process. They assumed that the critical velocity criterion was when adiabatic shear instability was attained, and summarized their FEA results into a simple expression for the critical velocity:

\[ v_{cr} = 667 - 14 \rho + 0.08 T_m + 0.1 \sigma_u - 0.4 T_i \]  \hspace{1cm} (2.2)

where \( \rho \) is the density in g/cm\(^3\), \( T_m \) is the melting temperature in °C, \( \sigma_u \) is the ultimate strength in MPa and \( T_i \) is the initial particle temperature in °C.

A schematic diagram of a typical cold spray system is illustrated in Figure 2.2 [21]. It normally consists of a high-pressure gas delivery system, gas heater, powder hopper, control console and cold spray gun. The gas delivery system supplies up to 170 m\(^3\)/h of air, nitrogen or helium at a pressure of 15-40 bar. In the cold spray process, one part of the high-pressure gas is heated by an electric gas heater to a maximum of 1023 K.
(800 °C), and the other part of the high-pressure gas propels the powder particles (normally in the size range of 5-45 microns) from the powder hopper to the gun. The reason for heating the cold spray process gas is to increase the sonic velocity of the gas in the ‘throat’ (point of smallest diameter) of the converging-diverging nozzle, which creates a higher spray jet velocity and reduces process gas consumption [4]. In the gun, momentum transfers from the supersonic gas jet to the particles, leading to high velocity particle jet. The high-speed particles impact and bond on the substrate, and create a dense layer of material. The console houses all the controls to meter the gas flow rates, pressures, powder feed rate, the robot controlled system (Fig. 2.3 (1)) and the cold spray gun part (Fig. 2.3 (b)). Figure 2.4 shows typical SEM micrographs of the coatings produced by cold spray.

![A schematic of a typical cold spray system](image1)

Figure 2.2 A schematic of a typical cold spray system [21]

![The robot controlled cold spray system](image2)

Figure 2.3 (a) the robot controlled cold spray system [22]; (b) the part of spray gun [23]
2.1.2 The advantages and disadvantages of cold spray

It is known that thermal spray technology has been extensively used in defense, aerospace and gas turbine industries, including fabrication of components, preparation of protective surfaces, refurbishment of mis-machined and service-damaged parts, etc [25, 26]. Recent years, cold spray has been introduced to produce various coatings (i.e. metal, alloy, and composite) with superior qualities [2, 5, 27]. As shown in Figure 2.5, the main difference between cold spray and well-known thermal sprays are in the aspects of particle velocity and gas temperature. Cold Spray uses high velocity rather than high temperature to produce coatings, and thereby produces coatings with many advantageous characteristics. Since high temperature is not involved, it is ideally suitable for spraying temperature-sensitive materials such as nano-structural and amorphous materials, oxygen-sensitive materials like aluminum, copper and titanium and phase-sensitive materials such as carbide composites [5, 10, 28, 29]. Moreover, some common problems with traditional thermal spray methods, such as high-temperature oxidation, evaporation, melting and gas release, are minimized or eliminated [5]. In addition, cold spray incorporates a micro shot peening effect, and hence the coatings are produced with compressive stresses rather than tensile stresses. Thus, ultra thick (up to several centimeters) coatings or bulk forms can be produced without failure at the interface with the substrate. The high energy-low temperature formation technique leads to a wrought-
like microstructure with near theoretical density values [1, 27, 30]. In the processing procedure, due to the small size of the nozzle (10-15 mm²) and the gun-substrate distance (5-25 mm), the size of the spray beam is very small, typically around 5 mm in diameter, which translates into precise control over the area of deposition over the substrate surface and results in high growth rate of coating thickness. Also a better control over area where the coating is deposited is possible, often with little need for masking as-sprayed part [6, 31, 32].

![Figure 2.5 The difference between cold spray process and thermal spray processes [21](image)](image)

Although cold spray offers important advantages over traditional thermal spray methods in some aspects, cold spray also has its limitations. First, since the spray particles are not melted but deformed in the solid state, the cold spray process is essentially limited to depositing ductile metals, e.g. aluminum, copper, steels, and nickel-based alloys, onto metal, ceramic, or other relatively hard substrate materials [8]. So, it is not possible to cold spray brittle materials, such as ceramics onto a brittle substrate. Second, much larger quantities of process gas is used in the cold spray process than in traditional thermal spray processes, typically of the order of 1-2m³/min [1]. When helium is necessarily applied, the expense could be a serious issue. Third, the spray beam is
small, and therefore the cold spray process is not as well suited for coating very large surface areas as compared with some of the traditional thermal spray processes, such as wire arc spray [5]. In addition, the extensive plastic deformation inherent during impact of particles hardens the sprayed materials, resulting near-zero ductility in the as-sprayed condition [33-35]. Finally, cold spray is a relatively new process and still considerable R&D efforts are needed to understand and control the process, as well as develop engineered coatings with desired properties for specific applications.

2.1.3 The applications of cold spray

Many metals (Al, Cu, Ni, Ti, Ag, Zn), alloys (SS, Inconels, Hastalloys, MCrAlYs) and composites (metal-metal like Cu-W, metal-carbides like Al-SiC, metaloxides like Al-Alumina) can be processed by cold spray to produce dense, pure and thick coatings [4, 5]. Figure 2.6 shows the SEM micrographs of various coatings produced by cold spray. Application of these coatings includes enhancing mechanical, thermal and electrical properties of surfaces, protecting from wear and/or corrosion, and repairing components [1, 4-6, 30]. For example, 6061 aluminum alloy based Al$_2$O$_3$ particle-reinforced composite coatings were cold sprayed on AZ91E substrates to improve the properties of corrosion and wear resistance [36]. Table 2.1 summarizes a broad range of coating materials and their applications [37].

![Figure 2.6 Microstructures of various cold sprayed coatings](image-url)

Figure 2.6 Microstructures of various cold sprayed coatings [30]
Cold spray has also been used to produce ultra-thick coatings, free-forms and near net shapes (NNS), as shown in Figure 2.7 [30] and Figure 2.8 [38]. Moreover, by controlling the feedstock composition, it is possible to vary the deposited microstructure and composition to produce functionally gradient materials (FGM) and other special structures, as shown in Figure 2.9 [39]. Moreover, using the ‘build up’ technique that has none of the thermal problems associated with welding or thermal spray methods, cold spray shows great potential for the optimization for aerospace alloys or components, as illustrated in Figure 2.10. It could significantly reduce the ‘buy-to-fly’ ratios, which is defined as the required input material weight divided by the finish machined part weight.

Table 2.1 Cold spray materials and their applications [37]

<table>
<thead>
<tr>
<th>Application</th>
<th>Coating Material</th>
<th>Industry Sector</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Cd-plating alternative</td>
<td>• Al alloys</td>
<td>• Aerospace</td>
</tr>
<tr>
<td>• Corrosion mitigation</td>
<td></td>
<td>• Oil &amp; gas</td>
</tr>
<tr>
<td>• Controlled potential coatings</td>
<td></td>
<td>• Petrochemical</td>
</tr>
<tr>
<td>• Pb-free bearing e.g. con-rods, turbochargers</td>
<td>• Al, Cu alloys</td>
<td>• Automotive</td>
</tr>
<tr>
<td>• Thermal management e.g. power hybrid devices, switchgear</td>
<td>• Cu, Al, Cu-W</td>
<td>• Motorsport</td>
</tr>
<tr>
<td>• Conductive tracks</td>
<td></td>
<td>• Aerospace</td>
</tr>
<tr>
<td>• Corrosion mitigation</td>
<td>• Ti, Ta, Nb, NiCrFeMo</td>
<td>• Oil &amp; gas</td>
</tr>
<tr>
<td>• High temperature corrosion and oxidation mitigation e.g. gas turbines</td>
<td>• Ni alloys, MCrAlYs</td>
<td>• Petrochemical</td>
</tr>
<tr>
<td>• Biocompatible coatings for medical devices</td>
<td>• Ti</td>
<td>• Power generation</td>
</tr>
<tr>
<td></td>
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</tbody>
</table>

9
Figure 2.7 Typical cold sprayed coatings and produced bulk forms (ASB Industries) [30]

Figure 2.8 Cold-spray produced near net shapes [38]

Figure 2.9 Tri-material sandwich built up from aluminum, copper and titanium [39]
2.2 Bonding Mechanism and Powder Consolidation due to Cold Spraying

2.2.1 Bonding mechanism

Early considerations regarding bonding included interfacial melting and atomic inter-diffusion as mechanisms. However, it is now thought that these do not play a significant role in the bonding process in cold spraying [7, 8].

As mentioned above, the bonding of sprayed particles can be directly related to adiabatic shear instabilities (ASI), i.e. when the conditions are such that ASI is initiated [2]. Figure 2.11 shows the simulation and experimental results of the interaction between particle and substrate [3]. Here, so-called ‘jet’ formation can be observed, which, according to the simulations, is due to ASI generated by the high temperatures of adiabatic heating by at the interface, at which point bonding will occur. Thus, in Figure 2.11c, the predicted critical velocity for Cu is between 400 and 500 m/s, which corresponds with experimental observations [3]. This means that the material loses its shear strength and undergoes severe deformation, resulting in a change in deformation mechanism from plastic to viscous flow. This type of mechanism has been suggested by
Grujicic et al. [7, 8] and Assadi et al. [2]. The viscous flow due to shear localization at impact interfaces is able to cause some type of nano/microlength-scale mechanical material mixing/interlocking structures (roll-ups and vortices) [8]. This can be considered as a kind of fluid flow phenomenon, leading to interface configurations, as shown schematically in Figure 2.12 (a). Such structures have been observed in explosive welding [40] and explosive cladding [41], as shown in Figure 2.12 (b) [41], but have not been observed in cold spray. In addition, the severe, localized, plastic deformation due to cold spray causes disruption of the thin oxide surface and enables and intimate conformal contact between the particles and the substrate material. This combined with high contact pressures are believed to be necessary conditions for bonding [5]. However, nearly all of these analyses are based on FEA numerical simulations [2, 7, 8] and a detailed microstructural investigation of the interfacial morphologies is currently lacking.

Figure 2.11 Jet formation at colliding interfaces: (a) temperature field 15 ns after impact, (b) 30 ns (c) temporal evolution of interface temperature calculated for different impact velocities, (d) cross-section of a single particle impact from a wipe-test [3]
2.2.2 Powder consolidation and coating formation

It is recognized that, during cold spraying, the powder is consolidated and very low levels of porosity can result. Steenkiste et al. [42] suggested that coating formation proceeded via four basic phenomena or stages, as illustrated in Figure 2.13. In the first stage, the substrate is cratered and the first layer of particles is built up. Then, the incoming particles are deformed, rotated and realigned. After that, inter-particle metallic bonds form in increasing numbers, leading to relatively thick coating and low porosity.
Finally, as the coating continues to build, the constant bombardment or peening leads to plastic deformation and work hardening and a further reduction of porosity. It should be noted that, at any given incident velocity, several of these stages can occur simultaneously.

The cold sprayability of the powder strongly depends on its materials properties. It is commonly recognized that a material that can be used for cold spray should have features of plasticity ensuring compression of the particle and shear of the surfaces [4]. Metals with FCC structure (aluminum, copper, silver, gold, platinum, nickel, and gamma-iron) have the highest number of slip planes, which is required for their high plasticity. Thus, high-density cold sprayed FCC metal coatings can be obtained, as shown in Figure 2.14 [14]. Metals with an HCP lattice (zinc, cobalt, magnesium, and alpha-titanium) have

![Figure 2.13 Stages of coating formation in the cold spray process [42]](image-url)
much fewer slip planes, which yield a lower plasticity. As shown in Figure 2.15 [43], a cold sprayed titanium coating prepared under similar conditions as for the coatings in Figure 2.14 shows much higher porosity. Metals with a BCC lattice (tungsten, tantalum, molybdenum, alpha-iron, and beta-titanium) also have lower plastic form ability compared to FCC structures, and are therefore more difficult to form dense coatings using cold spray. Additionally, for the same material, the porosity of coating is determined by the characteristics of the particles and processing parameters. For example, larger particle size creates more pores in the as-sprayed coating; higher particle velocity can decrease the coating porosity; higher gas temperature will soften powders and therefore decrease porosity [43, 44].

Figure 2.14 SEM micrographs in BSE mode of CS copper coatings: (a) Al, (b) Cu, (c) Ni. Interparticle interfaces show a dark contrast after etching. The arrow in (a) indicates a trapped jet. (Processing gas: Nitrogen; temperature: 380 °C; pressure: 25 bar) [14]

Figure 2.15 Polished (un-etched) optical micrograph of cold sprayed titanium coating (Processing gas: Nitrogen; temperature: 600 °C; pressure: 24 bar) [43]
2.3 Microstructural Evolution of Cold Sprayed Coatings

2.3.1 Thermo-mechanical processing mechanisms

In cold spray, due to high-velocity impact, the particles experience very large strains (up to 10) and strain rates (up to $10^9$/s) in the interfacial regions [2], leading to work hardening, i.e. the generation of dislocations and other defects. At the same time, the temperature rises, leading to the restoration processes of recovery and recrystallization. Recovery involves the reduction of the dislocation density without any other change in the microstructure. Dynamic recovery occurs concurrently with dislocation generation, i.e. during plastic deformation, whereas static recovery occurs after deformation when the metal is in the unloaded condition. Dynamic recovery happens in metals with high stacking fault energy (SFE) such as aluminum. Recrystallization leads to dislocation free structures by the formation of new grains by nucleation and growth into the deformed or recovered microstructure. In materials with low or medium SFE such as copper or stainless steel, in which recovery processes are relatively slow, dynamic recrystallization could takes place during the deformation. As implied from the above description of recovery, recrystallization can occur dynamically, or statically. Static recrystallization can also occur during post-deformation heat treatment, i.e. annealing. [45]

2.3.2 Microstructure characteristics of cold sprayed coatings

A large number of studies have been carried out using OM and SEM to study the morphology of deformed particles and as-sprayed coatings [46-48], as shown in Figure 2.16. In these characterizations, it is found that the coatings are relatively dense, interparticle boundaries can be fully or partially observed, and the porosities of these coatings are normally quite small. The particles are heavily deformed, showing flattened shapes mainly parallel to the substrate. However, very few papers have been reported on the evolution of sub-structures (i.e. grain and subgrains) of the particles during cold spraying. Using TEM, Borchers et al. [13, 14] observed very non-uniform features in cold-sprayed nickel and copper particles, as shown in Figure 2.17, revealing elongated
and equiaxed grains and subgrains with grain sizes ranging from a few microns to a few hundred nanometers. These complex structures indicate during cold spraying dynamic recrystallization is occurring in the form of grain refinement, as shown in region B of Figure 2.17 (1) and static recrystallization can also occur, as shown in region D.

Figure 2.16 Microstructures of cold-sprayed Cu coatings on Cu substrate (process gas: nitrogen). In (a, b), coating cross-sections are shown for the as-polished state (OM) whereas (c, d) display the etched state (c: OM, d: SEM/BSE mode). The arrows indicate the interface to the substrate material [49].

Comparing pure copper, nickel and aluminum samples processed, respectively, by cold spray [13, 14, 50, 51], cold rolling [50-53], hot rolling [45, 54-56], and equal channel angular pressing (ECAP) [57-62], it was found that the microstructure of cold sprayed samples have the following characteristics: 1) non-uniform microstructures (grain sizes ranging from a few microns to a few hundred nanometers, and elongated and equiaxed grains and subgrains); 2) smaller minimum grain size (~100 nm in copper and nickel); 3) very weak crystallographic texture (preferred grain orientation); 4) deformation twining could occur in cold sprayed copper; 5) amorphization could occur at impact interface of cold sprayed aluminum particles. In short, it is now recognized that a
broad range of structural differences from conventional plastic deformation processing is possible in the cold sprayed coatings. However, no systematic comparison between cold-spray deformation and other thermo-mechanical processing methods has been done to date.

Figure 2.17 (a) TEM micrograph of an inter-particle triple point in a CS copper coating showing typical microstructural features [13]; (b) TEM micrograph of a CS Ni coating. Particle-particle boundaries are marked with arrows. [14]

2.3.3 Effect of gas temperature

The quality of cold sprayed coatings is influenced by the particle velocity and particle temperature, which can be controlled mainly by process gas temperature (or inlet temperature) and gas pressure (or inlet pressure) [1, 3, 63]. This process involves preheating the gas flow (i.e. the ‘main’ gas flow) under the main gas temperature and combining it with the particles-gas mixture from the high-pressure powder feeder in a premixing chamber. The combination of gas and particles is generally injected axially through a de Laval type nozzle (i.e. converging-diverging nozzle) and the particles accelerate and impact on a flat surface of substrate due to drag effects from high-velocity
gas, as shown in Figure 2.18. The main gas temperature generates a gas velocity, which can be expressed by the equation [64]:

\[ v = \left( \frac{\gamma RT}{M_w} \right)^{1/2} \]  \hspace{1cm} (2.3)

where \( \gamma \) is the ratio of the constant-pressure and the constant-volume specific heats which is typically set to 1.66 for monoatomic gases like helium and 1.4 for diatomic gases like nitrogen and oxygen, respectively. \( R \) is the gas constant (8314 J/kmol·K), \( T \) is gas temperature, \( M_w \) is the molecular weight of the gas. When the particles impact on the substrate surface at high velocity, the particle’s kinetic energy is converted into mechanical deformation and thermal energy [5, 19]. Therefore, the first effect of temperature is to increase the velocity, all other things being equal. Although the particle velocity and the particle impact velocity strongly depend on gas velocity, the equations for these particle velocities are quite complex and more details can be found in ref. [64].

As shown in Figure 2.19, the copper coatings produced by the differences in particle velocity show different macroscopic features. The coating generated by condition 5, i.e. a particle velocity of about 650 m/s, shows a highly deformed and pore free structure compared to that of condition 1, which was generated at about 400 m/s. Moreover, the latter velocity is on the border of the critical velocity. However, more interesting is that the critical velocity appears to decrease with increasing particle (i.e. gas) temperature. It may be due to the effect of thermal softening. So far, nearly all the reports on the temperature effect are based on numerical simulation and/or characterization of macroscopic morphology, and the thermo-mechanical processing mechanism under difference gas temperatures is not well understood.
2.3.4 The role of post processing heat treatments in mechanical properties and microstructure

Any cold-sprayed metal exhibits high hardness and low ductility, leading to high brittleness and low formability [4, 5]. For example, hardness values as high as 225 HV and 325 HV have been reported by Lagerbom et al. for Ni and Ni20Cr, respectively [67]. Post processing heat treatment can obviously severely decrease the hardness of as-sprayed coatings. For example, the hardness value of cold sprayed copper decreased from 1.5 GPa to 0.7 GPa when annealed in 600 °C for one hour [35]. The hardness values decrease significantly to 100 HV and 200 HV by increasing heat treatment temperatures from 200 °C to 800 °C for Ni and Ni20Cr respectively [14]. Choi et al. [11] produced some cold sprayed aluminum specimens, and subsequently annealed them at 300 °C for 22 h in Ar or laboratory air. They found that annealing softened as-sprayed aluminum particles enough to promote ductile behavior, and even the flow stress is lowered below
that observed in bulk Aluminum 1100. Interestingly, as shown in Figure 2.20, vertical interfaces seem far more apparent than horizontal interfaces after Heat treatment (HT) in air, but HT in Ar seems to cause deterioration of all interfaces. This is not a normal mechanism associated with classical sintering of metal powder. In addition, Borchers et al. [35] observed dislocation loops of the extrinsic and intrinsic kind formed during cold spray do not heal out after annealing at 600 °C, as shown in Figure 2.21. These loops make the hardness of the samples does not fall as low as cold rolled sample after annealing. Although many studies have been reported on the recrystallization mechanism of the bulk metals after large strain deformation [68-70], the recrystallization phenomenon of cold sprayed materials in heat treatment process requires further systematic study.

Figure 2.20 Cross-sectional polished and etched SEM micrographs of coatings made from spherical (a, c, e) and globular (b, d, f) powders. Top row: as sprayed; middle row: HT in air; bottom row: HT in Ar. [11]
Figure 2.21 TEM micrographs of a CS Cu coating after heat-treatment of 1 h at 600 °C.

(a) Overview. There are no more nanosized grains, rather a recrystallized microstructure with micrometer-sized grains and recrystallization twins. Some have a coffee-bean-like contrast, very much like in the as-sprayed coating, one of which is marked with a white arrow. (b) Close-up of a grain with coffee-bean contrast (dislocation loops). [35]
Chapter 3 Materials and Experimental Methods

3.1 Materials

Commercially available gas-atomized nickel, copper and aluminum powder particles were used as feed stocks in the present study, as shown in Figures 3.1 (a) – (c), respectively. The size distributions of the particles are illustrated in Figure 3.1 (d). They are in spherical shape and the average size of them is about 30 µm. The nickel and copper powders were provided by H.C. Starck (Germany), and the aluminum powder was from Alfa-Aesar (USA).

Figure 3.1 SEM micrographs of as-received feedstock powder particles: (a) nickel, (b) copper, (c) aluminum and (d) the corresponding particle size distribution [71, 72].
The volume-weighted powder size distributions were measured using a laser diffraction particle size analyzer (LS320, Beckman Coulter, Miami, FL, USA). For depositing nickel and copper coatings, three mm thick carbon steel coupons (AISI 1022) were used as substrates. For aluminum coatings, Al-7075 alloy was used as the substrate.

3.2 Cold Spray Process

The coatings were produced by the cold spray system of CGT’s Kinetiks 3000, which is housed in McGill Aerospace Materials & Alloys Development Centre (MAMADC) at NRC- IMI in Boucherville, Quebec. The Kinetiks 3000 spray gun and the cold spray station in MAMADC are shown in Figure 3.2 (a) and (b), respectively. For the deposition of copper and nickel powders, the gun was held by a robot at a constant standoff distance of 4 cm and moved across the substrate surface at a transverse speed of 330 mm/s. The powder feeding rate was about ~20 g/min. Prior to deposition, the substrates were sand blasted and cleaned with alcohol. Ten gun passes were used over a given substrate to increase the coating thickness. The gas (nitrogen) pressure was maintained at 30 bar and the gas temperature was chosen as 200, 400 and 600 °C. For the conditions of producing the aluminum sample, the gas (nitrogen) temperature and pressure were fixed at 250 °C and 35 bar, respectively. The standoff distance, transverse speed powder feeding rate were 1 cm, 2 mm/s and 8-12 g/min, respectively. Prior to deposition aluminum, the substrates were blasted using grit alumina.

The average velocity of the particles at the onset of impact was measured by time-of-flight particle diagnostic system (DPV 2000) and has been described in [2]. The average velocity of copper particles under the gas temperatures 200, 400 and 600 °C are 624, 682 and 732 m/s, respectively, which are well above its critical velocity, about 500 m/s [2]. The average velocity of nickel particles under the gas temperatures 200, 400 and 600 °C are 596, 698 and 748 m/s, respectively, and its critical velocity is about 600 m/s [2]). For aluminum sample, the average velocity is 750 m/s, which is above its critical velocity (approx. 650 m/s).
3.3 Sample Preparation and Microstructural Characterization

3.3.1 Scanning electron microscopy

A Field Emission Gun Scanning Electron Microscope (Philips XL30) was used to characterize the morphologies of as-received powder particles and deformed particles on the first layer of as-sprayed coatings.

3.3.2 Electron backscattered diffraction

The as-sprayed coatings (Ni, Cu and Al) were cut parallel to the deposition direction using a diamond blade. For the EBSD observations, both the as-received powders and the as-sprayed coatings were cold mounted in a conductive resin, mechanically ground (400#, 600#, 800# and 1200# silicon carbon papers), polished (3 µm and 1µm diamond paste) and, vibratory polished using colloidal silica for 4 hours to remove the deformed surface layer.

The cross-sections of the as-received particles and the as-sprayed coating were characterized using Philips XL30 FEG-SEM fitted with TSL system [73]. The acceleration voltage and working distance used were 20 kV and 15 mm, respectively. The step size was chosen from 50 nm to 500 nm, depending on grain size. In the Euler angle maps presented in this paper, each point is colored according to crystal orientation, red
corresponds to the [001] direction, blue to [101] and green to [111]. High angle boundaries (HABs, >15°) are shown by black lines, and low angle boundaries (LABs, <15°) are depicted by white lines. To avoid misorientation noise, boundaries of less than 1° misorientation were cut off.

3.3.3 Transmission electron microscopy

Discs of 3 mm diameter were cut from the as-sprayed coatings along the deposition direction, using a slow diamond blade, and mechanically ground (400#, 600#, 800# and 1200# silicon carbon papers), polished (3 µm diamond paste) to a thickness of ~100 µm. The final thinning process by ion-beam milling was carried out using a Gatan Model 691 system. The TEM characterization was carried out using a Philips CM200 high-resolution transmission electron microscopy (TEM) system, which has a point-to-point resolution of 0.24 nm.
Chapter 4 Microstructural Evolution of Nickel Powder Particles Processed by Cold Spray

In this chapter, electron backscattered diffraction was used to investigate the microstructural evolution of nickel powder particles during cold spraying. Ultrafine grains in the scale of 100-200 nm were observed in the particle/particle bonding region. The formation of these nanometer-sized grains is interpreted in terms of dynamic recrystallization by lattice and subgrain rotation.

4.1 Introduction

As compared with the traditional thermal spray processes, cold spray is an evolving coating technology to form metallic coatings using low-temperature (300-800 °C) process gas and high-velocity (500-1200 m/s) feedstock powder particles [1-5]. In general, the bonding of particles is attributed to the extremely high strain-rate (up to $10^9$/s) plastic deformation and adiabatic shear instabilities that occur at the interfaces [2]. There are two types of interfaces: particle/substrate interface and particle/particle interface, both of which strongly affect the physical and mechanical properties of the as-sprayed materials [5, 12]. The particle/substrate interface has been extensively studied in recent years [2, 9, 74], but much less attention has been devoted to the particle/particle interface. Borchers et al. [14] observed non-uniform microstructure in the cold sprayed nickel coating by transmission electron microscopy (TEM). They found some elongated grains/subgrains and refined nanometer-sized grains with heavy strain contrast near the bonding regions, indicating the possibility of dynamic recrystallization during cold spraying. However, due to the lack of quantitative data and the limited examined areas of TEM, the relationship between the formed ultrafine grains and the original grains is not well understood. Compared with TEM, EBSD has the greater advantage of observing a larger area and therefore collecting more statistically significant data of crystal orientation, boundary misorientations, etc. [16, 18, 45, 75]. However, to the knowledge of the authors, no report has been made on studying microstructural evolution of powder particles during the cold spray process using EBSD.
4.2 Experimental

In the present study, a nickel coating was produced by a cold spray system (Kinetic 3000 CGT, Germany). Commercial gas-atomized nickel powder (5-22 µm in particle size), as shown in Figure 4.1a, was used as the feed stocks. Nitrogen was used as the process gas to achieve high impact of incident particles. The pressure and the temperature of nitrogen were maintained at $3 \times 10^6$ Pa and 873 K, respectively. The grit-blasted carbon steel was used as the substrate. For the EBSD observation, both the as-received powder and the as-sprayed coating were mounted in the conductive resin, mechanically ground, polished and, finally, vibratory polished using colloidal silica for 4 hours to remove the deformed surface layer.

The cross-sections of the as-received particles and the as-sprayed coating were characterized using Philips XL30 FEG-SEM fitted with TSL system [73]. For the spatial and angular resolutions of the EBSD system in FEG-SEM, some researchers demonstrated that they could reach $\sim 20$ nm and $\sim 0.5^\circ$, respectively, for aluminum [18, 76] [77]. Due to the larger atomic number of nickel, the resolutions for nickel could be higher [75]. The acceleration voltage used was 20 kV and the step size was 50 nm. In the Euler angle maps presented in this paper, each point is colored according to crystal orientation, red corresponds to the [001] direction, blue to [101] and green to [111]. High angle boundaries (HABs, $>15^\circ$) are shown by black lines, and low angle boundaries (LABs, $<15^\circ$) are depicted by white lines. To avoid misorientation noise, boundaries of less than $1^\circ$ misorientation were cut off. Pattern quality map obtained by the Kikuchi pattern qualities was used for a general measurement of the local defect density and lattice strain.

4.3 Results and Discussion

As seen in Figure 4.1b1, for the as-received particles, the Euler angle map shows typical crystallite in the size range of 1-5 µm. A relatively high pattern quality is seen in the pattern quality map (Fig. 1b2), indicating low defect density and lattice strain. To compare the morphology of the as-sprayed particles with the as-received ones, the bonded particles on the top surface of the coating are presented in Figure 4.1c.
In Figure 4.2, the cross-section of the as-sprayed coating, containing approximately 10 particles in this examined area, was characterized by EBSD. The deformation is clearly inhomogeneous as shown by the mixture of equiaxed grains and very elongated grains, i.e. some particles remain equiaxed while others are ‘pancaked’. Regardless of whether the particles remain equiaxed or are heavily deformed, a large number of ultrafine grains in the size of 100-200 nm are found in the region of particle/particle boundaries (Fig. 4.2a). As shown in the pattern quality map (Fig. 4.2b), the particle/particle interfacial regions have relatively lower pattern quality than the central regions of the impact particles. In addition to defect density and lattice strain, the low pattern quality could be due to the mixing of the overlapping EBSD patterns near or upon grain/subgrain boundaries [75]. To exclude these effects, the pattern quality values of the pixels in the center of the ultrafine grains were recorded. The obtained average pattern quality value in the center of the ultrafine grains is 136, much lower than that in the center region of the particle (224). This indicates that there is relatively high defect density and/or lattice strain inside the ultrafine grains in the bonding regions, consistent with the TEM observations previously introduced [14]. The EBSD observations imply that the formation of the ultrafine grains is attributed to dynamic recrystallization in the process of deformation, rather than static recrystallization during the heating and cooling process, because the typical feature of the grains formed by static recrystallization is nearly strain/defect free with, therefore, a high EBSD pattern quality [18].
Figure 4.2 EBSD characterization of the cross-section of the as-sprayed coating: (a) Euler angle map and (b) pattern quality map of the same area as 2 (a).

Figure 4.3 A close view of the box area in Figure 4.2a: (a) Euler angle map with four points (A, B, C and D) marked in a line from the center to the edge of the particle; (b) Misorientation profile, showing the point-to-point (the blue curve) and the point-to-origin (the red curve) along the path ABCD; (c) Tolerance angle map. The orientation of point A is selected as reference and the tolerance value is in the range of 0-25° (shown from
blue to red). The cubes in the map show the local crystal orientation; (d) Inverse pole figure of the points in the line ABCD.

There are two possible mechanisms for dynamic recrystallization: rotational and migrational types [78]. One way to determine which of these is operating is to consider the change in misorientation moving from the original grains to the recrystallized region [79]. Figure 4.3a is the Euler angle map corresponding to an area highlighted by the box in Figure 4.2a. The point-to-point and the point-to-origin misorientations are plotted versus distance along path ABCD from the center to the edge of the deformed particle, as shown in Figure 4.3b. It is seen that there are three apparently different regions divided by points A, B, C and D in Figures 4.3a and 4.3b, showing the distinct microstructures and the corresponding misorientation gradient.

In the central zone of the particle, as marked from A to B, subgrains are not well formed and there are only a small number of low angle boundaries. The misorientation gradient in this region is relatively low (20°/µm), meaning low lattice strain and defect density. Towards the particle/particle interface (from B to C), the strain increases and some elongated subgrains in the width of 100-200 nm are observed along the direction of shear or compression. The misorientation gradient in this region gradually increases, reaching an average value of 50°/µm. In the particle/particle interfacial region (from C to D), the misorientation reaches the highest value and some equiaxed, highly misoriented grains in the size of 100-200 nm are observed. As shown in Figures 4.3a and 4.3b, in the particle bonding region, high angle boundaries are formed and the point-to-point and the point-to-origin misorientations are up to 40° and 70°, respectively.

The difference of orientations relative to the center of the particle (point A) is shown in Figure 4.3c. To further reveal the deformation-induced lattice rotation in one grain, the tolerance angle map is illustrated using the color gradient from blue to red. It is seen that the lattice is gradually rotated from the center to the edge of the particle. The lattice rotation along the line ABCD is also illustrated using the orientations of the cubes in Figure 4.3c and the inverse pole figure (Fig. 4.3d). These results give sufficient evidences showing that the lattice in the particle is progressively rotated until high angle boundaries appear near the particle bonding region.
Assadi et al. [2] suggested that the bonding of particles was attributed to the adiabatic shear instability at the particle surfaces when the particle velocity exceeded a critical value. The similar feature of ultrafine grains and elongated subgrains in the present study was also observed in the adiabatic shear bands of the bulk materials under high strain-rate deformation [80-83]. Meyers and his coworkers [79, 84] proposed a model of rotational dynamic recrystallization to explain the microstructural revolution in the process of the high strain-rate deformation of bulk stainless steel and copper. Based on the present EBSD results, it seems reasonable to use this model to describe the formation of ultrafine grains in the cold sprayed nickel coating. A schematic diagram of this mechanism is shown in Figure 4.4. Before cold spraying, there is a low and uniform dislocation density (Fig. 4.4a), corresponding to Figure 4.1b2. As soon as the impact occurs, dislocations are propagated and the lattice is rotated progressively along the shear or compression direction (Fig. 4.4b). Due to the large number of dislocations accumulated and aligned in a short time, elongated subgrains are formed (Fig. 4.4c). These subgrains are subdivided into equiaxed subgrains due to the increased dislocation density (Fig. 4.4d). To accommodate the further strain induced by plastic deformation, the misorientations between adjacent subgrains gradually increase and, finally, the ultrafine grains with high angle boundaries are formed (Fig. 4.4e).

Experiments of dynamic recrystallization suggest that the recrystallized grain size \((D_R)\) may be estimated using a simple relationship:

\[
(\sigma/G)(D_R/b)^n = K [45]
\]  

where \(\sigma\) is applied stress, \(n\) and \(K\) are constants being 0.8 and 15, respectively, \(b\) is the Burgers vector (0.25 nm for nickel) and \(G\) is shear modulus (76 GPa for nickel). In the cold spray process, \(\sigma\) is the mean pressure during impact, which can be approximately calculated by \(\sigma = 1/2\rho u^2\) [13], where \(\rho\) is the density of materials (8908 kg/m\(^3\) for nickel) and \(u\) is the average velocity of the particles at the onset of impact (\(u = 750 \text{ m/s}, \) which was measured by time-of-flight particle diagnostic system (DPV 2000) and has been described in [72]). The estimated applied stress (\(\sigma\)) is about 5 GPa and the calculated dynamic recrystallized grain size (\(D_R\)) is about 200 nm, which is in good agreement with
the observed grain size by EBSD. This result further confirms that the dynamic recrystallization is a more possible mechanism for the formation of the ultrafine grains at the particle/particle interfacial region.

4.4 Conclusions

In summary, based on the EBSD technique, the non-uniform microstructure with the ultrafine grains in the size of 100-200 nm has been observed in the cold sprayed nickel coating. The formation of ultrafine grains is attributed to the dynamic recrystallization produced by lattice and subgrain rotation.
Chapter 5 Microstructure and Nanohardness of Cold Sprayed Nickel and Copper Coatings

In Chapter 4, electron backscattered diffraction was used to investigate the microstructural evolution of nickel powder particles during cold spraying. In this chapter, nanoindentation is conducted to identify how the local changes of microstructure influence the hardness distributions of cold sprayed nickel coating. The copper coating produced using the same cold spray processing conditions as the nickel coating is also investigated. The results show the hardness in the vicinity of nickel particle interfaces can be about 1.5 GPa higher than that in the particle interior, and this difference is attributed to the cold-spray induced grain boundaries and dislocation densities. The copper coating with lower activation energy for recrystallization shows a more uniform microstructure and hardness distribution, which can be attributed to static recrystallization.

5.1 Introduction

The past years have seen a significant advance in employing the cold spray process for the production of thick coatings and various bulk forms using high-velocity (500-1200 m/s) impact of solid metallic powder particles (1-50 µm) [4, 5, 27]. Based on finite element analysis (FEA), some researchers [2, 8, 9] predict that the particles experience heterogeneous strains ($\varepsilon$) and strain rates during impact: high level ($\varepsilon \sim 10$) on the outer edge of particles and low level ($\varepsilon < 1$) in the particle center. What is more, the heat generated in this process may cause partial or complete recrystallization of the as-sprayed materials immediately after impact or during cooling [8]. Such a localized thermo-mechanical process could lead to a very non-uniform microstructure and, therefore, significantly affects the properties of cold sprayed coatings. Using transmission electron microscopy (TEM), both micron-sized and submicron-sized grains/subgrains were observed in the cold sprayed coatings [13, 14]. Applying micro-hardness or fracture tests, a large amount of studies was carried out to investigate the mechanical performances of the entire as-sprayed coatings [12, 35, 85]. Despite the increasing prevalence of these characterizations and measurements, however, to our knowledge, no
studies have looked at the whole microstructure of a deformed particle and examined the uniformity of mechanical properties within the particle. Therefore, how the local changes of microstructure influence the mechanical properties in cold sprayed coatings are not clear.

Compared with TEM, EBSD has the advantage of observing a larger area and therefore collecting more statistically representative data on crystal orientation, image quality (IQ), boundary misorientations, etc [18]. Nanoindentation, using the Oliver and Pharr method [86], make it possible to measure the hardness and elastic modulus on a very small scale. In this paper, EBSD and the nanoindentation are employed to investigate the relationship between local microstructure and hardness in the cold sprayed Ni and Cu coatings.

5.2 Experimental

Spherical gas-atomized Ni and Cu powder particles with an average size of ~25 µm, as seen in Figures 5.1a1 and 5.1b1, were used as the feed stocks and cold sprayed according to the procedures and conditions described in Ref. [87]. In order to keep the same preparing procedure for the nanoindentation and EBSD testing, as-received powders and as-sprayed coatings were mounted in the same coupon, mechanically ground, polished and, finally, vibratory polished using colloidal silica for 4 hours to remove the deformed surface layers. The indentation experiments on the cross-sections of the Ni and Cu powders and coatings were conducted with a Hysitron Ubi3 nanoindenter, under a maximum load of 1 mN, a constant indentation loading rate of 0.2 µNs⁻¹ and a hold time of 1 s. A total number of 30 nominally identical indentation tests were carried on both the Ni and Cu powder particles. Matrices of 15×15 indents were carried out on every coating with the indent spacing of 3.5 µm. In each of the coatings, more than 4 areas after indentation were characterized by a Philips XL30 FEG-SEM fitted with EBSD-TSL system [73]. The procedures and analysis of EBSD data followed those described in Ref. [87]. In the Euler angle maps presented in this paper, high angle boundaries (HABs, >15°) are shown by black lines, and low angle boundaries (LABs,
<15°) are depicted by white lines. Image quality (IQ) maps were obtained by analyzing Kikuchi pattern quality and used as a general indicator of local dislocation density.

### 5.3 Results and Discussion

As shown in Figures 5.1a2 and 5.1b2, the Euler angle maps reveal typical crystallites in the size range of 1-5 µm in both as-received Ni and Cu particles. In Figure 5.1a3 and 5.1b3, IQ maps show relatively high image qualities for the as-received particles (average IQ\(_{\text{Ni}}\) = 246; average IQ\(_{\text{Cu}}\) = 258) and indicate low dislocation density before spraying.

![Figure 5.1 SEM micrographs, Euler angle maps and image quality (IQ) maps of as-received powder particles of Ni (a1, a2, a3) and Cu (b1, b2, b3).](image)

Figure 5.1 illustrates the hardness values for the as-received Ni and Cu powders and as-sprayed coatings. The red lines indicate average hardness for the as-received powders, and the error bars reflect the standard deviation of the hardness measurements. It shows that the hardness values for as-received Ni and Cu are 2.9 ± 0.2 GPa and 1.8 ± 0.2 GPa, respectively. For the as-sprayed coatings, it is found that Ni has a much wider hardness distribution than Cu, and the highest value in the Ni coating is about 5 GPa, nearly twice higher than the as-received one. However, the Cu coating shows a relatively narrow hardness distribution and the hardness is similar to the as-received one.

Figure 5.3a is the Euler angle map showing an indented area which contains approximately 6 Ni particles. Interestingly, we observed a roughly bimodal grain-size microstructure: micron-sized grains with a small amount of LABs are present in the particle interiors and have similar microstructure as the as-received one, while 100-200
nm sized grain/subgrains with a large number of LABs appear in the vicinity of inter-

particle interfaces (denoted by a circle) and form a “necklace-like” structure. The formation of these ultrafine grains could be the result of dynamic recrystallization during impact, which has been discussed in our previous paper [87]. For both cold sprayed Ni and Cu coatings, the average thicknesses are about 500 µm. The coatings were cross-sectioned parallel with the deposition direction. In the IQ map of the same area (Fig. 5.3b), the particle interiors show much higher image qualities (average IQ\textsubscript{Ni-center} = 225) than the particle/particle bonding regions (average IQ\textsubscript{Ni-edge} = 126, the effects of overlapping EBSD patterns near or upon grain/subgrain boundaries are excluded, as described in [87]). The EBSD observations imply that a large amount of dislocations are accumulated in the vicinity of particle interfaces, which might have been introduced by localized deformation during cold spraying. Figure 5.3c is the IQ map combined with the

Figure 5.2 The nanohardness distributions of the as-sprayed coatings determined from 15×15 indents. The red lines show the corresponding hardness of the as-received powder particles.
corresponding nanohardness. The circles indicate the locations of indentations and the numbers below the circles show the corresponding hardness values. In the 4 areas with more than 150 indents characterized by EBSD, it is found that the average hardness in the vicinity of particle interfaces \( (d_{\text{indent-to-edge}} < 1.5 \, \mu \text{m}) \) is 4.2 GPa, which is impressively higher than that in the particle interior \( (d_{\text{indent-to-edge}} > 1.5 \, \mu \text{m}, 3.2 \, \text{GPa}) \). For example, as shown in Figure 5.3c, the two indents denoted by triangles located near the particle interfaces are 1.0 -1.7 GPa higher in hardness than the two denoted by squares near the particle center. In order to give an approximation of the hardness in the cold sprayed particles, a linear superposition of various strengthening mechanisms is expressed as:

\[
H = H_i + H_{\Delta GB} + H_{\Delta \rho} \quad (5.1)
\]

where \( H_i \) is the initial average hardness of the as-received powder particles and should include the contributions of the lattice resistance, elements in the solid solution, dislocation hardening introduced by gas atomization, grain boundary (GB) hardening, grain orientation effect and indentation size effect \([88]\). \( H_{\Delta GB} \) is the additional hardening contribution owning to new GBs \( (\Delta GB) \) induced by cold spraying. \( H_{\Delta \rho} \) is the additional hardening component owning to the increased local dislocation density \( (\Delta \rho) \) induced by cold spraying. Following the procedure suggested by Nix and Gao \([88]\), we can get

\[
H_{\Delta \rho} = 3 \sqrt{3} \alpha \mu b \sqrt{\Delta \rho} \quad (5.2)
\]

where \( \alpha \) is a constant to be taken as 0.5, \( \mu \) is the shear modulus (76 GPa for Ni) and \( b \) is the Burgers vector (2.492 nm for Ni). So,

\[
H = H_i + H_{\Delta GB} + 3 \sqrt{3} \alpha \mu b \sqrt{\Delta \rho} \quad (5.3)
\]

For Ni particle interior, GB density is similar as in the as-received particles, so \( \Delta GB \approx 0 \), and the IQ value is also similar as the as-received one, so \( \Delta \rho \approx 0 \). Thus, \( H_{\text{Interior}} \approx H_i = 2.9 \pm 0.2 \, \text{GPa} \). For the vicinity of particle interfaces with high GB densities and low IQ
values, e.g. the two indents denoted by triangles in Figure 5.3c, both the effects of $\Delta GB$ and $\Delta \rho$ cannot be ignored. However, due to the complex structure in these regions and the very scanty data for nanoindentation of severely deformed materials, it is difficult to give an accurate calculation for $H_{\Delta GB}$ and $H_{\Delta \rho}$, respectively. In recent studies, Soer et al. [89] found that the hardness of GB region was $\sim$0.7 GPa higher than in the grain interior in Fe–14%Si and $\sim$0.8-1.2 GPa higher in Mo under a maximum load of 3 mN.

Additionally, Eliash, et al. [90] observed that the hardness in the GB region was strongly dependent on the load, and under the a maximum load of 1mN (the same condition we used in this paper) the GB region was about 1GPa harder than the grain interior in Mo. For a discussion, let us assume that the increased hardness due to cold-spray induced GBs is 1 GPa, i.e., $H_{\Delta GB} = 1$GPa. For $\Delta \rho$, although there is no report on the dislocation density of cold sprayed Ni, the dislocation density in the shock loaded Ni under the pressure of 10 GPa (the same impact pressure in the highly deformed regions of cold sprayed coating [6]) was reported to be $2 \times 10^{14}$ m$^{-2}$ [91]. This value can be used here to give a reasonably good estimation. Using these values, we can get the hardness near the particle interface ($H_{\text{interface}}$) of 4.6 ± 0.2 GPa, which is close to the result obtained in our nanoindentation tests. So the increased hardness near particle interfaces could be attributed to the increased numbers of both the grain boundaries and dislocation densities induced by cold spraying.

Figure 5.4a is the Euler angle map of the as-sprayed Cu coating. Compared with the Ni coating, the Cu coating does not show the “necklace-like” structure or obvious particle interfaces that illustrated the particle interactions at the impact, and the microstructure is relatively uniform. The grain size of the as-sprayed Cu is similar as in the as-received particles and most areas have only HABs. In Figure 5.4a, it is also worth noting that a lot of twin boundaries are present (denoted by arrows), which is a typical feature of annealed Cu. In Figure 5.4b, IQ map of the same area shows relatively high values of image qualities of the entire area (average IQ = 215), implying relatively low dislocation density in the Cu coating. Figure 5.4c is the IQ map combined with the corresponding hardness of the same area. It is seen that the hardness is more homogenously distributed in the coating and is 1.8 ± 0.3 GPa, which is close to the
hardness of as-received particles. These results further confirm that static recrystallization occurs in the cold sprayed Cu coating.

Figure 5.3 EBSD characterization of the cross-section of Ni coating after nanoindentation: (a) Euler angle map, (b) IQ map and (c) IQ map and the numbers below the circles showing the local hardness.

Figure 5.4 EBSD characterization of the cross-section of Cu coating after nanoindentation: (a) Euler angle map, (b) IQ map and (c) IQ map and the numbers below the circles showing the local hardness.
The recrystallization kinetics can be approximately estimated by the JAMK equation [45]:

\[ X(t) = 1 - \exp(-Bt^n) \]  

(5.4)

where \( X(t) \) is the time-dependent fraction of recrystallized area, \( n \) is a constant (JMAK exponent) and \( B \) is the temperature-dependent parameter. \( B \) can be expressed according to the Arrhenius law:

\[ B = B_0 \times \exp(-Q_R/RT) \]  

(5.5)

where \( B_0 \) is a constant, \( R \) is a gas constant and \( T \) is the absolute temperature in Kelvin grades. The processing parameters were maintained the same for the production of the Ni and Cu coatings, however, because Cu has much lower activation energy for recrystallization (\( Q_R \)) than Ni (\( Q_{R(Cu)} \) is reported to be 65-96 kJ mol\(^{-1} \) [92] and \( Q_{R(Ni)} \) is 650-790 kJ mol\(^{-1} \) [93]), so it is much easier for Cu to be recrystallized as a result of the rise of temperature within the coating that is caused by the mechanical deformation of particles and the temperature of process gas during spraying. The more details on recrystallization of the cold sprayed coatings will be discussed in our future paper.

5.4 Conclusions

In summary, using EBSD and nanoindentation techniques, the microstructural characteristics and hardness distributions of cold sprayed Ni and Cu coatings were investigated. Due to localized deformation at the impact interfaces, the Ni coating shows a large number of GBs and dislocations in the particle/particle bonding regions, and the vicinity of Ni particle interfaces can be about 1.5 GPa higher in hardness than the particle interiors. However, the cold sprayed Cu with lower activation energy for recrystallization shows the microstructure of static recrystallization and more homogenous hardness distribution.
Chapter 6 Microstructural Evolution and Bonding
Formation of Cold Sprayed Aluminum Coating

In Chapters 4 and 5, the microstructures of cold sprayed nickel and copper coatings were investigated. In this chapter, the microstructural characteristics and the particle/particle bonding characteristics of an aluminum coating is studied. The results show that nanometer-sized grains and interfacial perturbations can be observed in the particle/particle bonding region. The formation of these structures can be attributed to high strain and high strain-rate deformation combined with adiabatic shear instability at impact interfaces.

6.1 Introduction

In recent years, the cold spray process, using a high-velocity (500-1200 m/s) impact of solid powder particles (1-50 µm), has been attracting considerable interest for the production of coatings and bulk forms [4, 5, 27]. Various materials, i.e., pure metals, metallic alloys and composites, can be processed by cold spray. Using finite element analysis (FEA), the kinetic impact of particles has been extensively studied [2, 8, 9], and these results indicate that during cold spraying the particle/particle interfaces are subjected to high temperatures and high strains for an extremely short period of time (10-200 ns). This makes it difficult to understand the actual mechanism by which the solid metal particles deform and bond in the cold spray process. A prevalent opinion based on FEA indicates that the bonding of particles depends on the occurrence of adiabatic shear instability (ASI) at impact interfaces [2]. So far, few detailed microstructural investigations have been reported showing corresponding evidence in the particle/particle interfacial region. What is more, it is known that nanocrystalline (nc; d < 100 nm) grains can be produced by large strain plastic deformation, especially under high strain rate [79, 94]. Due to the extremely high strain rate (up to \(10^9/\text{s}\)) at impact interfaces during cold spraying [2, 8, 9], the particle/particle bonding process could also involve the formation of nc-grains. Although some researchers [13, 14] observed grains in the order of several
hundred nanometers in cold sprayed Cu, Ni and Al, true nc-grains, i.e., d < 100 nm, are expected to be formed during impact. The objective of this paper is to investigate the particle/particle bonding features and microstructural transformation in the interfacial region of Al powder particles processed by cold spraying.

6.2 Experimental

Spherical gas-atomized pure Al powder particles were used as the feed stock in this study. The Al particles were deposited on a grit-blasted Al-7075 alloy substrate by a cold spraying system (CGT’s Kinetiks 3000). Nitrogen was used as the process gas to accelerate Al particles under a gas temperature of 250 °C and gas pressure of $3.5 \times 10^6$ Pa. The average velocity of Al powder was 665 m/s as measured by a time-of-flight optical particle diagnostic system (Tecnar DPV 2000).

A Philips XL30 field emission scanning electron microscope (FEG-SEM) equipped with an EBSD-TSL system [73] was used to characterize the as-received Al particles and the as-sprayed coating. Specimens for transmission electron microscopy (TEM) characterization were taken from the coated Al. Discs of 3 mm diameter were cut and polished to a thickness of ~100 µm. The final thinning process by ion-beam milling was carried out using a Gatan Model 691 system. The TEM characterization was carried out in a Philips CM200 high-resolution system, which has a point-to-point resolution of 0.24 nm.

6.3 Results and Discussion

As seen in Figure 6.1a, the as-received Al powder particles are spherical and with an average size of 36 µm. The EBSD map (Fig. 6.1b) shows that the large Al particles are polycrystalline, having nearly equiaxed grains sized 5-20 µm, and the small ones are single crystals. The deformed particles on the top surface of the as-sprayed coating are shown in Figure 6.2a. In Figure 6.2b, it is seen that the cross-section of the coating is relatively dense and has an average thickness of ~300 µm. The EBSD map of the cross-section of the coating and the corresponding grain size distribution are revealed in Figure 6.2c and 6.2d, respectively, indicating impressive non-uniform microstructure with great
grain size and shape differences. The small dots in the EBSD map may be due to the areas which cannot be indexed by EBSD system.

Figure 6.1 SEM micrograph (a) and EBSD map (b) of as-received Al powder particles. In the EBSD map, each point is colored according to crystal orientation, red corresponds to the [0 0 1] direction, blue to [1 1 1] and green to [1 0 1].

Figure 6.2 SEM micrographs of the top surface (a) and the cross-section (b) of as-sprayed
coating; EBSD map of the cross-section of as-sprayed coating (c) and its corresponding grain size distribution (d).

A typical TEM image (Fig. 6.3a) shows a small region in the as-sprayed coating. The bright areas are holes made by ion milling. The distinct contrast between the left and right and the cracked morphologies in the middle indicate that this region is right at the impact zone between two particles (denoted by 1 and 2). The morphology in the bonding region is shown in higher magnification images of box i and ii, as seen in Figure 6.3b and 6.3c, respectively. In Figure 6.3b, a lot of roll-ups and bulges in the size of ~100 nm (indicated by a circle) appear on the edges of the particles, showing the morphology of strong perturbation. In the contacted area of the particles, as shown in Figure 6.3c, the perturbations, i.e., roll-ups and bulges (denoted by arrows), can be also observed and cause blurring and mixing of the original interfaces. It is interesting to find that these roll-ups and bulges are almost equidistantly distributed and interlocked and form a “zipper-like” structure. This indicates that a mechanical bonding could occur between the two particles.

Schmidt et al. [3] did a FEA simulation and suggested that there was a critical particle velocity in cold spraying above which ASI forms at impact interface. For Al/Al impact, the critical particle velocity is about 620 m/s [3]. The tested average velocity of Al particles in our experiment is 665 m/s, which is above the critical value. Adiabatic heating causes the materials to soften and deform locally easily creating shear instabilities, which can give rise to viscous flow [2]. Under such circumstances the interfacial instability can be explained using the Kelvin–Helmholtz instability phenomenon, as suggested by Grujicic et al. [8] based on FEA. If there is a sufficient velocity difference across the interface between two materials during impact, the interface will not be stable and a centrifugal force is generated. This force can make materials flow easily, give rise to interfacial roll-ups and bulges and lead to strongly interlocked particles. A schematic diagram of this process is presented in Figure 6.4.
Figure 6.3 (a) Typical TEM image of the bonding region between two Al particles, as denoted by 1 and 2; (b) and (c) are closer observations of the boxed regions i and ii, respectively. The circle in (b) indicates the morphology of roll-ups and bulges. The arrows in (c) show the interfacial perturbations between particle 1 and 2.
To estimate the time period ($\tau$) needed to form unstable perturbation, an equation developed by Grujicic et al. [8] is used, which can be expressed as:

$$\tau = (\alpha^2 R_e J)^{-1} \quad (6.1)$$

where $\alpha = 2\pi/\lambda$, $\lambda$ is the wavelength of the perturbation, i.e., the diameter of roll-ups and bulges (about 100 nm, according to our TEM observation), $J$ is a function of the viscosity ratio and the thickness ratio of two materials, which is in the order of $10^2$ to $10^4$ m$^2$/s [95], and $R_e$ is the Reynolds number as:

$$R_e = \frac{\rho V L}{\mu} \quad (6.2)$$

where $\rho$ the density of the materials (2700 kg/m$^3$ for Al), $V$ the mean fluid velocity, i.e., the particle impact velocity (about 665 m/s), $L$ a length of the object that the flow material is going through or around, i.e., the scale of impact region (in the order of 1 µm) and $\mu$ the dynamic viscosity of the materials (about $10^5$ kg/m·s as estimated using FEA analysis [8]). Using the above values, the time period $\tau$ for yielding the unstable perturbation is about $10^{-12}$ to $10^{-14}$ s, which is under the time scale of the particle/particle collision event (in the scale of nano seconds). This indicates that perturbations could be formed at impact and continue to move, mix and interlock during the time of collision. Therefore, ASI could be a possible mechanism for the bonding formation in the cold spray process.

In addition to the interfacial morphology, it is also interesting to see that a large number of nc-grains are present on both sides of the particles, as shown in Figure 6.3a. Outside the nc-grain region, grain sizes are in the range of 100-500 nm (denoted by arrows). Figure 6.5a and 6.5b are bright field image and dark field image of the boxed region-iii in Figure 6.3a, respectively. In this region, grain size is non-uniformly distributed - grains as small as ~5 nm are present near the interface, but larger ones in the size of ~60 nm are farther from it. The selected area electron diffraction (SAD) pattern in Figure 6.5a confirms that the bonding region is completely nanocrystalline Al. A high-
resolution TEM (HRTEM) image of the nc-grains (Fig. 6.5c) shows that there is a high misorientation angle between nc-Al grains.

![Diagram](image)

Figure 6.4 Schematic diagram of the morphology formed due to ASI in the cold spray process: (a1) as soon as impact, two particles 1 and 2 have different velocities across the interface; (a2) Due to ASI, the interface is not stable and centrifugal force can be generated; (a3) interfacial roll-ups and bulges are formed by the generated centrifugal force, leading to interlocked particles; (b) Kelvin–Helmholtz instability rendered visible by clouds (Source of (b): English Wikipedia: http://en.wikipedia.org/wiki/Image:Wavecloudsduval.jpg, Permission is granted to copy, distribute and/or modify this document)

The feature of nc-grains or ultrafine grains in the bonding region, i.e., a high-velocity impact zone, in the present study seems similar as those in the adiabatic shear bands of the bulk materials under high strain-rate deformations [80-83]. Meyers et al. [79] and Hines et al. [81] suggested that the grains within adiabatic shear bands were refined by rotational dynamic recrystallization. Under the similar high strain and high strain-rate conditions in the bonding region, it seems reasonable to use rotational dynamic recrystallization to describe the formation of nc-grains in the cold sprayed Al, as schematically shown in Figure 6.6. Before cold spraying the grain size is relatively large
with a low dislocation density. As soon as impact occurs, a large number of dislocations and vacancies are introduced, and then the dislocations accumulate and rearrange into low angle boundaries, forming subgrains. To accommodate increasing strain, the misorientation angle of the subgrain boundaries increases, the subgrains rotate, and then high angle boundaries and randomly oriented fine grains are formed.

Figure 6.5 Bright field image (a) and dark field image (b) of the boxed region-iii in Fig. 6.3a; the corner of (a) showing the corresponding selected area electron diffraction (SAD) pattern; (c) HRTEM image of nc-grains near the bonding region.

Figure 6.6 Schematic diagram showing dynamic recrystallization produced by subgrain rotation during the particle/particle bonding process: (a) a relatively large grain has a low dislocation density before cold spraying; (b) with increasing strain during impact, a large number of dislocations are introduced, accumulated and rearranged into low angle boundaries, and then subgrains are formed; (c) to accommodate increasing strain, misorientations of the subgrain boundaries increase and the subgrains rotate, forming high angle boundaries and randomly oriented fine grains.
In order to determine whether the nc-grains were formed during the impact of particles or the subsequent cooling process, it is necessary to determine how quickly the new grains could be achieved by subgrain rotation at a given condition of cold spray. The period of time \( t \) for subgrain rotation can be approximately predicted by a kinetics model for subgrain rotation proposed by Doherty and Szpunar [96]:

\[
\begin{align*}
  t &= \frac{l^3}{3E_0Bb} \\
  \text{where } E_0 &= \frac{G\beta}{4\pi(1-\nu)} \text{ with } G \text{ the shear modulus (26 GPa for Al), } b \text{ the Burgers vector (0.29 nm for Al) and } \nu \text{ Poisson’s ratio (0.35), } l \text{ is the subgrain size (about 10 nm) and } B \text{ is the dislocation climb mobility by bulk diffusion, calculated by } B = 4dbD/lkT, \text{ where } d \text{ is about } 180b, \text{ } k \text{ is the Boltzmann constant, } T \text{ is the temperature in the highly deformed region( estimated at 900 K from Ref. [9]) and } D \text{ is the bulk diffusion coefficient under } T \text{ (approximately } 10^{-12} \text{ m}^2/\text{s}) [96]. \text{ The detail of the calculation procedures can be found in Ref. [96]. Under this condition the predicted time of the subgrain rotation is about 200-300 ns, which is close to the impact time calculated by the simulations [2, 3]. Therefore, the whole process schematically shown in Figure 6.4 can be achieved during the impact of particles.}
\end{align*}
\]

The recrystallized grain size \( D_R \) in dynamic recrystallization process is approximately dependent upon the applied stress \( \sigma \), which can be estimated using a simple relationship:

\[
\begin{align*}
  \left(\frac{\sigma}{G}\right) \cdot \left(\frac{D_R}{b}\right)^n &= K \quad [45] \\
  \text{where } n \text{ and } K \text{ are constants (being 0.8 and 15, respectively). In the cold spray process, } \sigma \text{ is the impact pressure calculated as 5-10 GPa in the highly deformed regions in the numerical simulation as reported in Ref. [8]. So the predicted dynamic recrystallized grain size } (D_R) \text{ is about 20-60 nm. This coincides with the grain size observed by TEM. Moreover, due to the decreased pressure towards the internal region of the particles [2], the } D_R \text{ can be increased from the interfacial region to the internal region. This can be}
\end{align*}
\]
used to explain the observed grain size difference in the nc-grain region and the appearance of the grains in the size of hundreds of nanometers.

6.4 Conclusions

Perturbations in the form of roll-ups and bulges were observed in the particle/particle bonding region of cold sprayed Al powder particles. This morphology could be induced by the ASI at the impact interfaces and lead to strongly interlocked particles. In addition, a large number of nc-grains were found within the bonding region and the formation of the nc-grains is attributed to the dynamic recrystallization produced by subgrain rotation.
Chapter 7 Effect of Gas Temperature on the Microstructure and Properties of Cold Sprayed Copper Coatings

In Chapters 4, 5 and 6, the microstructures of cold sprayed nickel, copper and aluminum coatings produced under certain process condition were investigated. In this chapter, the effect of gas temperature on the microstructure and hardness of cold sprayed copper coatings are studied. Copper coatings were produced under the same gas pressure (30 bar) but different gas temperatures (100, 200, 400 and 600 °C). The results show that, with increasing gas temperature, the deposition efficiency was increased and the porosity was decreased. The microhardness of the coatings is increased below the gas temperature of 400 °C, but decreased above 400 °C. This phenomenon is interpreted in terms of static recrystallization in the cold spray process.

7.1 Introduction

Cold spray technology is a relatively new method for the production of dense and tightly bonded coatings or free-standing structures, particularly suitable for the materials that are sensitive to heat and oxidation [1, 2, 4, 5]. During this process, metallic powder particles are accelerated to supersonic velocity by high-pressure gas, and they impact the substrate or previously deposited particles to form coatings due to severe plastic deformation and related phenomena at the interfaces [2]. The quality of the as-sprayed coating is influenced by the particle velocity and particle temperature, which can be controlled by main gas temperature (or inlet temperature) and gas pressure (or inlet pressure) [2-5]. A typical cold spray system is shown in Figure 7.1. The process involves preheating the gas flow under the main gas temperature and combining it with the particles-gas mixture from the high-pressure powder feeder in a premixing chamber. When the particles impact the substrate surface at high velocity, the particle’s kinetic energy is converted into mechanical deformation and thermal energy. The main gas
temperature plays a significant role in particle velocity, which can be expressed by the equation [5]:

\[ v = \left(\frac{\gamma RT}{M_w}\right)^{1/2} \]  

(7.1)

Where \( \gamma \) is the ratio of specific heats, \( R \) is the gas constant (8314 J/kmolK), \( T \) is gas temperature, \( M_w \) is the molecular weight of the gas. So particle velocity (i.e. gas velocity) was increased by the increased gas temperature. The main gas temperature can also increase the particle temperature, which can introduce thermal energy to the substrate during the impact [5, 19]. Both the mechanical deformation and thermal energy caused by gas temperature can influence the microstructure and further the properties of the as-sprayed coatings. However, nearly all the reports [3, 13, 97, 98] on the temperature effect so far are based on numerical simulation or macroscopic morphology characterization, in which the particles are presumed as continuity without considering the sub-structures in sprayed particles. In this paper, microstructural transformation in the particle during the process is considered and the effect of gas temperature on the properties of as-sprayed coatings is investigated.

![Figure 7.1. Schematic diagram of the cold spray system](image)

7.2 Experimental

Commercial gas-atomized copper powder was used as the feed stocks in the present study. The powder was deposited to form coatings by a cold spray system
Nitrogen was used as the process gas. To investigate the temperature effect, the gas pressure (P inlet) was maintained at 30 bar and the gas temperature (T inlet) was chosen as 100, 200, 400 and 600 °C, respectively. The average velocities (V) of particles at onset of impact were tested using a DPV-2000. Deposition efficiency (DE) is calculated by the weight of deposited powder over the weight of the total powder used. For the porosity measurement, the cross-sections of as-sprayed coatings were examined using backscatter electron mode in JEOL-840 electron scanning microscopy (SEM). Micro-hardness measurement of the cross-section of as-sprayed coating was performed Clark™ micro-hardness machine. The spraying parameters for experiments and properties of the as-sprayed coatings are summarized in Table 1.

Table 7.1 The spraying parameters for experiments and properties of the as-sprayed coatings (more details in Reference [71])

<table>
<thead>
<tr>
<th>No.</th>
<th>T inlet (°C)</th>
<th>P inlet (bar)</th>
<th>Processing gas</th>
<th>V (m/s)</th>
<th>DE (%)</th>
<th>Porosity (%)</th>
<th>Micro-hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>30</td>
<td>N₂</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>30</td>
<td>N₂</td>
<td>624</td>
<td>68.5</td>
<td>1.8</td>
<td>142</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>30</td>
<td>N₂</td>
<td>682</td>
<td>97.6</td>
<td>0.6</td>
<td>144</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>30</td>
<td>N₂</td>
<td>732</td>
<td>97.5</td>
<td>0.1</td>
<td>134</td>
</tr>
</tbody>
</table>

The as-received powder morphology, the top surfaces and cross-sections of as-sprayed coatings were characterized by a Philips XL30 FEG-SEM system. For electron backscattered diffraction (EBSD) characterization, both the as-received powder and as-sprayed coating were mounted, mechanically grounded, polished, and finally polished in colloidal silica to remove the deformed surface layer. The voltage was 20 KV and the step size was 50 nm. In the Euler angle maps presented in this paper, blue, red and green levels are proportional to the three Euler angles, respectively. EBSD pattern quality maps...
obtained by the Kikuchi pattern quality were used for a general measurement of the local defect density and lattice strain.

7.3 Results and Discussion

Figure 7.2 The effect of gas temperature on coating properties: (a) average particle velocity, (b) deposition efficiency (DE), (c) porosity and (d) microhardness

The effect of gas temperature on the average particle velocity, deposition efficiency, porosity and micro-hardness are shown in Figure 7.2. It is seen that in Figure 7.2a that the average particle velocity is increased with increasing gas temperature. It is
because that higher temperature causes higher gas velocities, as shown in equation (1), leading to higher particle velocities. As shown in Figure 7.2b, the deposition efficiency was increased from 68.5 % to 97.6 % with the gas temperature increased from 200 to 400 °C, but it reached the deposition limit in the temperature above 400 °C. The increased deposition efficiency could be caused by the higher plastic deformation and more thermal effect in the interfaces due to increased particle velocities and particle temperature. As shown in Figure 7.2c, the porosity of the as-sprayed coatings was decreased as increased gas temperature. Higher gas temperature increases the particle velocity, and more kinetic energy were converted into other forms of energy such as plastic deformation, void consolidation, particle-particle rotation, etc. [5]. These can reduce the void between particles and decrease the porosity of as-sprayed coatings.

The relationship between micro-hardness and gas temperature is illustrated in Figure 7.2d. Interestingly, the hardness is nearly constant (about 143 HV) when the gas temperature is in the range of 200-400 °C, but the hardness was decreased when the gas temperature above 400 °C. Both the increased particle temperature and the particle velocities can influence the hardness of the as-sprayed coatings. On one hand, the work hardening effect due to increasing particle velocity can increase the hardness of as-sprayed coatings. On the other hand, the increased gas temperature could soften as-sprayed coatings by recrystallization during or after the impact. So the final hardness is the determined by the effects of work hardening and recrystallization under different gas temperatures.

Figure 7.3 As-received copper powder: (a) SEM micrograph and (b) particle size distribution
As seen in Figure 7.3a, as-received copper powder particles are in spherical, with the average particle size of 25 µm, and the size distribution is shown in Figure 7.3b. Inverse pole figure (IPF) map (Figure 7.4b) shows typical crystallite of feedstock particles is nearly equaxed and in the size range of 1-10µm. The image quality (IQ) map (Figure 7.4a) shows relatively high pattern quality of the grains in as-received powder, implying low defect density and lattice strain. A comparison of as-received powder to as-sprayed coating, discussed later in this paper, distinguishes the implication of grain size and defect density distribution towards explaining the microstructural evolution after cold spraying.

Figure 7.4 EBSD characterization of powder particles: (a) IQ map and (b) IPF map (c) color coded reference: [001] Inverse pole figure of copper

To compare the morphology of as-sprayed coatings under different gas temperature, both the top surfaces and the cross-sections are characterized by SEM, as shown in Figures 7.5 and 7.6, respectively. As shown in Figure 7.5a, the bonded particles on the top surface exhibit irregular shapes with relatively flat morphology, implying most of the particles are rebounded. On the coating produced in the higher temperature conditions, the bonded particles are more spherical and the gaps between the particles are fewer and smaller. As shown in Figure 7.5d, particles were bonded tightly and nearly no gap between them, implying good bonding of particles and low porosity.
Figure 7.5 SEM micrographs of the top surfaces of as-sprayed coatings under the gas temperatures of (a) 100 °C, (b) 200 °C, (c) 400 °C and (d) 600 °C
Figure 7.6 SEM micrographs of the cross-sections of as-sprayed coatings under the gas temperature of (a) 100 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C

The morphologies of the cross-sections of as-sprayed coatings are shown in Figure 7.6. As shown in Figure 7.6a, the coating with the thickness of 100 µm is not well bonded with the substrate. Under the gas temperature higher than 200 °C, the coatings with the thickness more than 500 µm were obtained. In addition, the porosity is decreased with the increasing temperature. Nearly no obvious pore is observed in the coating sprayed under the gas temperature of 600 °C.

EBSD maps of the as-sprayed coatings produced in the gas temperatures of 200 °C and 600 °C (i.e. Samples 2 and 4) are shown in Figure 7.7. Inverse pole figure maps with grain boundaries (Figures 7.7a and 7.7b) indicate Sample 4 has less low angle boundaries than Sample 2. Image quality (IQ) maps (Figures 7.7c and 7.7d) exhibit Sample 4 has more high IQ regions (bright area) than Sample 2, implying there are more strain/defect free grains in Sample 4. These phenomena indicate that higher fraction of recrystallization could occur in Sample 4. To further confirm this, Kernel Average Misorientation (KAM) maps are used to illustrate fully recrystallized grains with low KAM value areas (blue regions). It is obvious to see more grains are fully recrystallized in Sample 4, as shown in Figure 7.7e and 7.7f. Large magnification of a region in Sample 2 (Fig. 7.8 in appendix) shows a obvious microstructure of partial recrystallization: deformed regions (e.g. the boxed area) have low IQ value and high KAM value, i.e. high strain and defect density, and grain size in the range of sub-microns; recrystallized regions showing high IQ value and low KAM value, i.e. low strain and defect density,
and micron-sized grains with annealing twins. The average grain size and recrystallization fraction measured by EBSD are illustrated in Figure 7.9 in appendix. So, the coating produced in higher gas temperature has more recrystallization, which can be used to explain the decreased microhardness in higher gas temperature. The recrystallization phenomenon in the as-sprayed coatings may be due to the thermal energy caused by the high-energy impact or/and the particle temperature higher than the recrystallization temperature of copper.

Figure 7.7 EBSD IPF (a, b), IQ (c, d), KAM (e, f) maps of Sample 2: (a) (c) (e) and Sample 4: (b) (d) (f).
Our later TEM results show there are more complex structures in the cold sprayed coatings produced in different temperatures. In sample 2, 3 and 4, a large number of deformation bands and nanometer-sized deformation twins can be observed, as shown in Figures 7.10 and 7.11, respectively. In sample 1, a large fraction of nanometer-sized grains can be found, as shown in Figure 7.12. Those structures could be formed due to different strains, strain rates, and temperatures in the local regions of particle during high impact. Generally, lower gas temperature induces lower particle velocity and low surface temperature, leading to low deposition efficiency, which makes more peening effect on the coating, and more grain refinement, as illustrated in Figure 7.13a. However, high gas temperature makes higher particle velocity and higher surface temperature, causing high deposition efficiency and more recrystallization, as illustrated in Figure 7.13b. More theoretical and experimental work is needed to explain the mechanisms of the formation of different structures in cold sprayed coatings.

7.4 Conclusions

In the cold spray process, gas temperature plays an important role in the microstructure and properties of the as-sprayed copper coatings. The deposition efficiency is increased in higher gas temperature and reaches the limit when the gas temperature is over 400 °C. The porosity is decreased with increasing gas temperature and can be as low as 0.1% under the gas temperature of 600 °C. The microhardness does not change when the gas temperature is in the range of 200-400 °C but decreased at the temperature of 600 °C, which can be explained by the recrystallization that occurs in the cold spray process. In addition, nanometer-sized twins and grains can be found in cold sprayed copper, which could be attributed to the high strain, high strain-rate deformation in the cold spray process.
7.5 Appendix

Figure 7.8. EBSD characterization of the as-sprayed coating (gas temperature 200 °C): (a) IPF map, (b) IQ maps, (c) KAM map and (d) twin boundary maps

Figure 7.9. (a) Average grain size and (b) recrystallization fraction measured by EBSD software
Figure 7.10 Low angle boundaries and deformation bands are observed in copper sample produced in the gas temperature of 600 °C.

Figure 7.11 Deformation twins observed in the sample produced in the gas temperature of 200 °C and 400 °C.
Figure 7.12 Nano-sized grains observed in the copper sample produced in the gas temperature of 100 °C.

Figure 7.13 (a) More strain, grain refinement, low DE (%), and low surface temperature induced by low gas temperature (b) Less grain refinement, more recrystallization, high DE (%) and high surface temperature induced by high gas temperature
Chapter 8 The Role of Annealing in the Microstructural Transformation and Mechanical Properties of Cold Sprayed Nickel Coatings

In the previous four chapters, the microstructure of as-sprayed coatings was studied. In this chapter, the role of post processing heat treatment on cold sprayed nickel coatings is investigated. The results show the microstructure of the nickel coatings became uniform and the hardness was much reduced after annealing in 400 °C for one hour due to recrystallization. Continuous recrystallization, as opposed to nucleation and growth or discontinuous recrystallization occurred in the cold sprayed nickel coating during annealing.

8.1 Introduction

Cold spray is a technique used to build up layers by spraying metal powders onto a substrate at relatively low temperatures [2, 3, 99], without thermal problems associated with well known thermal spray technologies. However, metal powders are heavily work hardened after spraying [2, 100], which leads to very brittle material with high hardness and low ductility. Moreover, the microstructure of as-sprayed powder particles is non-uniform due to different strains and strain rates between the particle interface and particle centre [2]. This inhomogeneous microstructure would leave more mechanical residual stresses in the particle bonding interface and reduce mechanical properties in its application.

Figure 8.1 Schematic diagram of the cold spray system
Post processing heat treatment is an obvious approach to homogenize the deformed microstructure and release the residual stresses. Some publications [85, 101, 102] show substructure was removed through recovery and recrystallization by grain boundary migration and the ductility was significantly improved by annealing. Although some researchers [69, 70] discussed about the recrystallization mechanism of the bulk metals after large strain deformation, the recrystallization mechanism of the metal powder particles under high strain deformation is still not understood well. In this paper, EBSD was first systematically used to characterize the microstructure of as-sprayed and annealed coatings.

8.2 Experimental

Nickel coatings were fabricated by the cold spray system of Kinetiks 3000 CGT Technologies (Figure 8.1) using commercially available gas-atomized nickel powder, as shown in Figure 8.2. Gas pressure was 30 bar and gas temperature was 600 °C in the present study. The nozzle stand-off distance was kept constant at 4 cm while the powder feed rate was 20 g/min and the traverse speed was 330 mm/s. As-sprayed coatings were annealed in inert gas for one hour in different temperatures of 200, 400 and 600 °C. Vickers-hardness tests were carried out on both as-sprayed and annealed coatings.

![Figure 8.2](image_url)

(a) (b)

Figure 8.2. Morphology of nickel powder (a) and particle size distribution (b)

The morphology of nickel powder and coatings were characterized by Philips XL30 FEG-SEM. The microstructure, stresses distribution and micro-texture of the
powdered particles, as-sprayed coatings and annealed coatings were characterized using high resolution EBSD in the FEG-SEM instrument, fitted with TSL system. In data acquisition procedure, the scanning step sizes were between 0.05-1 µm depending on the magnification, and the EBSD data were subsequently analyzed by TSL OIM ANALYSIS 4 software. In all the EBSD maps, boundaries with misorientations between 2° and 15° were defined as low angle grain boundaries (LAGB), depicted as white lines, and those misorientations larger than 15° as high angle grain boundaries (HAGB), depicted as black lines. In the inverse pole figure (IPF) maps presented in this paper, the grains are colored according to orientation, with blue, red and green levels proportional to the three Euler angles. The image quality (IQ) maps are constructed by the quality of an electron backscatter diffraction pattern during beam scanning. It should be noted that in all the EBSD experiments all the samples were prepared by the same procedure and the settings of hardware and software were kept constant.

8.3 Results and Discussion

Figure 8.3a shows the SEM micrograph and EBSD map of the cross-section of nickel powder particles. In the EBSD map, various colors indicate different grains. As shown in Figure 8.3a, grains in the nickel particle are nearly equiaxed. Figure 8.3b shows the morphology of as-sprayed coating surface, in which highly deformed nickel powder particles can be easily observed.

Figure 8.3 (a) SEM micrograph (left) and EBSD map (right) of the cross-section of nickel particles, (b) SEM micrograph of the surface of as-sprayed coating
Figure 8.4a shows EBSD IPF map of the cross-section of as-sprayed nickel coating, in which various colors indicate different crystal orientation. In this map, elongated grains, subgrains and sub-micron grains can be easily observed in different regions of the particles, indicating non-uniform microstructure after spraying.

Figure 8.4b shows the IQ map of the cross-section of the same region as Figure 8.4a. In the IQ map, lower IQ value was shown in darker color, indicating higher crystal strain; higher IQ value was shown in brighter color, indicating lower crystal strain in this region. As shown in this figure, more strain is remained in the particle/particle bonding regions after spraying.

Figures 8.5a and 8.5b are the IPF map and IQ map of the coating annealed in 400 °C for one hour, and Figures 8.5c and 8.5d are larger magnification of the same coating. It is found that grain size is significantly decreased, and HABs and LABs are almost uniformly distributed. So the microstructure became more uniform after annealing in 400 °C for one hour. As shown in the IQ maps, there is no obvious dark region with low IQ value, which means the residual stresses in the particle bond interface are nearly released after annealing in 400 °C for one hour.

Figures 8.6a and 8.6b show the microstructure of cold sprayed coating annealed in 600 °C for one hour. As shown in Figure 8.6a, the microstructure becomes more uniform without sub-structures in the grains and the grain size is increased compared to the coating annealed in 400 °C for one hour. The IQ map of Figure 8.6b shows no obvious
particle bond interface can be observed and the residual stresses are nearly released after annealing at 600 °C for one hour.

Figure 8.5 IPF map (a) and IQ map (b) of the cross-section of cold spray nickel coating annealed in 400 °C for one hour, (c) and (d) are IPF map and IQ map in higher magnification

Figure 8.6 IPF map (a) and IQ map (b) of the cross-section of cold spray nickel coating annealed in 600 °C for one hour
Different from classic recrystallization, termed as recovery, nucleation and grain growth, a microstructure of fine grains consisting predominantly of high-angle grain boundaries is found. No recognizable “nucleation” of the recrystallized grains occurs, and the microstructure evolves homogeneously throughout the material, which process can reasonably be classified as continuous recrystallization [69]. Since this phenomenon normally occurs in materials after large strain deformation [69] and cold spray is a large strain deformation process at elevated temperatures [2], so the continuous recrystallization could caused by high dislocation density under large strain and high dislocation move ability at elevated temperature.

Figure 8.7 shows the morphologies of Vickers hardness indents on the as-sprayed coating and annealed coatings. As shown in Figure 8.7, many cracks can be easily observed on the edge of the indent, but the annealed coatings have relatively smooth indent edges without obvious cracks around. Although the hardness is decreased after annealing, the ductility and formability of cold sprayed coatings are significantly improved.

Figure 8.7  Morphologies of Vickers hardness indents of (a) as-sprayed coating, (b) coating annealed in 400 °C for one hour and (c) 600 °C for one hour

8.4 Conclusions

After annealing, the microstructure of cold sprayed nickel coating transforms to be uniform and the residual stresses in the particle bond interface are released. The ductility and formability are improved due to the annealing processing. Continuous recrystallization after large strain deformation could occur in the annealing process, followed by normal grain growth.
Chapter 9 Conclusions and Future Work

9.1 Conclusions

- Cold sprayed nickel coating (gas temperature: 600 °C, gas pressure: 30 bar) shows non-uniform microstructure with ultrafine grains in the size range of 100-200 nm in the particle/particle bonding region, and the micro-sized grains in the particle interior regions. Formation of these ultrafine grains is attributed to the dynamic recrystallization produced by subgrain rotation. The hardness in the vicinity of nickel particle interfaces can be about 1.5 GPa higher in hardness than the hardness in the particle interiors.

- Cold sprayed copper coating (gas temperature: 600 °C, gas pressure: 30 bar) shows more uniform microstructure than the nickel coating. The grain size is in the scale of microns and annealing twins are revealed. Due to lower activation energy for recrystallization, the cold sprayed copper coating shows the microstructure that can be characterized as of static recrystallization and has more homogenous hardness distribution.

- Cold sprayed aluminum coating (gas temperature: 250 °C, gas pressure: 35 bar) shows non-uniform microstructure with the grains in the size range of 10-60 nm in the particle/particle bonding region, and the micro-sized grains in the particle interior regions. The Perturbations in the form of roll-ups and bulges were observed in the particle/particle bonding region using TEM. This morphology could be induced by the adiabatic shear instabilities at the impact interfaces and lead to strongly interlocked particles.

- In the cold spray process, gas temperature plays an important role in the microstructure and properties of the as-sprayed copper coatings. The deposition efficiency is increased in higher gas temperature and reaches the limit when the gas temperature is over 400 °C. The porosity is decreased with increasing gas temperature and can be as low as 0.1 % under the gas temperature of 600 °C. The microhardness does not change when the gas temperature is in the range of 200-400 °C but decreased at the temperature of 600 °C, which can be explained by the
recrystallization that occurs during cold spraying. In addition, nanometer-sized twins and grains can be found in cold sprayed copper, which could be attributed to the high strain, high strain-rate deformation in the cold spray process.

- After post processing heat treatment, the microstructure of cold sprayed nickel coating transforms to be more uniform, and the residual stresses in the particle bond interface are released. The ductility and formability are improved. Continuous recrystallization after large strain deformation occurs in the annealing process, followed by normal grain growth.

9.2 Future Work

- Systematic comparison of differences between deformation mechanisms in cold spray and other thermo-mechanical process processes.

- Comparing microstructural evolution between FCC metals (copper, aluminum and nickel), BCC metals (steel) and HCP metals (alpha-titanium).

- Optimization of the processing parameters (i.e. powder characteristics, gas temperature, gas pressure, substrate temperature and post treatment procedures) to decrease porosity and improve mechanical properties.

- Finite element analysis of the effect of strain, strain rate and temperature on the deformation behaviors of metal powder particles to obtain better equation for critical velocity; molecule dynamic (MD) simulation of dislocation activities during impact, such as interaction and migration of dislocations.
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