INFLUENCE OF PRE-PROCESS WORK HARDENING OF NICKEL ENCAPSULATED HEXAGONAL BORON NITRIDE POWDERS ON COLD SPRAY COATINGS

A Dissertation in

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by

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Unlike conventional coating methods typically performed at high temperatures, cold spray is a low temperature process to apply coatings on different surfaces. This method introduces a unique opportunity to deposit materials that are sensitive to high temperatures, such as self-lubricating coatings. Current research studies on cold spray coatings focus primarily on the deposition of pure metal or metallic alloy particles. In this study, the performance of composite self-lubricating particles of Hexagonal-Boron-Nitride encapsulated with nickel (hBN-Ni), and deposited onto aluminum 6061 substrates was examined. Such coated substrates showed great improvement in wear resistance and reduction of surface friction. Moreover, unexpectedly high bond strength was achieved, which was close to that of standard high strength epoxies. The exact reason for this high bond strength was not understood at the beginning. Based on the present findings, and comparing to cold sprayed layers of composite nickel-nickel (nickel particles encapsulated with nickel; Ni-Ni), a hypothesis for the bonding mechanism of hBN-Ni particles to aluminum was developed. This hypothesis relates the high bond strength between the coating and substrate to the initial ductility and work hardening of the particles through plastic deformation during cold spray. To prove the hypothesis, a set of parametric studies was performed in which the initial hardness of hBN-Ni particles before coating was changed by ball milling, through work hardening of the nickel encapsulation, as well as reducing the amount of air pockets that were introduced in the particle agglomerates during nickel encapsulation. For this, hBN-Ni powder was low- and high-energy ball milled at different durations. The resulting materials were cold sprayed onto aluminum
6061 substrates using nitrogen and helium as carrier gas. The test results showed that, by increasing the initial hardness of the milled particles, the coating thickness was reduced. Image analysis of coating layer cross sections indicates that unaltered particles were flattened more than the milled ones. That is, the aspect ratio of particles in sprayed layers was reduced when the milling time was increased. Furthermore, larger amounts of pores and segregations resulted between the particles in the coating layers. When bond strength tests were performed for the samples coated with unaltered particles, failure mostly occurred at the interface between the coating and aluminum 6061 (adhesion failure). However, for coated samples with milled particles, bonds failed within the coating layers (cohesion failure). Examining the hardness of the coating layers, perpendicular to the sample’s cross sections, showed that unaltered particles were generally more hardened than milled particles, as a result of plastic deformation during cold spray. These results indicated that increasing the initial hardness with ball milling reduced the deformability of the particles, which in turn, resulted in poor interlocking between the particles in the coating layers.
# TABLE OF CONTENTS

- LIST OF FIGURES ix
- LIST OF TABLES xv
- Acknowledgement xvi

Chapter 1 Introduction 1

1.1 Background 1

1.2 Problem Statement 3

1.3 Objectives 4

1.4 Scope 4

1.5 Dissertation Outline 4

Chapter 2 Literature Review and Background 6

2.1 High Velocity Particle Consolidation Method 6

2.2 Interaction of Particles with the Substrates 8

2.3 Parameters Affecting Coating Bond Strength in Cold Spray 11

2.4 Self-lubricating Coating 17

2.5 Summary 18

Chapter 3 Equipment and Experimental Procedures 19

3.1 Introduction 19

3.2 Preparation of Encapsulated Hexagonal Boron Nitride with Nickel 19

3.2.1 Hexagonal Boron Nitride and Chemicals for Nickel Deposition 19
3.2.2 Encapsulated Powder Preparation

3.3 Testing Devices
   3.3.1 Weight and pH Measurements
   3.3.2 Particle Size Analysis
   3.3.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)
   3.3.4 Grinder and Polisher
   3.3.5 Focused Ion Beam (FIB)
   3.3.6 BET Surface Area Measurement
   3.3.7 Pycnometer Density Measurement
   3.3.8 Micro Hardness Measurement
   3.3.9 X-Ray Diffraction

3.4 Ball Milling

3.5 Cold Spray

3.6 Wear Resistance and Coefficient of Friction

3.7 Bonding Test

3.8 Image Analysis

3.9 Summary

Chapter 4 Development and Optimization of Self-lubricating Coatings

4.1 Introduction

4.2 Initial Study
   4.2.1 Encapsulation of hBN with Nickel (hBN-Ni)
   4.2.2 Application of Coating
4.2.3 Evaluation of Coated Surface

4.2.4 Encapsulating Nickel with Nickel (Ni-Ni)

4.2.5 Determining Crystallinity with XRD

4.3 Hypothesis

4.4 Summary

Chapter 5 Results and Discussion

5.1 Introduction

5.2 Case 1: Low- vs. High-Energy Ball Milling

  5.2.1 Scanning Electron Microscopy and EDS Results
  5.2.2 BET Surface Area Measurement
  5.2.3 Particle Size Analysis
  5.2.4 Hardness

5.3 Case 2: Duration of Ball Milling Particles with Low-Energy Method (LEM)

  5.3.1 Low-Energy Ball Milling for 1 and 24 Hours
  5.3.2 Low-Energy Ball Milling for other Intermediate Times
  5.3.3 Bond Strength
  5.3.4 Hardness in Coating Layers

5.4 Summary

Chapter 6 Conclusions and Recommendations

6.1 Summary and Conclusions

6.2 Salient Points

6.3 Recommendations for Future Studies
References 137

Appendix: Additional Tables 143
LIST OF FIGURES

Figure 1-1 Temperature ranges for various coating methods including cold spray (Sakaki et al. 2004, Wolfe et al. 2005) .............................................................................................................................................. 2

Figure 1-2 ARL cold spray facility at Penn State University .......................................................................................................................... 3

Figure 2-1 Schematic of cold spray system .................................................................................................................................................. 6

Figure 2-2 Impact simulation of two 5 µm size particles with 600 m/s impact velocity at 5, 10, and 15 ns after the initial contact of the first particle (Assadi et al. 2003) ................................................................. 12

Figure 2-3 SEM of surface morphologies (a-c) and cross sections (d-f) of individual nickel particle impact onto copper, aluminum 6061-T6 and SKH 51 steel substrates, respectively (Bae et al. 2008) .......................................................................................................................... 16

Figure 3-1 Pre-treatment and electroless nickel deposition process on hBN surfaces (Stark 2010) .......................................................... 20

Figure 3-2 Temperature at which reaction happened and nickel started to deposit on hBN ........................................................................ 23

Figure 3-3 Schematic of the structure of Horiba LA 950 (Horiba Company) .......................................................... 25

Figure 3-4 Schematics of low-energy (left) and high-energy (right) ball milling equipment .......................................................... 29

Figure 3-5 Cold Spray Equipment at ARL Facility ................................................................................................................................. 31

Figure 3-6 Aluminum 6061 substrate cold sprayed samples ........................................................................................................................... 32

Figure 3-7 Reciprocating wear test machine (ASTM International 2010) and the wear scar after the test (Stark 2010) .......................................................................................................................... 34

Figure 3-8 a) Uncoated slug; b) Cold sprayed slug; c) Bonded slugs .................................................................................................................. 35

Figure 4-1 hBN particles before encapsulation with nickel ......................................................................................................................... 38

Figure 4-2 Cross section of nickel encapsulated hBN particles .................................................................................................................. 39

Figure 4-3 SEM and optical microscope images of coating layer for coating aluminum 6061 samples (Stark 2010) ........................................................................................................................................... 40
Figure 4-4 Comparison of the coefficient of friction of pure nickel and hBN-Ni, Size of flat squares are 2.54 cm×2.54 cm (Stark 2010) ........................................................................................................ 41

Figure 4-5 (a) Wear of uncoated aluminum 6061 substrate; (b) wear of aluminum 6061 substrate coated with pure nickel; (c) wear of aluminum 6061 substrate coated with hBN-Ni. 43

Figure 4-6 Comparison of bond strength for self-lubricating coating hBN-Ni compared to pure nickel and epoxy (Stark 2010) .......................................................... 45

Figure 4-7 EDS image of pure nickel coating (Stark 2010) .......................................................... 46

Figure 4-8 EDS image of hBN-Ni coating (Stark 2010) .................................................................. 46

Figure 4-9 SEM image of Ni-Ni particles in different magnifications: (a) 2000x; (b) 5000x ... 47

Figure 4-10 SEM image of the cross section of a Ni-Ni particle ................................................ 48

Figure 4-11 EDS image of Ni-Ni coating .................................................................................. 48

Figure 4-12 Cross section of aluminum 6061 sample coated with Ni-Ni .................................. 49

Figure 4-13 EDS mapping of the cross section of a Ni-Ni cold sprayed coating .................. 50

Figure 4-14 XRD Spectra of as-received pure nickel .............................................................. 51

Figure 4-15 XRD Spectra of electroless deposited nickel ....................................................... 52

Figure 5-1 (a) SEM images of as-received hBN powders; (b) Encapsulated hBN-Ni clusters . 58

Figure 5-2 Agglomeration map .......................................................... 60

Figure 5-3 hBN-Ni Particles, a) Unaltered, b) Low-energy milled (LEM), c) High-energy milled (HEM) ........................................................................................................ 61

Figure 5-4 EDS pattern of unaltered hBN-Ni powder .............................................................. 63

Figure 5-5 EDS pattern of LEM milled hBN-Ni powder ........................................................... 63

Figure 5-6 EDS pattern of HEM milled hBN-Ni powder .......................................................... 64

Figure 5-7 Surface area per gram of the unaltered and the ball milled (low- and high-energy) powders 65
Figure 5-8 Particle size distribution of as-received hBN particles .................................................. 66
Figure 5-9 Particle size distribution for unaltered hBN-Ni powder .................................................. 67
Figure 5-10 Average particle size distribution for low-energy milled (LEM) hBN-Ni ............ 67
Figure 5-11 Average particle size distribution for high-energy milled (HEM) hBN-Ni ........... 68
Figure 5-12 Standard deviation for particle size distributions ......................................................... 68
Figure 5-13 Average hardness measurements for unaltered and milled hBN-Ni ................. 69
Figure 5-14 SEM image of 1 hour milled hBN-Ni particles ......................................................... 71
Figure 5-15 SEM image of 24 hour milled hBN-Ni particles ......................................................... 72
Figure 5-16 EDS pattern of 1 hour milled hBN-Ni powder ............................................................ 73
Figure 5-17 EDS pattern of 24 hour milled hBN-Ni powder ............................................................ 73
Figure 5-18 Surface area per grams of unaltered and milled powders for 1 and 24 hours ...... 74
Figure 5-19 Density of unaltered and milled powders for 1 and 24 hours ................................. 75
Figure 5-20 Average particle size distribution for 1 hour milled hBN-Ni ................................. 76
Figure 5-21 Average particle size distribution for 24 hour milled hBN-Ni ................................. 76
Figure 5-22 SEM image of cross section of aluminum 6061 substrate coated with 24 hour milled hBN-Ni powders ........................................................................................................... 78
Figure 5-23 Average particle size distribution for 2 hour milled hBN-Ni ................................. 79
Figure 5-24 Average particle size distribution for 3 hour milled hBN-Ni ................................. 79
Figure 5-25 Average particle size distribution for 4 hour milled hBN-Ni ................................. 80
Figure 5-26 Average particle size distribution for 5 hour milled hBN-Ni ................................. 80
Figure 5-27 Average particle size distribution for 6 hour milled hBN-Ni ................................. 81
Figure 5-28 Average particle size distribution for 12 hour milled hBN-Ni ............................... 81
Figure 5-29 Average particle sizes .............................................................................................. 82
Figure 5-30 Standard deviation for particle size distributions ................................................. 83
Figure 5-31 Average hardness measurements for unaltered and milled hBN-Ni particles .... 84
Figure 5-32 SEM image of 2 hour milled hBN-Ni particles .................................................. 85
Figure 5-33 EDS pattern of 2 hour milled hBN-Ni powder .................................................... 86
Figure 5-34 SEM image of cross section of aluminum 6061 substrate coated with unaltered hBN-Ni, with (a) nitrogen, and (b) helium .............................................................. 87
Figure 5-35 SEM image of cross section of aluminum 6061 substrate coated with 1 hour milled hBN-Ni, with (a) nitrogen, and (b) helium .............................................................. 88
Figure 5-36 SEM image of cross section of aluminum 6061 substrate coated with 2 hour milled hBN-Ni, with (a) nitrogen, and (b) helium .............................................................. 89
Figure 5-37 Comparison of the average thickness of cold spray layers ................................. 90
Figure 5-38 Impact velocities for hBN-Ni particles for cold spraying with nitrogen and helium 92
Figure 5-39 Bond slugs after bonding test for unaltered hBN-Ni after cold spraying with nitrogen 94
Figure 5-40 Bond slugs after bonding test for 1 hour milled hBN-Ni after cold spraying with nitrogen 95
Figure 5-41 Bond slugs after bonding test for 2 hour milled hBN-Ni after cold spraying with nitrogen 96
Figure 5-42 A close up view with SEM for cross section of aluminum 6061 substrate coated with unaltered hBN-Ni, with nitrogen .............................................................. 98
Figure 5-43 A close up view with SEM for cross section of aluminum 6061 substrate coated with 1 hour milled hBN-Ni, with nitrogen .............................................................. 98
Figure 5-44 A close up view with SEM for cross section of aluminum 6061 substrate coated with 2 hour milled hBN-Ni, with nitrogen .............................................................. 99
Figure 5-45 Bond strengths, cold spray with nitrogen .......................................................... 100
Figure 5-46 Comparison of particle size, average bond strength, and particle hardens for unaltered and milled hBN-Ni particles, cold sprayed with nitrogen........................................... 102
Figure 5-47 Comparison of average coating layer thickness, average bond strength, and particle hardens for unaltered and milled hBN-Ni particles, cold sprayed with nitrogen.................. 103
Figure 5-48 Optical microscopy image of unaltered hBN-Ni particles cold sprayed on aluminum 6061 substrate .................................................................................................................. 105
Figure 5-49 Superimposed image for the unaltered hBN-Ni particles and their circumscribing ellipses ................................................................. 105
Figure 5-50 Aspect ratio histogram of unaltered hBN-Ni particles ............................................. 106
Figure 5-51 Optical microscopy image of 1 hour milled hBN-Ni particles cold sprayed on aluminum 6061 substrate .................................................................................................................. 106
Figure 5-52 Superimposed images for the 1 hour milled hBN-Ni particles and their circumscribing ellipses .................................................................................................................. 107
Figure 5-53 Aspect ratio histogram of 1 hour milled hBN-Ni particles ......................................... 107
Figure 5-54 SEM image of 2 hour milled hBN-Ni particles cold sprayed on aluminum 6061 substrate ................................................................. 108
Figure 5-55 Superimposed images for the 2 hour milled hBN-Ni particles and their circumscribing ellipses .................................................................................................................. 108
Figure 5-56 Aspect ratio histogram for 2 hour milled hBN-Ni particles ....................................... 109
Figure 5-57 Area percentage porosity of coating layers with Nitrogen ........................................ 110
Figure 5-58 Bond slugs after bonding test for unaltered hBN-Ni after cold spraying with helium 111
Figure 5-59 Bond slugs after bonding test for 1 hour milled hBN-Ni after cold spraying with helium 112
Figure 5-60 Bond slugs after bonding test for 2 hour milled hBN-Ni after cold spraying with helium 113

Figure 5-61 Bond strengths, cold spray with helium .......................................................... 114

Figure 5-62 A close up view of cross section of aluminum 6061 substrate coated with unaltered hBN-Ni powders, with helium ........................................................................................................ 116

Figure 5-63 A close up view of cross section of aluminum 6061 substrate coated with 1 hour milled hBN-Ni with helium ........................................................................................................ 117

Figure 5-64 A close up view of cross section of aluminum 6061 substrate coated with 2 hour milled hBN-Ni with helium ........................................................................................................ 117

Figure 5-65 Area percentage porosity of coating layers with Helium ................................. 118

Figure 5-66 Average hardness measurements for cold spray layer of unaltered hBN-Ni, with nitrogen 120

Figure 5-67 Average hardness measurements for cold spray layer of 1 hour milled hBN-Ni, with nitrogen 120

Figure 5-68 Average hardness measurements for cold spray layer of 2 hour milled hBN-Ni, with nitrogen 121

Figure 5-69 Average hardness measurements for cold spray layer of unaltered hBN-Ni, with helium 123

Figure 5-70 Average hardness measurements for cold spray layer of 1 hour milled hBN-Ni, with helium 123

Figure 5-71 Average hardness measurements for cold spray layer of 2 hour milled hBN-Ni, with helium 124
LIST OF TABLES

Table 3-1 Composition of electroless nickel deposition bath in 1st step ........................................ 22
Table 3-2 Composition of electroless nickel deposition bath in 2nd step ......................................... 23
Table 3-3 Cold spray coating and condition ......................................................................................... 32
Table 4-1 Wear scar volume data for reciprocating wear tests ......................................................... 44
Table 4-2 Grain size (crystallinity) ....................................................................................................... 52
Table 5-1 Bond strengths, cold spray with nitrogen .......................................................................... 100
Table 5-2 Aspect ratio of the particles after coating aluminum 6061 substrate .............................. 104
Table 5-3 Bond strengths, cold spray with helium .............................................................................. 114
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my brothers, Majid and Masoud, and my sister, Mahdieh.

My great sources of dream, happiness and strength.
Chapter 1  Introduction

1.1  Background

Different types of coatings can be employed to improve the wear and fretting resistance of surfaces and to increase component durability and reduce maintenance costs. For applying coatings to surfaces, many techniques exist. Some of the most conventional techniques are: Arc Spray, Plasma Spray, and High Velocity Oxy Fuel (HVOF). Undesirably, high operating temperatures in all these processes can lead to melting, evaporation, gas release, crystallization, de-bonding and oxidation of the coating materials. Crystallization and gas release may preclude coatings from bonding to the surfaces. For self-lubricating coatings, such as hexagonal boron nitride (hBN), high temperatures may also destroy the lubricous phase. In addition, deleterious residual stresses are induced in the substrate material due to thermal gradients, mismatch in thermal expansion, and/or phase transformation, which are very likely to happen under high temperature conditions. Moreover, for a surface that is coated using conventional techniques, it cannot be repaired in-situ with another layer of coating if the surface is damaged (Papyrin et al. 2006, Kim et al. 2009, Wang et al. 2010).

In recent years, a new method of coating has been introduced known as cold spray. This method can be used in many of the situations where conventional coating techniques are not applicable because of the previously mentioned limitations. Figure 1-1 compares the working temperature for conventional thermal spray techniques to cold spray. Due to the low temperatures utilized in cold spray, the coating particles and the substrate undergo minimal microstructural changes (Kumar, et al. 2009, Yoon et al. 2011, Smid, et al. 2012). Therefore, different ductile particles, composites, polymers, and metal alloys such as copper, aluminum, nickel, and nickel alloys can be deposited via this process without losing their beneficial
properties. For instance, self-lubricating coatings, which are vulnerable at high temperatures, can be applied using cold spray.

Figure 1-1  Temperature ranges for various coating methods including cold spray (Sakaki et al. 2004, Wolfe et al. 2006)

Based on observations, there was a critical velocity ($v_{cr}$) where particles deform plastically after hitting the substrate, and then bond (Papyrin et al. 2006, Ning et al. 2007, King et al. 2009a). The equipment used for application of cold spray coating is shown in Figure 1-2. The whole deposition process occurs in a short period of time ($10^{-8}$ sec). In this research, the cold spray deposition method was used to apply a self-lubricating coating powder, which was composed of micro-scale lubricant particles of hexagonal boron nitride (hBN) encapsulated with a metallic matrix of nickel (hBN-Ni).
1.2 Problem Statement

In a recent study conducted by Stark (2010), self-lubricating coating particles of hBN-Ni, were used to coat aluminum 6061 substrates via cold spray. Results showed significant improvement in wear resistance and reduced surface friction. Coated samples also demonstrated unexpectedly high bond strength, which was much higher than bond strength of pure nickel coating on aluminum, and closed to that of high strength epoxies. However, the main reason for this high coating bond strength could not be explained based on the existing theories for bonding mechanism in cold spray coatings, which were developed primarily by investigating behavior of pure metal or metallic alloy particles. Understanding and explaining the reason for having such a good result for cold spray coating of the composite particles of hBN-Ni on the aluminum 6061 substrates was the principal focus of this study.
1.3 Objectives

The primary objective of this research was to identify the reason for the unexpectedly high bond strength and high performance of hBN-Ni coated substrates. One plausible theory was that this improved behavior was related to the initial ductility of the composite hBN-Ni particles, which makes it possible for the encapsulating nickel to deform plastically during cold spray and form a uniform and hardened coating layer on the substrate. Accordingly, this research aimed to examine the influence of the initial ductility of hBN-Ni particles on the performance of cold sprayed coatings. Once this is determined, it could be possible to better control cold spray deposition, to produce a more uniform coating and increase deposition efficiency, and also to improve the properties of the coating material, especially to further increase the bond strength between the coating and the substrate.

1.4 Scope

The influence of initial ductility of hBN-Ni particles was examined by changing these attributes through work hardening, using low- and high-energy ball milling for different durations. Size, density, and surface area of the milled particles were compared to those of unaltered particles. The particles were cold sprayed on aluminum 6061 samples using nitrogen and helium as the process or carrier gas. The coated samples were characterized in terms of coating layer thickness, hardness, and bond strength.

1.5 Dissertation Outline

This dissertation consists of six chapters with a major focus on results from laboratory experiments that were completed to fulfill the objectives of this study. Following this introductory chapter:
• Literature was reviewed pertaining to: cold spray deposition, interaction of particles with substrates in cold spray process, parameters affecting the bond strength between coating layers and substrates (Chapter 2).

• The equipment and the experimental procedures used in Chapter 4 and Chapter 5 for producing coating particles, ball milling, and characterization of the particles and coated surfaces in terms of hardness, density, porosity, material composition, friction and wear resistance, and bond strength were described (Chapter 3).

• An initial study was completed to investigate the bonding mechanism of coatings with aluminum 6061 substrates. Different coating powders were sprayed on aluminum 6061 and their performance was examined. Based on the result from these initial studies, a hypothesis was developed to explain the main reason for the high bond strength between hBN-Ni coating layer and the aluminum 6061 substrates (Chapter 4).

• A set of experimental parametric studies were completed to prove the hypothesis developed in Chapter 4. This was accomplished by varying some characteristic parameters (i.e. initial ductility and hardenability) of the hBN-Ni particles and examining the particles and the coated layer before and after cold spray coating, in terms of thickness, and bond strength (Chapter 5).

• All significant findings obtained from the studies in the previous chapters were summarized and recommendations for future research were provided (Chapter 6).
Chapter 2  Literature Review and Background

In this chapter, the background related to the cold spray coating method is addressed. Then, the mechanisms of the interaction of coating powders with different substrates are discussed. Finally, studies that investigated the influence of different physical and chemical properties of the coating powders on the performance are reviewed and the most important findings as they relate to the scope of work in the present study are summarized.

2.1  High Velocity Particle Consolidation Method

High Velocity Particle Consolidation or Cold Spray is a relatively new deposition method that can be used for coating various substrates, such as alloys, ceramics, and even plastics. In this method micron-sized solid phase particles, which are typically in the range of 1 to 50 μm diameter, are accelerated with a process or carrier gas and then sprayed at a velocity ranging between 300 to 1200 m/s through a converging diverging DeLaval type nozzle towards a substrate (see Figure 2-1) (Grujicic et al. 2004, Xiong et al. 2008).

Figure 2-1 Schematic of cold spray system
Helium (He), nitrogen (N₂), or mixtures of both, are commonly used as the process gas in cold spray. Often, the process gas is heated to a certain temperature prior to accelerating the particles in flight. This is done to achieve higher flow velocities for the process gas, and also to raise the temperature of particles before coating to improve coating efficiency by decreasing the critical velocity (Grujicic et al. 2004, Fukanuma and Huang 2009). The gas temperature remains below the particle and substrate melting point, and therefore, the powders are in solid state upon impact.

There is a critical velocity \( v_{cr} \) where particles deform plastically when they impact and bond to the surface of substrate or a previously deposited layer. It has been observed that the particles at impact velocities in the range of 300-1200 m/s deform plastically and then bond with the substrate (Xiong et al. 2008). In other words, the bond between the coating particles and the substrate occurs primarily due to the kinetic energy and ductility of the powder. The value of the critical velocity \( v_{cr} \) varies based on the adhesion–rebound energy of the particles, the particle size, and physical, mechanical, and thermo-mechanical properties of the particles. For instance, particles with higher yield strength and melting temperature have a higher critical velocity. However, by increasing the density and temperature of the particle, the critical velocity decreases. Experimental and computational studies by Assadi et al. (2003) showed that density and temperature have a larger effect on the critical velocity than the yield strength and melting temperature. They suggested the relationship in Equation (2-1) for calculating the critical velocity for different particles. Copper powder was used as the reference material for developing this equation. The equation was also validated based on experimental results for critical velocity of aluminum powder. It should be noted that this equation is only valid for small variations of involved parameters with respect to those of the reference material.
\[ v_{cr} = 667 - 14\rho + 0.08T_m + 0.1\sigma_u - 0.4T_i \]  \hspace{1cm} (2 - 1)

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

If the velocity of the particles is less than the critical velocity (\( v_{cr} \)), densification and abrasion of the substrate will occur. Given these complex factors, the most important challenge for the cold spray coating is how to form strong bonds between particles and substrate. Therefore, it is of high importance to improve the bonding by optimizing the coating process and material properties.

### 2.2 Interaction of Particles with the Substrates

This section addresses the studies that investigated the adhesion mechanism between the cold sprayed particles and substrate surfaces. There are generally two theories for adhesion mechanisms. First, Assadi et al. (2003) explained that the bonding between the particles and substrate is generated as a result of adiabatic shear instability (ASI) of the particles, which occurs at the particle-substrate or particle-particle interfaces at high velocities or under severe plastic deformation of the particles. That is, the high plastic strain of the particles at or above the critical velocity (\( v_{cr} \)) occurs in a very short period of time (50 ns), so that the produced heat cannot be dissipated (Schmidt et al. 2009) and this leads to softening under which the shear strength of the material falls to zero. The softening effect of adiabatic shear instability is dominant to the hardening effect at high strain rate deformation of the particles at the interfaces, and therefore results in bonding. The authors showed that for small particles at high speed, impact heat conduction was very slow when compared to what was predicted by the diffusive heat equation. Therefore, it was logical to assume that the process of bonding was adiabatic such that no heat transfer could occur. Accordingly, it was shown that more than 90%
of the kinetic energy of the in-flight particles was converted into heat energy in the impact zone, and this led to a strong bond between the particles and the substrate. Moreover, the study demonstrated that the adiabatic shear instability between the particles and the substrate always happened in the softer material (particles or substrate). Aside from formation of bonding, they showed that there were some other parameters in the coating process that could lead to rebounding of the particles after impacting on the substrate surface. For instance, when the contact time was insufficient the particles bounced back from the substrate rather than bonding to it. In addition, when the particles were sprayed onto the surface at an angle, the temperature increased at the contact zone due to the frictional dissipation. Moreover, the tangential component of particle’s momentum resulted in a tensile force at the contact zone. Although higher temperatures could facilitate the process of shear instability of the particles, the tangential tensile force was so large that it separated the bonded particle from the surface regardless of the existence of shear instability at the contact zone.

The second theory for the bonding mechanism in cold spray was developed by Wu et al. (2006). This theory is based on conversion of kinetic energy of the particles to adhesion energy at the impact zone. More specifically, Wu et al. (2006) believed that the particle shear instability and bonding were the result of the high kinetic energy of the particles rather than the elevated temperature at the impact zone in the adiabatic process. It was indicated that the cold spray coating had an elastic-plastic loading nature. This implies that if the kinetic energy is sufficient, the particles deform plastically and bonding forms. Moreover, the rebound phenomenon is inevitable because of the elastic unloading in this process. When the adhesion energy is greater than the rebound energy at the particle-surface interface, deposition can result.
Another important finding from Wu et al. (2006) was the relationship for the rebound energy, which is also known as the recoverable energy, shown in Equations 2-2 and 2-3.

\[ R_e = \frac{1}{2} e_r m_p v_p^2 \]  \hspace{1cm} (2 - 2)

\[ e_r = 11.47 \left( \frac{\sigma_y}{E^*} \right) \left( \frac{\rho_p v_p^2}{\sigma_y} \right)^{-1/4} \]  \hspace{1cm} (2 - 3)

where, \( \rho_p, v_p, e_r \) and \( m_p \) are the density, velocity of impacting particle, recoil coefficient, and molecular weight, respectively. Additionally, \( \sigma_y \) and \( E^* \) are the effective yield stress and conventional elastic modules of particle and substrate, respectively.

Other studies (e.g. Bae et al. 2010, Kumar et al. 2009) have demonstrated that the condition of both the particles and the substrates before and during the deposition process are important to form a strong bond. In fact, Bae et al. (2008) demonstrated that material instability happened as a result of strain rate hardening and thermal softening of the particles and substrate. They showed that contact temperature, area, and time had marked influence on the bonding mechanism and the generation of the adhesion energy in cold spray. Furthermore, the conditions of the particles before deposition such as size, shape, temperature, impact angle, and velocity affected the amount of plastic deformation in the particles. Among these factors, impact velocities could be adjusted by controlling the temperature and the pressure of the process gas (Richer et al. 2006, Ajdelsztajn et al. 2006). Although the impact velocity had an important effect on the plastic deformation and size of the contact area, properties of the particles and substrates and available kinetic energy played the main role in generating high contact stress and particle strain and strain rate in the deposition process.
2.3 Parameters Affecting Coating Bond Strength in Cold Spray

As explained in Chapter 1, one of the most important challenges of the cold spray method is to create strong bonding between the coating and the substrate. Different studies have addressed the influence of various parameters on the coating bond strength. The main criterion for having a successful bonding in explosive welding is the formation of a jet at the contact zone. In a similar fashion, it can be assumed that the formation of the jet at the interface in cold spray coating is a criterion for having successful bonding (Assadi et al. 2003). Figure 2-2 demonstrates a three-dimensional simulation of the impact zone of two particles with high velocity. As seen in this figure, a jet-type ring is formed along the contact zone of the particle-substrate. In addition, the jet-type ring of the second particle is formed because of impact on the zone that was covered with the first flattened particle. In other words, particle bonding in cold spray can be influenced by the surface morphology of the previous layer. King et al. (2009b) demonstrated that jetting in the particle can be suppressed by absorption of the impact energy through the deformation of substrates. The particles are, however, trapped inside the craters formed on the surface of the substrates at high velocities. This results in higher deposition efficiencies.
Figure 2-2 Impact simulation of two 5 µm size particles with 600 m/s impact velocity at 5, 10, and 15 ns after the initial contact of the first particle (Assadi et al. 2003)

Grujicic et al. 2004 completed a set of analytical studies, using nonlinear regression analysis method, and developed the relationships to compute gas flow velocity and particle’s impact velocity for different process gases and particles. They explained that helium as carrier gas has a better performance in cold spray coating than nitrogen due to lower molecular weight of this gas which results in higher impact velocities in the particles for the same gas temperature. They also indicated that for large and heavy particles the impact velocity is small,
because they are not sufficiently accelerated with the process gas. In addition, they showed that for very small and light particles (smaller than 2 µm) the impact velocity reduces with reducing the particle size. This was due to high deceleration that occurs for these particles within a stagnation bubble zone, which forms adjacent to the surface of substrate.

Champagne et al. (2007) conducted an analytical study to develop a simple analytical model that predicts the influence of particle’s impact velocity on the degree of flattening of the particles through cold spray, and also porosity of the resulting coating layer. They validated this model with experimental results based on cold spray coating of aluminum powders, with two different particle size ranges, on aluminum substrates. They showed that particles with smaller sizes attain larger impact velocities, and therefore become more flattened and produce a coating layer with smaller amount of pores.

In a later study, Champagne et al. (2010) investigated the influence of particles impact velocity on hardening of the particles through cold spray. They explained that cold spray increases the hardness of particles as a result of severe deformation during impact, and results in higher hardness values than what can be obtained using the conventional work hardening methods. By increasing the impact velocity of the particles, larger deformation and higher hardness values are resulted in the coated particles. An analytical model was developed in this study to predict hardness values of the coated particles as a function of impact velocity. The model was validated based on experimental results for cold spray coating of aluminum and copper powders on aluminum samples.

Kumar et al. (2009) indicated that surface adhesion was an important property for improving the bond strength in cold spray. The researchers showed that by mixing nano/microscale particles and increasing the mechanical interlocking, interfacial bonding could be
increased. Furthermore, the authors found that interfacial reactions depend on mechanical interlocking, metallic interaction, and physical adhesion between particles and substrates. In addition, it was reported by Kumar et al. (2009) that grit blasting of the surface before coating had a significant influence on hard substrates with soft particles, or vice versa. That is, grit blasting increased the deformation, deposition efficiency (the weight fraction of the deposited coatings over the total consumed powder), and flattening ratio of the particles (the ratio between the largest diameter of the deposited particle on the substrate to that of the particle with the same volume, before coating). Furthermore, Kumar et al. (2009) deposited copper particles on smooth and roughened aluminum 6061 substrates. Copper powders were sprayed on substrates with roughness values equal to half, same as, and twice the particle crest size. The best deformation was observed for the substrates with a roughness similar to the particle size. The authors also showed that the contact time could be extended by increasing the roughness. Moreover, experimental results showed that both contact area and time increased with impact velocity.

Yin et al. 2011 completed a set of numerical studies for copper particles cold sprayed on aluminum, nickel and stainless steel substrates. They showed that the hardness of the substrate has an important effect on the behavior and bonding mechanism of the incident copper particles. Higher compression ratio and larger deformation of the incident particles were achieved for harder substrates (stainless steel). For cold spray coating on soft substrates (e.g. aluminum) part of the kinetic energy of the particles was absorbed through plastic deformation of the substrate. This effect was more severe for smaller coating thicknesses. However, by increasing the thickness of the coatings, particles deformation became independent of the hardness of substrate. In addition the study explained that by increasing the impact velocity of
the copper (more than 900 m/s in this research) excessive deformation occurred in the substrate or the formed coating layer.

Similarly, Xiong et al. (2010) explained that roughening or grit blasting of substrates could result in a higher mechanical anchorage property, greater particle deformation, and stronger bonding compared to those with the smooth surface. With a rougher surface, higher strain values and temperatures were achieved and the initial deposition efficiency increased.

According to the physical and mechanical properties of the particles and substrates, there are four possible combinations of particle/substrate: hard/hard, soft/soft, soft/hard, and hard/soft. Bae et al. (2008) showed that during the deposition process, the primary kinetic energy of the in-flight particles was dissipated through plastic deformation of the soft matching part and frictional work of the particles and substrates. Part of the initial energy was also found to be stored as elastic strain energy in both impacting particles and substrates. The authors found that a high temperature (near the melting point) was created on the soft side (particle or substrate) due to the severe deformation of this zone, which led to forming a reliable metallurgical bonding. In another study by Bae et al. (2008), 35 µm pure nickel particles were used to coat three different substrates: copper, aluminum 6061-T6, and SKH 51 steel. Using these substrates, three different combinations were examined, which were denoted as: soft/soft, hard/soft, and soft/hard, according to the deformability of the nickel particles relative to the properties of the substrates (copper, aluminum and steel). Figure 2-3 shows Scanning Electron Microscopy (SEM) images for surface morphologies and cross sections of the individual nickel particle after impact onto the three substrates. In the first case, using Ni/Cu, comparable deformations occurred at the copper substrate and the particles, whereas in the second case, Ni/Al, slight deformation of the nickel particles and severe deformation of the aluminum
substrate was observed. In the last case, Ni/steel, severe plastic deformation of the nickel particles, without any deformation of the substrate, was observed. After testing, the deposition efficiency was measured using image analysis. Maximum value was found for the first case, with Ni/Cu, where both the nickel particles and the substrate underwent severe deformations.

Bae et al. (2010) examined the influence of different carrier gases such as helium and nitrogen on the bond strengths of pure nickel particles (26-44 µm size) on steel substrates. Results showed that the maximum bond strength was obtained when helium was used as the carrier gas. Using this gas, the bond strength was observed to be 85 MPa, which was close to that of standard high strength epoxies. This effect was most likely related to the higher impact velocity of the particles with helium.

The effects of particle shape and size on coating bond strength was examined by Bae et al. (2010). Three different nickel powders with primary size distributions of: $S_1=26-44$ µm, $S_2=37-52$ µm, and $S_3=52-74$ µm were examined for cold spray coating of steel substrates.
Results showed that $S_1$ coating, with smaller particle sizes, demonstrated better mechanical performance with a more uniformly flattened coating layer, higher bond strength, and greater deposition efficiency, compared to those for the other coatings with larger particle sizes. For $S_2$ poor coating properties were observed due to dynamic compressive and shear failure of the particles in cold spray deposition. For $S_3$ coating, although enhanced bonding was obtained as a result of higher “adiabacity” and highly localized temperature rise at the contact area, the deposition efficiency was low (70%), which means that this coating was not economical. Furthermore, Bae et al. (2010) revealed that coatings with coarser nickel particles had a higher porosity, whereas, fine nickel particles resulted in denser coatings.

### 2.4 Self-lubricating Coating

Application of self-lubricating coatings on different metallic substrates has been studied by many researchers. It has been generally shown that a thin lubricant film could largely protect the substrates from damage by significantly increasing wear resistance, and reducing surface friction (Weyant 2008, Stark et al. 2012). The following summarizes the studies that investigated application of self-lubricating coatings on different substrates, using cold spray.

Walia (2006), investigated application of a molybdenum disulfide (MoS$_2$) lubricant film on a turbine blade dovetail joints to increase their wear resistance. Given the fact that MoS$_2$ particles are vulnerable at high temperatures, cold spray was used for deposition. The thin lubricant film of MoS$_2$ increased wear resistance and significantly reduced the coefficient of friction of coated surfaces on the dovetail joints.

In a more recent study, Stark (2010) reported the performance of hexagonal boron nitride (hBN) lubricant coatings on aluminum 6061 substrates. This material was selected for its lubricious property at high pressures and temperatures. In spite of good lubricating
properties, bare hBN particles are considered a poor candidate for cold spray coating, since, due to their lubricious nature, they slide on the surface of the substrate rather than bonding to it. In order to achieve the deformation required and create a bond between the particles and the substrate, the hBN particles were encapsulated with nickel. The encapsulating nickel provided a ductile medium, which led to a metallurgical bond between the particles and the substrate. In general, the results from this study demonstrated promising attributes for the coating, with high bond strength between the coating and substrate, low friction, and high wear resistance.

2.5 Summary

Literature was reviewed in this chapter pertaining to: cold spray deposition, interaction of particles with substrates in cold spray process, parameters affecting the bond strength between coating layers and substrates.
Chapter 3  Equipment and Experimental Procedures

3.1  Introduction

In this chapter the testing equipment and procedures used for the experimental studies in Chapter 4 and Chapter 5, are addressed. The same testing equipment were used and the materials were ordered from the same manufacturers for all experiments to avoid any additional impact on the test results.

3.2  Preparation of Encapsulated Hexagonal Boron Nitride with Nickel

3.2.1  Hexagonal Boron Nitride and Chemicals for Nickel Deposition

Commercially available hexagonal Boron Nitride (hBN) powders were purchased from the Atlantic Equipment Engineers Company. The powders were characterized for shape and size distribution. Sodium citrate, nickel sulfate hexahydrate and sodium hypophosphate monohydrate were purchased from J. T. Baker, Alfa Aesar and Sigma Aldrich, respectively. Hydrochloric acid and ammonium hydroxide were ordered from BDH Chemicals. These materials were used to produce nickel encapsulated hexagonal boron nitride particles (hBN-Ni), based on the procedure adopted from the previous study by Stark (2010).

3.2.2  Encapsulated Powder Preparation

Commonly used encapsulation methods include vapor deposition, electroplating, and electroless plating. Hu et al. (2009), indicated that electroless plating demonstrated higher corrosion and wear resistance than the other encapsulation methods. In this method, catalytic metals are deposited onto encapsulated particles in a metal salt solution. This deposition method was used by Challahan (2011) to encapsulate aluminum particles with nickel. The success of deposition depends on different parameters such as the composition of the plating
bath, pH, temperature, and the compatibility of the depositing metal with the encapsulated particles (Sahoo 2009).

In the present study, electroless nickel plating was used to encapsulate micrometer-sized hexagonal boron nitride particles (approximately 7 µm in size). Figure 3-1 shows the main steps for the nickel encapsulation process.

![Figure 3-1](image)

**Figure 3-1 Pre-treatment and electroless nickel deposition process on hBN surfaces (Stark 2010)**

First, all debris on the surface of hBN powder was removed with a washing solution made of nitric acid to prevent interference with the deposition process. To do so, the powder was added to 70% nitric acid in a beaker, with a weight ratio of 5:1 for acid to powder, and stayed there for at least 30 minutes. After that, filtration was performed to remove the cleaned powder from the solution. The retained powder on the filter papers was rinsed three times with distilled water (dH₂O), and then placed in an oven for 12 hours, at approximately 80-90 °C, to dry.
Next, the surface of hBN particles was activated with tin chloride (SnCl₂) followed by palladium chloride (PdCl₂) solutions. For the first step, hBN powder was soaked in a 0.044 M tin (II) chloride and 0.12 M hydrochloric acid solution. In order to prepare the solution, 9.928 g of stannous chloride dehydrate was dissolved in approximately 500 ml dH₂O. Then, 40 ml of 3 M hydrochloric acid was added. The solution was diluted with additional dH₂O to a total volume of 1000 ml. In the second step, the tin-activated hBN powder was soaked in a solution of 5.6×10⁻⁴ M palladium and 0.12 M hydrochloric acid. The solution was prepared by dissolving 0.0993 g palladium (II) chloride in approximately 500 ml of dH₂O, and then adding 40 ml of 3 M hydrochloric acid. It was then diluted with dH₂O to a final volume of 1000 ml. Catalytic layers of tin and palladium ions on the surface of hBN particles provided sites for nickel deposition.

Before starting the process of nickel deposition, the surfaces of all glass wares used for this process were cleaned by a two-step standard solution method. In the first step, a basic solution (pH 11) was used to remove all organic contaminants. For this solution, five parts of distilled water were added to one part of ammonium hydroxide and hydrogen peroxide. The filled glass surfaces were heated up to 60-70 °C for about 15 minutes. Then, they were rinsed with distilled water at least three times. In the second step, an acidic solution (pH 7) was used to remove all metallic contaminants. For this solution, five parts of distilled water were added to one part of hydrochloric acid and hydrogen peroxide. The glass surfaces were heated up to 60-70 °C for about 15 minutes, and then were rinsed with distilled water at least three times.

Nickel deposition was completed in two steps. In the first step, a thin layer of nickel was deposited around the Sn-Pd-activated hBN particles. For this step, following Baudrand and Bengston (1995), nickel sulfate was used as a source for nickel ions, and sodium hypophosphite
was used as a reducing agent to provide sufficient electrons for the reaction. Ammonium was used as a complexing agent to produce a complex with nickel and preclude extra free nickel ion concentration. It also stabilized the solution by acting as a pH buffer. Sodium citrate was also used to play the role of stabilizer, to prevent unwanted homogeneous reactions that could cause subsequent decomposition of the nickel solution (Jappes et al. 2005). A 2500 ml solution was produced by adding these salts and distilled water to an Erlenmeyer flask, with the solution composition shown in Table 3-1. The Erlenmeyer flask was then placed in an ultrasonic bath. After everything was well dissolved, 0.1 g of hBN powder was added to the solution and stirred. Sonication was started simultaneously with setting the stirrer. An Immersion heater increased the temperature of the bath and helped start the reaction. As the solution heated up, the temperature was recorded every 10 minutes (see Figure 3-2). The reaction occurred at 58 °C. The solution turned dark green and started bubbling when it was reacting.

Table 3-1 Composition of electroless nickel deposition bath in 1st step

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>H₂O</td>
<td>2500mL</td>
</tr>
<tr>
<td>Sodium Citrate</td>
<td>C₆H₇NaO₇</td>
<td>141.1g</td>
</tr>
<tr>
<td>Nickel Sulfate Hexahydrate</td>
<td>NiSO₄·6H₂O</td>
<td>126.3g</td>
</tr>
<tr>
<td>Sodium Hypophosphate Monohydrate</td>
<td>NaPO₂H₂·H₂O</td>
<td>126.8g</td>
</tr>
<tr>
<td>Ammonium Hydroxide</td>
<td>NH₄OH</td>
<td>55mL</td>
</tr>
</tbody>
</table>
The second step of nickel deposition was completed to increase the thickness of the encapsulation layer around hBN particles. For this step, a 400 ml solution was prepared with the composition shown in Table 3-2. This solution was added to the Erlenmeyer in volumes of 100 ml at 10 minute intervals. After the completion of the reaction in the second step, the ultrasonic unit heater and the immersion heater were turned off. The solution remained in the bath for 12 hours at 25-27 °C. Then, the solution was filtered using Pall Corporation filter papers (with less than 0.2 µm pores) and then placed in the oven for 12 hours at 80-90 °C to dry. The weight of the resulting powder after drying was between 38-42 g, which included 1.0 wt% hBN.

Table 3-2 Composition of electroless nickel deposition bath in 2nd step

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>H₂O</td>
<td>400mL</td>
</tr>
<tr>
<td>Nickel Sulfate Hexahydrate</td>
<td>NiSO₄·6H₂O</td>
<td>126.3g</td>
</tr>
<tr>
<td>Sodium Hypophosphate Monohydrate</td>
<td>NaPO₂H₂·H₂O</td>
<td>126.8g</td>
</tr>
<tr>
<td>Ammonium Hydroxide</td>
<td>NH₄OH</td>
<td>95mL</td>
</tr>
</tbody>
</table>
3.3 Testing Devices

3.3.1 Weight and pH Measurements

The weight of chemicals of more than 5 grams was measured on a Mettler Toledo PB 303 digital scale (0.02-310g). Chemicals of less than 5 grams were weighed on a Mettler AE200 digital scale (0.0001-200.0000g). BDH-35312.607 pH strip indicators were used to measure the pH of the solutions used in the electroless nickel plating process.

3.3.2 Particle Size Analysis

In order to measure the size of the particles before and after milling, the Horiba LA-950 laser diffraction particle size analyzer was used (Figure 3-3). Using this system, the particle size distribution was determined based on the scattering of light by powders dispersed in a fluid medium. Isopropanol was used as a dispersant and a droplet of soap was used as a surfactant. Helium and neon lasers and a tungsten lamp were used to brighten the particles dispersed in the fluid medium.

The data was analyzed and the average particle size distribution for each sample was obtained. The device and the procedure used in this study were suitable for measuring particle sizes in the range of 10 nanometers to 30 millimeters.
3.3.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)

In order to study the surface morphology and microstructure of the particles and the coating layers, a scanning electron microscope (FEI Quanta 200 Environmental SEM) with a resolution of 10 nm was used. Using this system, SEM images were obtained through the interaction of electrons with the surface of samples.

An energy dispersive X-ray spectroscopy (EDS) detector (manufactured by Oxford Instruments) was used to characterize particles in terms of material composition. The device was composed of a silicon-lithium detector with a 10 mm area.

3.3.4 Grinder and Polisher

Grinding and polishing were performed on samples before SEM and hardness tests occurred. The grinder was composed of power-driven wheels covered with silicon carbide
paper disks (240, 320, 400, 600, 800, 1200 and 2400-grit abrasives). The grinding was performed under a load of 5-10 N. The surface of the specimens was cleaned in an ultrasonic bath between and after grinding steps to remove remaining materials. In addition, to remove the scratches that remained from grinding on the surface, diamond polishing was performed. This was done using a nylon cloth charged with 3μm diamond paste and an alcohol based lubricant, with both the platen and head rotating in the same direction under a load of 5-10 N. The last step was oxide polishing with 0.06 colloidal silica suspensions with a Struers MD-Chem pad for 2 minutes. During this step, the platen and head were rotating in opposite directions under a load of 5-10 N.

3.3.5 Focused Ion Beam (FIB)

A focused ion beam (FIB), equipped with a Quanta 200 3D Dual beam, was used to explore the surface and inside of the particles. In order to prepare the samples for analysis, a small amount of powder was placed on a disk of carbon tape. First, a layer of platinum was deposited on the surface of a single hBN-Ni particle via a gas injection system (GIS). Then the surface layer (platinum and nickel) was removed from that particle by adjusting the size and location of the focused beam to expose the particle’s hBN-Ni core.

3.3.6 BET Surface Area Measurement

A Coulter SA 3100 system was used in order to measure the surface area of the particles through a Brunauer-Emmett-Teller (BET) test based on the amount of nitrogen adsorbed by the surface.
3.3.7 **Pycnometer Density Measurement**

The density of the powders was determined with a Quanta Chrome Multi-Pycnometer, using a pycnometer density measurement technique. In this technique, a known quantity of helium flows from a known reference volume into a micro cell that contains a powder sample. The volume of the sample was obtained by measuring the pressure difference due to the gas displacement. Since helium can penetrate the finest pores between the particles, maximum accuracy was assured. The weight of the sample was measured on a Mettler AE 200 digital scale, and the density was calculated accordingly. This procedure was repeated for different samples 5 times from the same powder and the results were averaged. Note that prior to measuring the density of the powders, the machine was calibrated with stainless steel calibration balls with known volume and density.

3.3.8 **Micro Hardness Measurement**

Micro-hardness was measured as the resistance of the surface of samples to indentation. In this study, the hardness of the samples was determined based on the Vickers hardness testing method, using a Leco M-400-H Vickers Micro-hardness Indenter. This method is known to be more reliable than the other conventional hardness testing methods (e.g. Brinell and Rockwell tests). Since the indenter in the Vickers test penetrates close to two times deeper than the other test indenters, this method is less sensitive to surface conditions. The indentation was created on the surface of the samples by pressing the indenter against the surface under 1.96 N applied force. The diagonals in the scar were measured with the Leco Akashi Video Line Micrometer (VL-101) and averaged. The Vickers Hardness number (HV) was calculated by dividing applied force by the surface area of the indentation using Equation 3-1.
\[ HV = \frac{2P}{d^2 \sin \frac{\alpha}{2}} \]  

where, \( d \) is the average diagonal in millimeters, \( P \) is the applied load in gram force, and \( \alpha = 136^\circ \) \((\sin \frac{\alpha}{2} = 1854.4)\) is the angle between the faces of the indenter (Dowling 2007).

### 3.3.9 X-Ray Diffraction

X-ray diffraction (XRD) is a nondestructive method to measure the average spacing between layers or rows of atoms. Using this machine, it is possible to identify crystalline phases and orientation, and also to measure the size, shape and internal stress of small crystalline regions. In this study, Panalytical Empyrean XRD, using CuK\(_\alpha\) radiation source at 40 mA and 45 kV, was used to obtain XRD spectrum of as-received and generated powders. For this test, the scanning speed and scanning range of the machine were set at 0.02 and 5-70 degrees, respectively.

### 3.4 Ball Milling

Ball milling is conventionally used in the alloying process to create homogenous alloys. As explained in the previous chapter, the main objective of this study was to investigate the influence of initial ductility and potential hardenability of hBN-Ni particles on the bond strength between the particles and aluminum 6061 substrate after coating. Ball milling was primarily used to impart strain in the encapsulated particles and therefore to increase their initial hardness. It also helped break clusters or agglomerations of encapsulated particles before coating, to produce more uniform particle sizes. Low- and high-energy ball milling methods were used in this study. For the low-energy ball milling, a low-energy horizontal steel ball milling instrument (Paul O Abbe Inc., JRM model) was used. In this method, particles were placed in a PVC jar (cylinder with a different diameter and height). Then, grade 440 C stainless
Steel milling balls (with a 4.75 mm diameter and weight ratio of 1:3 for powder to balls) were added to the jar and milling was run at different speeds and times. Hardened steel balls were used to minimize contamination of the particles. In addition, the milling jars were filled with argon and sealed to avoid oxidation during milling. Figure 3-4 (left figure) shows the schematics of the low-energy ball milling equipment. As indicated, in this technique the PVC jar is rotated with two rollers.

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**Figure 3-4 Schematics of low-energy (left) and high-energy (right) ball milling equipment**

For high-energy ball milling, two-station planetary ball milling equipment (Fritsch Planetary Micro Mill Pluverisette 7) was used. Particles were placed in two steel jars (cylinders with a diameter of 4 cm and a height of 4 cm). Grade 440 C stainless steel milling balls (diameter 4.75 mm and weight ratio of 1:10 for powder to balls) were added to the jar and
milling was performed. Again, hardened steel balls were used and the milling jars were filled with argon and sealed to minimize contamination or oxidation of the particles during milling. Figure 3-4 (right figure) depicts the schematics of the high-energy ball milling equipment. As shown, in this technique the steel jars spin around their own axis, while they also rotate in a large cylinder (similar to the motion of planets around the sun).

3.5 Cold Spray

Cold spray coatings were completed at the Applied Research Laboratory (ARL) at the Pennsylvania State University. The cold spray unit is located in an acoustic room provided by the Industrial Acoustics Company (Figure 3-5). The unit is equipped with a ventilation system and an automated robotic arm (IRB2400), which is programmable and can move across the substrate during coating. The robotic arm operates at an offset distance of 1.27 cm from the substrate, with a horizontal spray step of 1 mm, and a vertical speed of 100 mm/second.

For the cold spray operation, substrates are fixed using a vise under the Sulzer Mecto Spray hood with a dust collection system. The cold spray system is equipped with a 153 mm tungsten carbide De-Laval type nozzle, which has a 3 mm throat for all trails. Nitrogen and helium were used as process or carrier gases. Because of low cost and relatively low reactivity of nitrogen, it is more commonly used for cold spray coating. However, due to its high density (1.2506 g/L) in some cases (i.e. for particles with large size and density), nitrogen cannot provide the driving force required for the inflight powder to reach the critical velocity. For those cases, helium (density = 0.1785 g/L) is used (Wong et al. 2010). Both carrier gases were used in this study for cold spray coating of unaltered, 1 and 24 hour milled particles, and their performances were compared. The gas is first heated to a specific temperature (up to 500°C). Coating powder is then poured in the heated cylindrical hopper. The hopper is fitted with a
Praxair feeder (Model 126HP powder) and can work at a pressure up to 3.45 MPa. Feed rate and wheel speed for the powder flow are controlled and adjusted with a data acquisition and control system. A 240-hole powder feed wheel at various powder feed rates is operated inside the hopper. In this study, aluminum 6061 was used as the substrate, with different shapes and sizes (see Figure 3-6). These included 2.54 cm×2.54 cm flat square samples with different thicknesses, and 2.54 cm diameter cylindrical bond slugs with a length of 3.8 cm. Table 3-3 shows the parameters used for cold spraying the different samples. Before coating, the samples were grit blasted using 16 grit alumina oxide at 0.86 MPa and a 45° angle, and then cleaned in an ultrasonic bath of ethanol for 30 minutes.

Figure 3-5 Cold Spray Equipment at ARL Facility
Flat Square
[2.54 cm×2.54 cm (1.0 in. ×1.0 in.)]

Cylindrical Bond Slug
[2.54 cm (1 in.) diameter]

Figure 3-6 Aluminum 6061 substrate cold sprayed samples

Table 3-3 Cold spray coating and condition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (cm)</th>
<th>Carrier Gas</th>
<th>Pressure of the Carrier Gas (MPa)</th>
<th>Temperature of the Carrier Gas (°C)</th>
<th>Number of Passes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat square aluminum 6061 substrate</td>
<td>2.54×2.54</td>
<td>N₂</td>
<td>2.41</td>
<td>480</td>
<td>5</td>
</tr>
<tr>
<td>Flat square aluminum 6061 substrate</td>
<td>2.54×2.54</td>
<td>He</td>
<td>2.06</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>Bond Slug</td>
<td>2.54 diameter</td>
<td>N₂</td>
<td>2.41</td>
<td>480</td>
<td>5</td>
</tr>
<tr>
<td>Bond Slug</td>
<td>2.54 diameter</td>
<td>He</td>
<td>2.06</td>
<td>200</td>
<td>5</td>
</tr>
</tbody>
</table>
3.6 **Wear Resistance and Coefficient of Friction**

Wear resistance and the coefficient of friction of coated samples were examined according to ASTM G133-05, *Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear* (ASTM 2010), using a reciprocating wear test machine (Plint High Frequency Friction Machine). The testing sample (2.54 cm×2.54 cm square sample) and 302 stainless steel balls (diameter: 7.95 mm) were first cleaned in an ultrasonic bath of acetone for 5 minutes. The sample was then fitted in a machine fixture and placed under an adjustable force transducer. An oscillating drive arm with the stainless steel ball was set to slide on the top of the surface of the sample. The normal force was set to 24 N and the oscillation frequency was adjusted to 5 Hz. The test continued for 17 minutes. Figure 3-7 shows a schematic view of the reciprocating wear test machine, and also a sample with the remaining scar from the wear test. The first three minutes of the test was considered as wear-in period, and were ignored. After that, the coefficient of friction was calculated for each second using Equation (3-2).

\[ \mu = \frac{F}{N} \]  

where, \( F \) is the measured force of friction and \( N \) is the applied load.

After the wear test, wear scars were evaluated using a Zygo 7300 Optical profilometer. This equipment provided the topography of the worn surfaces and measured the volume and depth of the scars.
3.7 Bonding Test

Bond strength between coating layers and aluminum substrates was measured, following ASTM C633-13, *Standard Test Method for Adhesion or Cohesion Strength of Thermal Spray Coatings* (ASTM 2013). For this test, cylindrical aluminum 6061 bond slugs with a diameter of 2.54 cm and a length of 3.8 cm were used. The surfaces of the bond slugs were first cleaned with ethanol in an ultrasonic bath, for about 5 minutes. Then, a coated slug was mated with an uncoated one by placing a sheet of Cytec Engineered Materials FM1000 adhesive film between the adjoining surfaces. Figure 3-8 shows uncoated and coated bond slug surfaces before and after bonding to each other with FM1000 film. The slugs remained connected to each other, using a fixture system with built-in spring elements to provide the required compression force to hold the bond slugs together (see Figure 3-8c). They were placed in an oven for 4 hours at 200°C. Then, the oven was shut off, and left to slowly cool down for 12 hours. The following day, the bond slugs were released from the fixture system. Bond
strength tests were performed using 584 Instron Tensile Machine with a displacement rate of 1.27 cm/min, at room temperature. An increasing tensile load was applied to the adjoining slugs, at the constant rate of 12.7 mm/sec, until the bond failed. The maximum tensile strength that caused bond failure was recorded. If the bond failed at the interface between the bond slug and the coating layer, the measurement represented the adhesive strength; otherwise, it reflected the cohesive strength of the coating.

![Figure 3-8](image)

*Figure 3-8 a) Uncoated slug; b) Cold sprayed slug; c) Bonded slugs*

### 3.8 Image Analysis

The coated aluminum 6061 samples were sectioned and mounted in resin to expose the cross section of the coating layer. The mounted samples were polished for the image analysis. ImageJ version 1.46r (2012) software was used to analyze the particles’ aspect ratios in the coating layer. The software recognized the boundaries of the coated particles and drew a circumscribing ellipse around each particle. The aspect ratios of the particles were then determined with ImageJ “analyze particles” command. This ratio was equal to \( \frac{d_1}{d_2} \) where \( d_1 \) and \( d_2 \) were the major and minor diameters of the ellipse, respectively.
3.9 Summary

In this chapter, the equipment and the experimental procedures used in Chapter 4 and Chapter 5 for producing coating particles, ball milling, and characterization of the particles and coated surfaces in terms of hardness, density, porosity, material composition, friction and wear resistance, and bond strength were described.
Chapter 4  Development and Optimization of Self-lubricating Coatings

4.1  Introduction

Self-lubricating coatings can be used on lightweight aluminum 6061 components to provide desirable properties for wear, friction, and therefore to extend the life-time and reduce maintenance. Conventional methods of coating (e.g. Arc Spray, Plasma Spray, and High Velocity Oxy Fuel) are done at higher temperatures which may destroy the lubricous phase. One possible solution for application of self-lubricating coating is the cold spray, given its relatively low temperature requirements.

As explained in Chapter 1, an important issue with respect to the use of cold spray to apply self-lubricating coatings is the bond strength among the coated particles, and also between the coating layer and the substrate. Therefore it is of great interest to find an optimized technique for cold spraying of self-lubricating materials on aluminum 6061 substrates to form strong bonding.

4.2  Initial Study

The cold spray coating method used in an initial study, was adopted from Stark (2010) to coat aluminum 6061 substrates, with a self-lubricating coating material composed of hexagonal Boron Nitride particles encapsulated with nickel (hBN-Ni). This coating was a composite material in which hBN particles play the role of lubricant and nickel is the matrix that forms the bonding between the composite particles and the substrate. Nickel was selected for the matrix phase because it has a relatively high temperature capability, potential hardenability, and a demonstrated compatibility with aluminum 6061. It also results in coating layers with high corrosion and wear resistance due to its low oxygen content and low porosity.
(Marx et al. 2006, Raletz et al. 2004). A brief summary for procedures developed and the most important findings from that study is provided in the following sections.

4.2.1 Encapsulation of hBN with Nickel (hBN-Ni)

The hBN-Ni coating powder, with 1.0 wt% of hBN, was produced, following the two solution deposition method outlined in Section 3.2.2. SEM images for the hBN particles before encapsulation with nickel, and also the cross section of the particles after the encapsulation are shown in Figure 4-1 and Figure 4-2, respectively. When a sufficient amount of the coating powder was generated, they were deposited on aluminum 6061 substrates via cold spray.

![Figure 4-1 hBN particles before encapsulation with nickel](image-url)
4.2.2 Application of Coating

Three different procedures were considered in the initial study for coating the aluminum 6061 substrates. In the first case, the samples were coated with a single, 508 microns thick layer of hexagonal boron nitride encapsulated with nickel (hBN-Ni). To examine the influence of hexagonal boron nitride (hBN) on coating performance for the second case, the samples were coated with a single layer of pure nickel. Finally, in the third case the samples were coated with two coating layers; pure nickel at the bottom and hBN-Ni at the top. Figure 4-3 shows SEM and optical microscope images of the three coating types. For all three cases, relatively uniform coating distributions were formed on the substrate surfaces.
4.2.3 Evaluation of Coated Surface

The coated samples were examined for mechanical and tribological properties, such as wear, coefficient of friction, bond strength, and micro-hardness. Friction and wear were examined quantitatively for different coated substrates using a reciprocating wear test machine, following the procedure explained in Section 3.6.
The wear test was continuously run for 17 minutes and the coefficient of friction (COF) for different coated samples was recorded. Figure 4-4 compares the COF’s of the samples coated with pure nickel and hBN-Ni. As indicated in this figure, the COF of the sample with pure nickel coating is approximately twice that of the sample coated with hBN-Ni. It should be noted that the COF values for the sample with two layers of coating (one layer of pure nickel as a bond-coat and hBN-Ni on top; not shown in Figure 4-4) were, as expected, close to those of the sample with single layer of hBN-Ni. The figure also illustrated the larger wear scar observed in the pure nickel coating.

![Figure 4-4 Comparison of the coefficient of friction of pure nickel and hBN-Ni, Size of flat squares are 2.54 cm×2.54 cm (Stark 2010)](image)

To examine the wear resistance of the samples with different coating types, the wear scars were evaluated using a profilometer. Figure 4-5 shows the depth profiles for uncoated aluminum 6061 samples and aluminum coated with single layers of either pure nickel or hBN-Ni. As shown in this figure the wear scar of the pure nickel coating was much deeper (maximum depth = 1000 µm) than the sample protected with hBN-Ni (maximum depth = 200 µm). In addition, Table 4-1 compares the wear volumes of the aluminum 6061 samples coated
with pure nickel and hBN-Ni against an uncoated aluminum 6061 sample which was considered as the base line. Again, the wear volume of the sample coated with hBN-Ni was much smaller than those in the other two samples. Therefore, the addition of hBN particles in the coating powder, aside from reducing friction by creating a self-lubricating surface, can significantly improve the surface wear resistance. Note that the wear volume of the sample coated with pure nickel in Table 4-1 was even larger than that for the uncoated aluminum 6061 sample. The reason for this can be explained considering the fact that pure nickel coating is very soft. Therefore the wear test created a deeper scar on the nickel coated sample, relative to the uncoated sample, by removing the entire coating layer and part of the substrate surface.
Figure 4-5 (a) Wear of uncoated aluminum 6061 substrate; (b) wear of aluminum 6061 substrate coated with pure nickel; (c) wear of aluminum 6061 substrate coated with hBN-Ni
Table 4-1 Wear scar volume data for reciprocating wear tests

<table>
<thead>
<tr>
<th>Material</th>
<th>Wear Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated aluminum 6061</td>
<td>13.91 mm$^3$</td>
</tr>
<tr>
<td>Aluminum 6061 substrate coated with pure nickel</td>
<td>23.8 mm$^3$</td>
</tr>
<tr>
<td>Aluminum 6061 substrate coated with hBN-Ni</td>
<td>2.13 mm$^3$</td>
</tr>
</tbody>
</table>

Bond strengths of the three different coatings were examined by performing adhesion tests using cylindrical slugs following the procedure explained in Section 3.7. Figure 4-6 compares the bond strength values of the three different coatings, all of which were used to coat aluminum 6061. As shown in this figure, the average bond strength for hBN-Ni coating was 71.67 MPa, which was approximately threefold greater than those of pure nickel (average strength = 21.91 MP), as well as, the two layers of pure nickel and hBN-Ni (average strength = 24.19 MP). It is also noteworthy that for the aluminum 6061 substrate which was coated with pure nickel, the bond failure was of the cohesive type. The results in Figure 4-6 indicate the bond strength of hBN-Ni was very close to the high-strength standard epoxy. It should be noted that the bond strength of hBN-Ni was not expected to be this high. In fact, due to the presence of hBN in the coating composition, the bond strength of this coating was expected to be less than that of pure nickel. However, the tests showed completely different results.
Figure 4-6 Comparison of bond strength for self-lubricating coating hBN-Ni compared to pure nickel and epoxy (Stark 2010)

Apparently the inclusion of hBN particles resulted in a clearly superior bond strength of the hBN-Ni coatings in comparison with pure nickel as explained in the previous paragraphs. This indicates that something in the nickel matrix and substrate interaction had changed either during encapsulation or deposition. In order to determine the underlying reasons, the coated surfaces were examined using Energy Dispersion X-ray Spectroscopy (EDS). Figure 4-7 and Figure 4-8 show the EDS images for pure nickel and hBN-Ni coatings. As can be observed in these two figures, the electroless encapsulation of hBN-Ni particles introduces an addition of phosphorus to the nickel matrix which is not found in pure nickel coatings. Therefore, the improved performance of hBN-Ni coating was initially thought to be due to existence of phosphorous in these coatings. To verify this, another study was completed in the following section to examine the influence of the additional phosphorus in the coating powder on the bond strength.
Figure 4-7 EDS image of pure nickel coating (Stark 2010)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.30</td>
<td>1.43</td>
</tr>
<tr>
<td>Fe</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>Ni</td>
<td>99.35</td>
<td>98.35</td>
</tr>
</tbody>
</table>

Figure 4-8 EDS image of hBN-Ni coating (Stark 2010)

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.98</td>
<td>3.29</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>7.71</td>
<td>13.35</td>
</tr>
<tr>
<td>Nickel</td>
<td>91.31</td>
<td>83.36</td>
</tr>
</tbody>
</table>
4.2.4 **Encapsulating Nickel with Nickel (Ni-Ni)**

The aforementioned procedures, originally used for the preparation of hBN-Ni powder in Section 4.2.1, were repeated to encapsulate pure nickel particles with nickel (Ni-Ni). This was done to find out whether or not the high bond strength was caused by the existence of phosphorous which was generated during electroless encapsulation. Figure 4-9 shows the SEM images of the Ni-Ni particles. In addition, Figure 4-10 shows the SEM image of the cross section of a Ni-Ni particle that was cut using Focused Ion Beam (FIB). No agglomeration of particles is detectable in these figures. The reason for this can be speculated to be the size or the surface roughness of the pure nickel particles, used as the core in the Ni-Ni powder. Note that these effects were not examined in this study.

![Figure 4-9 SEM image of Ni-Ni particles in different magnifications: (a) 2000x; (b) 5000x](image)
The Ni-Ni particles were sprayed on aluminum 6061 substrates and then the coated surfaces were evaluated. An EDS image for the Ni-Ni coating is shown in Figure 4-11. According to this figure, the coating exhibited more phosphorous in the composition as originally believed.
The SEM image for the cross section of the coated sample is shown in Figure 4-12. In addition, Figure 4-13 shows SEM images from a cross section of the Ni-Ni cold sprayed coating which was taken using the mapping method. This figure shows the cross sections of the nickel coating layer (upper left image), aluminum 6061 substrate (upper right image), phosphorus content of the coating layer (lower left image), and the cross section of the substrate with coating. It is evident that the Ni-Ni sprayed coating in comparison with pure nickel resulted in a non-uniform and porous layer. These results indicate that the coating with Ni-Ni particles was not as successful as had been originally hoped. The sample was barely coated, with only isolated lines of coating formed on the surface.

*Figure 4-12 Cross section of aluminum 6061 sample coated with Ni-Ni*
It should be noted that, the upper right corner image of Figure 4-13 shows existence of aluminum in the coating layer near the substrate interface. In fact, due to the high impact velocity of the Ni-Ni particles, viscous mixing between coating and substrate may have been occurred. Champagne et al. 2005 demonstrated this effect for cold spray coating of copper particles on aluminum 6061 substrate.

4.2.5 Determining Crystallinity with XRD

The XRD patterns of as-received pure nickel powder and nickel encapsulated on hBN particles are shown in Figure 4-14 and Figure 4-15. As observed, the XRD pattern in Figure 4-15 for electroless deposited nickel has a much wider peak than the pure nickel (Figure 4-14). Therefore, it can be concluded that electroless nickel is near amorphous and much softer than the as-received nickel, which has a crystalline microstructure.
Using these patterns the grain size (i.e. crystallinity) of the two coating powders were
determined based on Scherrer's equation (Equation 4-1), and the results are compared in
Table 4-2. It should be noted here that Scherrer's equation can analyze the crystallinity of
materials, with high accuracy, when grain size is in the range of 0.1 µm to 0.2 µm (Singh 2005).

\[
\beta = \frac{0.9 \lambda}{(t \cos \theta)} \tag{4 - 1}
\]

where, \( \lambda \) is the X-ray wavelength of copper (K\( \alpha \)=1.543 µm); \( t \) is the line broadening at half of
the maximum intensity in Figure 4-14 and Figure 4-15; and \( \theta \) is Bragg’s angle (22.35°).

*Figure 4-14 XRD Spectra of as-received pure nickel*
Based on the results shown in Table 4-2 the grain size of the electroless deposited nickel was estimated to be 1.5 orders of magnitude smaller than that of as-received nickel powders. Thus, it can be concluded that electroless nickel is near amorphous and much softer than the as-received nickel, which has a crystalline microstructure.

It can be inferred from these results that one possibility for the promising performance of hBN-Ni coating, contrary to the Ni-Ni coatings, on aluminum 6061 can be explained based on the initial ductility and potential hardenability of these coating powders. That is, nickel electroless-deposited on hBN particles was understood to be initially very soft (i.e. low initial
yield strength and stiffness), but had the potential to be hardened through the coating process. On the other hand, hBN particles were soft with a layered structure, and this let the deposited nickel and the composite particles have significant deformation before hardening. As a result of the significant deformation, the particles were able to retain their deformed shape even after impacting the substrate, due to the lack of elastic recovery. While the resulting cold sprayed layer retained its highly deformed state, it also had a relatively high density, stiffness, and strength as a consequence of the hardenability of nickel. On the other hand, for Ni-Ni particles the encapsulated nickel was shown to be initially hard, so the possibility of having significant plastic deformation and subsequently forming a strong bond upon impacting the substrate was relatively low. It is also believed that there was a rebound effect for the encapsulated nickel after impact, trying to regain the elastic deformation. This phenomenon is summarized in the form of a hypothesis in the following section.

4.3 Hypothesis

Encapsulation of hBN particles with nickel gives the composite powder an amorphous-like soft surface, with a ductile metallic skeleton, which results in high deformability of the particles, and subsequently high bond strength to the substrate, primarily due to work hardening of the encapsulating nickel during impact.

4.4 Summary

An initial study was completed in this chapter to investigate the bonding mechanism of cold sprayed coatings with aluminum 6061 substrates. Different coating powders were sprayed on aluminum 6061 and their performances were examined. Based on the result from these initial studies, a hypothesis was developed to explain the main reason for the high bond strength between hBN-Ni coating layer and the aluminum 6061 substrates. In order to prove
this hypothesis, the influence of the initial ductility and the hardenability of hBN particles encapsulated with nickel were examined by changing these attributes through ball milling at different energy levels and different durations. The findings from these studies are addressed in Chapter 5.
Chapter 5  Results and Discussion

5.1  Introduction

When aluminum 6061 substrates were coated with hBN-Ni, the results showed rather high bond strength. Initial studies completed in Chapter 4 indicated that the high bond strength may be related to the initial ductility of the particles and their potential work hardening through plastic deformation during cold spray. This is explained in the hypothesis in Section 4.3.

In order to prove the hypothesis, the influence of the initial ductility of hBN-Ni on bond strength of the coating were examined by changing the powders’ attributes through ball milling at different energy levels and various durations. Due to the plastic deformation of the particles during ball milling, the hardness of the particles increases. This increase in the initial hardness translates into a lower residual work hardening in the hBN-Ni particles, which is believed to influence bond formation between the encapsulated particles and the substrate. A reduction of initial ductility in the nickel matrix is expected to adversely affect the bond strength of cold sprayed layers.

In the ball milling process, structural refinement can be achieved by shearing and fracturing particles, followed by recrystallization. This process is referred to as “welding-fracturing-welding,” which results in a more uniform dispersion and smaller particle sizes (Weeber et al. 1988, Shen et al. 1995, Zhao et al. 2003, Sivasankaran et al. 2010). Having smaller sizes, the particles can gain larger impact velocities in the cold spray process and therefore, undergo a more significant plastic deformation resulting in better bonding to the substrate (Champagne et al. 2007, Bae et al. 2010). In other words, ball milling can have both a positive and negative influence on the particles’ properties and their potential to form a strong
bond with the substrate through cold spray. This influence was examined in the following sections in the form of two case studies.

5.2 Case 1: Low- vs. High-Energy Ball Milling

The objective was to determine an optimal method to increase the initial hardness of the hBN-Ni particles before coating. For this, low- and high-energy ball milling methods were examined. The results from this case study are discussed in the following. These results are also published by Neshastehriz et al. (2014).

It is important to mention that “classical” hardenability of ferrous metal components, such as steel, can be explained based on the capacity of these components to harden in depth under thermal quenching. To measure the hardenability of ferrous alloys, the Jominy test is conventionally used (Dobrzański et al. 1998). In this setup, a round metal bar is first heat treated to fully austenitize the structure. Then, the sample is placed on a rig in which one end of the bar is quenched with a water jet. The hardenability is determined by sectioning the sample and measuring the hardness at different distances from the surface. That is, for a sample with higher hardenability, hardness develops further away from the quenched area (Llewellyn and Hudd 1998, Marrow 2001). The hardenability in the present study, however, relates to the work hardening of the particles through cold spray.

hBN-Ni powders were produced in a multiple-step encapsulation procedure as described in Section 3.2. The resulting hBN-Ni particles were milled using low- and high-energy ball milling following the procedure explained in Section 3.4. For low-energy ball milling (LEM), 5 grams of powder and 15 grams of 0.5 cm stainless steel milling balls (weight ratio of 1:3) were added to a PVC jar (cylinder with a diameter of 3 cm and height of 4 cm) and
the milling was run for 15 min at 100 rpm. For high-energy ball milling (HEM), 5 grams of powder and 50 grams of 0.5 cm stainless steel balls (weight ratio of 1:10) were added to a steel jar (cylinder with diameter of 4 cm and height of 4 cm) and milled for 15 min at 500 rpm. The particles, before and after ball milling, were characterized by means of Scanning Electron Microscopy, Energy Dispersive X-ray spectroscopy, BET, and hardness testing. The results are presented in the following sections.

5.2.1 Scanning Electron Microscopy and EDS Results

5.2.1.1 Unaltered Particles

To compare the morphology of the particles before and after ball milling, SEM images were taken. The particles were sprinkled on carbon tape. Figure 5-1 (a) shows SEM images of hBN particles before encapsulation. Figure 5-1 (b) indicates hBN particles after encapsulation with nickel. As evidenced by the SEM images, the particles were agglomerated and formed large clusters. Air pockets were entrapped inside the agglomerations during the encapsulation process, and produced a soft metallic microstructure. Note that for the Ni-Ni particles, which were examined in Section 4.2.4, no agglomeration of particles was detected in the SEM images (see Figure 4-10).
Figure 5-1 (a) SEM images of as-received hBN powders; (b) Encapsulated hBN-Ni clusters
Figure 5-2 depicts the agglomeration steps for the hBN-Ni particles. It also shows the cross section of a single hBN-Ni particle taken by Focused Ion Beam (FIB). A cluster of agglomerated hBN-Ni particles was formed after the first reaction step in the encapsulation process. During the later stages of the encapsulation, more nickel was deposited on the exterior surface of the agglomerates. The step for adding concentrated solution (see Table 3-2) to the bath was repeated four times.

To determine the time when agglomeration occurred, the electroless nickel plating was stopped one minute into the reaction. The average size of the resulting particles was 140 µm. Ultraonication was then used to separate the loosely packed particles, which reduced the average particle size to 21.6 µm. This size was achieved after 12 minutes. Longer ultrasonication did not appear to change the average particle size any further. When continuing to add concentrated solution to deposit more nickel, the cluster size increased from 21.6 to 30.8 µm.
1\textsuperscript{st} step: Initial agglomeration

Image of agglomerated particles

2\textsuperscript{nd} step: Initial nickel encapsulation of hBN particles

3\textsuperscript{rd} step: Continued nickel deposition

Image of cross section of one hBN-Ni particle after Focused Ion Beam etching

*Figure 5-2 Agglomeration map*
5.2.1.2 Low- and High-Energy Milled Particles

Figure 5-3 compares SEM images for unaltered (Figure 5-3a) and milled particles Figure 5-3b and Figure 5-3c. Figure 5-3b shows that milled particles using low energy ball milling (LEM) still contained agglomerates. These agglomerates were compacted in LEM, but remained unbroken. That is, the hBN-Ni particles were not destroyed or de-agglomerated, only the air pockets between the sub-particulates were reduced (i.e., the agglomerates were “deflated”). This was most likely due to the fact that the electroless deposited nickel was soft, so, it did not fracture during LEM, but rather it deformed plastically together with the clustered, encapsulated hBN. This can be seen in the SEM images of the milled particles, where the hBN particles remained encapsulated with nickel, and there is only minor breaking up of clusters. This means that deflation occurred within the clusters of the encapsulated particles.

Encapsulated hBN; voids exist inside the clusters; average particle size 30.80 µm

Compacted clusters; voids were eliminated; average particle size 26.00 µm

De-agglomerated, nickel encapsulant partially fractured, average particle size 9.80 µm

Figure 5-3 hBN-Ni Particles, a) Unaltered, b) Low-energy milled (LEM), c) High-energy milled (HEM)
Figure 5-3c shows that almost all hBN-Ni clusters were fractured after HEM, resulting in smaller particles. Further, often the encapsulating nickel in these clusters was destroyed and hBN was squeezed out. Existence of bare, non-encapsulated hBN particles after HEM was confirmed by EDS. Figure 5-4 to Figure 5-6 show the EDS patterns of unaltered and milled particles with high- and low-energy methods. In the EDS pattern of hBN-Ni particles, nitrogen and boron elements of hBN particles were not detectable. Only nickel and some phosphorus were seen in this pattern (Figure 5-4). This was due to the complete encapsulation that was obtained as a result of electroless nickel plating. Figure 5-5 and Figure 5-6 show the EDS patterns for LEM and HEM of hBN-Ni, respectively. As seen in the figures, the basic composition of milled particles remained almost unchanged. The only difference found was that boron and nitrogen became detectable after HEM. This means that clusters, as well as nickel encapsulant, were broken during HEM. It is noteworthy that the phosphorous content, measured by EDS, for unaltered and milled particles remained almost unchanged (between 8.50 to 9.50 wt%).
Figure 5-4 EDS pattern of unaltered hBN-Ni powder

Figure 5-5 EDS pattern of LEM milled hBN-Ni powder
5.2.2 BET Surface Area Measurement

The surface areas of the unaltered and ball milled hBN-Ni samples were measured following the procedure described in Section 3.3.6 and compared in Figure 5-7. The surface area of the particles decreased from 0.56 m$^2$/g, to 0.44 m$^2$/g after LEM. It is believed that the original clusters contained entrapped air pockets, which compacted during LEM. However, HEM resulted in a larger surface area (0.73 m$^2$/g). This is due to the fact that the original clusters have been fractured and the total surface area of the particles increased. It should be noted that 10 measurements per sample were taken, and for all, the correlation factor was 0.99 or better.
5.2.3 Particle Size Analysis

Particle sizes were measured before and after ball milling. For each sample, a size distribution and a cumulative distribution were obtained. The size of the as-received particles of hBN was measured using a LA-950 laser diffraction particle size analyzer following the procedure explained in Section 3.3.2. Due to the nature of these particles, which had a high tendency to agglomerate, the method of powder dispersion had a significant effect on the particle size distribution. Therefore, in this test Isopropanol was used as a carrier liquid. Since the hBN particles were not permeable by Isopropanol, one droplet of soap was added as a surfactant (dispersing agent) to the powders and mixed before adding Isopropanol. To avoid measuring the size of agglomeration of materials instead of the powders, ultrasonic energy treatment with a probe (sonication) was applied in the solution for one minute and then the powder was added to the machine. The average size distribution of the particles was obtained after five tests and is reported in Figure 5-8. Based on the result, it is clear that as-received hBN particles demonstrated a bi-modal distribution with two mean values at 0.61 and 7.34 microns.
It is believed that the small particles with the mean of 0.61 microns were produced as a result of fracturing the larger ones during the sonication.

![Graph of particle size distribution](image)

*Figure 5-8 Particle size distribution of as-received hBN particles*

As already explained, the mean particle size of as-received hBN particles was 7.34 µm. This value after encapsulation with nickel reached 30.80 µm, due to nickel deposition as well as formation of clusters (agglomeration). Figure 5-9 shows the particle size distribution of the encapsulated hBN-Ni powders. Nickel was deposited in multiple reaction steps (see Figure 5-2). Figure 5-10 shows the particle size distribution for low-energy milled particles. The mean particle size for this sample was found to be 26.00 µm. This means that by using LEM for 15 minutes, the size of the particles was reduced as a result of compacting or deflating clusters. It is assumed that in LEM the breaking up of clusters occurred to a minor extent only.
The particle sizes of the high-energy milled powder are shown in Figure 5-11; the mean size of these particles decreased from 30.80 μm to 9.80 μm after milling for 15 minutes with HEM. This means that in HEM, not only the clusters were de-agglomerated, but also the encapsulant of individual hBN-Ni particles was fractured. These results are consistent with findings obtained from SEM, EDS and BET tests.
Figure 5-11 Average particle size distribution for high-energy milled (HEM) hBN-Ni

Figure 5-12 compares the standard deviations for the particle size distributions shown in Figure 5-9 to Figure 5-11 for the unaltered and milled particles. The standard deviation for the low energy milled particles was almost the same as that for the unaltered particles. However, the standard deviation was dramatically reduced as a result of high energy ball milling.

Figure 5-12 Standard deviation for particle size distributions
5.2.4 Hardness

Vickers Hardness numbers (HV) for the unaltered and milled particles were measured following the procedure explained in Section 3.3.8. For each test, 0.2 g of the powders were mounted in Diallyl Phthalate powder (copper filled) and the test was run 10 times under 1.96 N loads. Figure 5-13 shows the average hardness for different powders. As originally expected, milling caused the Vickers hardness of the particles to increase. This happened by work hardening of the encapsulating nickel layer, as well reducing the entrapped air pockets in the particle agglomerations. Milling the particles in LEM, even for a short time (15 minutes), significantly increased the hardness (approximately 11%, compared with the unaltered particles). This increase in hardness was even more evident for HEM, where the average hardness of the particles increased approximately 18%, when compared with the unaltered particles.

![Figure 5-13 Average hardness measurements for unaltered and milled hBN-Ni](image)

*Figure 5-13 Average hardness measurements for unaltered and milled hBN-Ni*
5.3 Case 2: Duration of Ball Milling Particles with Low-Energy Method (LEM)

The results from the studies in Case 1 indicated that milling the encapsulated particles resulted in smaller particle sizes. In addition, the initial hardness of the encapsulated particles was found to significantly increase by milling the particles with low- or high-energy methods for only 15 minutes.

The objective of the studies in Case 2 was to determine the influence of changing the initial hardness of hBN-Ni particles on the bond strength between the coating layer and aluminum 6061 substrates after cold spray. To change the initial hardness, particles were milled for different time durations to create different levels of hardness. As understood from the studies in Case 1, high-energy milling equipment, significantly increased the hardness of the particles, it also destroyed the particles, such that the encapsulating nickel was fractured and hBN was squeezed out. Therefore, in Case 2 only the low-energy ball milling technique was used. Similar to the studies for Case 1, the particles were characterized after milling for different time durations, with Scanning Electron Microscopy, BET, and hardness testing. Moreover, the effect of changing the hardness of the particles on coating bond strength with aluminum 6061 substrate was examined by measuring this parameter after cold spray.

5.3.1 Low-Energy Ball Milling for 1 and 24 Hours

For the first stage of this study, two time durations: 1 and 24 hours, were arbitrarily chosen to mill hBN-Ni particles with the low-energy milling equipment at 180 rpm. The test results are discussed in the following sections.
5.3.1.1 Scanning Electron Microscopy and EDS

SEM image of the particles after 1 hour milling with LEM is shown in Figure 5-14. Similar to what was seen for the Case 1 studies, milled particles still contained agglomerates. These agglomerates were compacted in LEM after 1 hour, and remained almost unbroken. A SEM image of 24 hour milled particles is shown in Figure 5-15. As seen in the figure, almost all hBN-Ni agglomerates were fractured after 24 hour of milling and smaller clusters formed. In fact, during the ball milling process, fracturing and welding are two major phenomena. This experiment indicated that fracturing through milling dominated the cold welding for 24 hours milling.

![Figure 5-14 SEM image of 1 hour milled hBN-Ni particles](image)

*Figure 5-14 SEM image of 1 hour milled hBN-Ni particles*
The EDS patterns of milled hBN particles after 1 and 24 hours are shown in Figure 5-16 and Figure 5-17. As seen, for 1 hour milled particles only nickel and phosphorus were detectable, which verified the understanding that hBN particles remained encapsulated after this milling process (see Figure 5-16). However, for the 24 hour milling, in addition to the basic composition of the milled particles (nickel and phosphorus), a small quantity of nitrogen and boron were also detected in the EDS pattern (see Figure 5-17). This means that, similar to what happened under high-energy milling in the Case 1 studies, but to a smaller extent, clusters as well as nickel encapsulant were broken and some hBN particles were squeezed out during milling for 24 hours. It is also noteworthy that the hardened stainless steel balls used for milling did not add iron to the powder, even after milling for 24 hours. In addition, the phosphorous content, measured by EDS, for unaltered and milled particles remained almost unchanged (between 8.50 to 9.50 wt%).
5.3.1.2 BET Surface Area Measurement

The surface area of the unaltered and ball milled hBN-Ni powder was measured following the procedure outlined in Section 3.3.6 and are compared in Figure 5-18. As
indicated, the surface area of the particles decreased from 0.56 m²/g to 0.51 m²/g after 1 hour of milling. This is due to the fact that the original clusters contained entrapped air pockets, which compacted during milling and therefore resulted in reduction of the surface area. However, milling for 24 hours resulted in a larger surface area (0.57 m²/g). This again, showed that the original clusters were fractured after a longer time of milling even with low-energy equipment. Note that 10 measurements per sample were taken for this test, and for all the correlation factor was 0.99 or better.

![Surface Area Per Grams of Unaltered and Milled Powders for 1 and 24 Hours](image)

*Figure 5-18* Surface area per grams of unaltered and milled powders for 1 and 24 hours

5.3.1.3 Density

The density of the powders before and after milling for 1 and 24 hours were measured following the procedure described in Section 3.3.7 with the results compared in Figure 5-19. As shown, milling for 1 hour slightly increased the density of the particles, which was mainly due to the aforementioned compaction of the air pockets entrapped between the particles. However,
continuing the milling for a longer time did not have a marked influence on density of the particles.

![Figure 5-19 Density of unaltered and milled powders for 1 and 24 hours](image)

**Figure 5-19 Density of unaltered and milled powders for 1 and 24 hours**

### 5.3.1.4 Particle Size Analysis

The particle size for the milled particles for 1 and 24 hours was measured based on the procedure explained in Section 3.3.2. For each sample, a size and cumulative distributions were obtained. As discussed earlier in this chapter, the mean particle size of as-received hBN particles was 7.34 µm (see Figure 5-8); after encapsulation with nickel, it reached 30.8 µm (see Figure 5-9). Figure 5-20 shows the particle size distribution after 1 hour of milling with low-energy equipment. The mean particle size for this sample was found to be 17.8 µm. By using LEM for 1 hour, the size of the particles was reduced as a result of compacting or deflecting clusters. The particle sizes of milled powder after 24 hours of milling are shown in Figure 5-21; the mean size of these particles decreased from 30.8 µm for unaltered to 7.5 µm after milling. This was a dramatic change in the particle size, which was due to the de-agglomeration of the clusters, as well as the detachment of the nickel encapsulant from hBN particles.
Figure 5-20 Average particle size distribution for 1 hour milled hBN-Ni

Figure 5-21 Average particle size distribution for 24 hour milled hBN-Ni

5.3.1.5 Cold Spray Coating of 1 and 24 Hour Milled Particles

As explained earlier, the objective of the studies in Case 2 was to determine the influence of changing the initial hardness of the particles through ball milling process on variation of the bond strength between the coating layer and aluminum 6061 substrates.
Therefore, after characterization of the 1 and 24 hour milled particles, they were cold sprayed on aluminum 6061 samples using the equipment and the testing procedure described in Section 3.5.

According to the test observations during cold spray coating using 24 hour milled particles, low quality coating was built-up on the substrate surface. In fact, only the first pass of sprayed particles bonded to the aluminum surface; all subsequent failed to bond. The reason for this effect can be explained based on the excessive increase in the initial hardness of the particles, which reduced their capability to have plastic deformation, and the deterioration of the nickel encapsulation in some particles after 24 hours of milling. Since aluminum 6061 is a soft material, bonding was only formed between the first layer of the milled particles and the substrate primarily through plastic deformation of the substrate. Figure 5-22 shows the SEM image from the cross section of the coated sample with 24 hour milled particles. As indicated, the resulting coating layer was so thin that measurement of coating characteristic parameters (i.e. thickness, and bond strength) was impossible. Therefore to accomplish the objective of this study, other intermediate ball milling durations were examined, as discussed in the following section. Note that the test results for the coatings with unaltered and 1 hour milled particles are discussed later in this chapter.
5.3.2 **Low-Energy Ball Milling for other Intermediate Times**

To determine the optimum time duration for milling particles in order to examine the effects that variation of initial hardness had on coating performance, 100 g of hBN-Ni particles were generated based on the procedure explained in Section 3.2. Size distribution measurement was performed on the particles after 2, 3, 4, 5, 6, and 12 hours of milling using LEM. The results are shown in Figure 5-23 to Figure 5-28. These results were obtained following the procedure outlined in Section 3.3.2.
Figure 5-23 Average particle size distribution for 2 hour milled hBN-Ni

Figure 5-24 Average particle size distribution for 3 hour milled hBN-Ni
Figure 5-25 Average particle size distribution for 4 hour milled hBN-Ni

Figure 5-26 Average particle size distribution for 5 hour milled hBN-Ni
The average particle sizes and the standard deviations of the particle size distributions for the milled particles are compared in Figure 5-29 and Figure 5-30, respectively. The results for the as-received hBN, unaltered hBN-Ni, and milled hBN-Ni for 15 min, 1 hour and 24 hours were also included in these figures for reference. As indicated, both the average particle size and the standard deviations showed descending trends, with increasing the duration of
milling. The rate of change in these parameters was faster at the beginning, up to 2 hours of milling, and then it slowed down for longer times. These results indicated that milling produced smaller particle sizes with more uniform distributions.

*Figure 5-29 Average particle sizes*
It is worth mentioning that cold spraying of particles with a size below 10 µm would have required readjustment of some parameters for coating onto aluminum 6061. This might have induced additional impact on the test results, not related to the variation of coating powder properties only. Having that known, 2 hour time duration for milling was found to be the best choice, since it resulted in an average particle size of slightly more than 10 µm (12.3 µm).

Next, the Vickers Hardness (HV) of the powders after different milling durations was examined using the procedure described in Section 3.3.8. Figure 5-31 shows these results for unaltered and milled particles after 1, 2 and 24 hours of milling. As seen, milling generally caused the Vickers Hardness (HV) of the powders to increase. As explained, this occurred due to compaction of the air pockets inside particle agglomerations, and also work hardening of the nickel encapsulation. The rate of the increase in hardness was faster at the beginning (increased by 11% after 1 hour) and then it somewhat slowed down (13% after 2 hours, and 16% after 24
hours, when compared with the unaltered particles). As stated earlier, the objective of this study was to examine the effect of change in the initial hardness of particles on coating bond strength. The results in Figure 5-31 indicated that milling more than 2 hours did not change the hardness significantly.

![Figure 5-31 Average hardness measurements for unaltered and milled hBN-Ni particles](image)

*Figure 5-31 Average hardness measurements for unaltered and milled hBN-Ni particles*

The hardness number for nickel encapsulated with nickel (Ni-Ni) particles is included in Figure 5-31 for comparison. These particles were examined on aluminum 6061 substrates in Section 4.2.4, and it was found that the substrate was barely coated after cold spray; it is believed to be due to the high hardness of the core pure nickel. Figure 5-31 also indicated that the hardness of Ni-Ni particles was approximately 30% higher than that of the unaltered hBN-Ni particles. This reconfirmed the aforementioned understanding for the behavior of Ni-Ni particles and, at the same time, verified the method used for measuring the hardness of the particles in this study. It is worth mentioning that, the agglomeration of the particles and the
entrapped air pockets which produced a soft microstructure for the hBN-Ni particles were not detectable for the Ni-Ni particles (see Figure 4-10).

Finally, Figure 5-32 and Figure 5-33 show the SEM image and EDS pattern for 2 hour milled particles respectively. As indicated only nickel and phosphorus were detectable, which verified that hBN particles remained encapsulated and were not damaged by 2 hours of milling. Given the understanding that continuing the milling process for a longer time can undesirably result in fracturing and deterioration of nickel encapsulation, 2 hour milling using LEM was chosen as the optimal milling option for the next studies in the following sections.

*Figure 5-32 SEM image of 2 hour milled hBN-Ni particles*
5.3.2.1 Cold Spray Coating of 1 and 2 Hour Milled Particles

The aluminum 6061 samples were coated with sufficient amount of unaltered, as well as 1 and 2 hour milled powders (about 400 g from each powder). Both nitrogen and helium were used as carrier or process gases during the cold spray. Figure 5-34 to Figure 5-36 show SEM images from the cross section of each coated sample.

Figure 5-33 EDS pattern of 2 hour milled hBN-Ni powder
Figure 5-34  SEM image of cross section of aluminum 6061 substrate coated with unaltered hBN-Ni, with (a) nitrogen, and (b) helium
Figure 5-35  SEM image of cross section of aluminum 6061 substrate coated with 1 hour milled hBN-Ni, with (a) nitrogen, and (b) helium
Figure 5-36  SEM image of cross section of aluminum 6061 substrate coated with 2 hour milled hBN-Ni, with (a) nitrogen, and (b) helium
The average thicknesses of cold spray layers for different samples were measured using SEM images with the results compared in Figure 5-37. This figure shows the total thickness of coating layer, after 5 passes of coating for each powder. Note that, evolution of coating thickness per cold spray pass was not examined. As indicated, milling the particles before coating generally resulted in a reduction of the cold spray coating thickness, primarily because of the increase in the initial hardness of particles and corresponding reduction in their capacity for plastic deformation during cold spray. The figure also shows the error bars that represent the variation in the coating thickness measurements, with respect to the reported average values. As shown, there were relatively larger variations in the coating thickness for the milled particles, compared to the unaltered particles. This means that the unaltered particles resulted in a more uniform coating thickness on the surface of substrate.

![Figure 5-37 Comparison of the average thickness of cold spray layers](image)

90
As explained earlier in this chapter, ball milling also resulted in smaller particle sizes, which was expected to increase particles deformation during cold spray and improve coating (Champagne et al. 2007, Bae et al. 2010). However, as understood from the results in Figure 5-37, the positive influence of having a more uniform size distribution was outweighed by the negative influence of increasing the initial hardness. It should be again noted that for the samples that were coated with 24 hour milled particles, the thickness of the coating layer was not measurable with the SEM. It is also worth mentioning that coating efficiency, which is defined as the weight fraction of the deposited particles over the total consumed powder, was not directly measured in this study. However, since the number of passes for cold spray coating was kept constant for all types of powders (5 passes), reduction in the thickness of the resulting coating layer corresponds to lower deposition efficiency as a result of ball milling.

In the cold spray process the particles need to be accelerated with the carrier gas to or beyond a critical velocity, so that bonding between the particles and the substrate is formed. Hence, there is always a range with a lower bound (critical velocity) and an upper bound (erosion velocity), within which the cold spray process is operable. Below the critical velocity the particles do not have sufficient kinetic energy to deform plastically after hitting the surface. Above the erosion velocity, the energy of particles is so high that they deflect or rebound after hitting the substrate surface. In addition, as a result of this excessive energy the particles may cause erosion or abrasion to the substrate (Papyrin et al. 2006).

The equipment that was used in the present study for cold spray was not able to measure impact velocity of the particles during coating. However, using a numerical code, impact velocities for hBN-Ni were estimated, based on the coating parameters addressed in Table 3-3. These values are shown in Figure 5-38 for different particle sizes, and for nitrogen and helium.
as carrier gas. The numerical code was supplied by the US Army Research Laboratory in Aberdeen, MD, and has been verified with a particle velocity measurement device. The critical and erosion velocities were also estimated for these particles using the numerical code, and are included in Figure 5-38. As indicated impact velocity has a generally descending trend by increasing the particle size. The plot shows that when nitrogen was used as carrier gas the impact velocity was reduced for particles smaller than 4 µm. The reason for this was explained by Grujicic et al. (2004) to be because, in cold spray process very small and light particles are decelerated within a stagnation bubble zone, which forms adjacent to the surface substrate. This effect results in reduction of the impact velocity for these particles.

![Figure 5-38 Impact velocities for hBN-Ni particles for cold spraying with nitrogen and helium](image)

*Figure 5-38 Impact velocities for hBN-Ni particles for cold spraying with nitrogen and helium*

The results in Figure 5-37 indicated that the average thickness of the coating layers for the different powders sprayed with helium were generally lower than those with nitrogen. In addition, a higher reduction in coating thickness was observed with helium, as a result of milling. As shown in Figure 5-38, helium as a carrier gas generally produced higher impact
velocities than nitrogen in the cold spray process. For the smaller particles in each powder, helium was believed to have increased the impact velocities more than the erosion velocity. Therefore, those particles rebounded after hitting the surface instead of deforming plastically and bonding to it. This resulted in reduction of coating layer thicknesses compared to the coatings with nitrogen. Such effects are discussed in further detail in Section 5.3.3.

5.3.3 Bond Strength

Bond testing in tension was used to evaluate the bond strength of the deposited layers for different powders. The samples coated with unaltered and milled powders (after 1 and 2 hours) were tested under a tensile force, normal to the surface, following the procedure outlined in Section 3.7. If the layer failed at the interface between the substrate and the coating layer, the measurement represented the adhesive strength between the cold sprayed coating and aluminum 6061; otherwise it was considered to be the cohesive strength between the deposited particles. Three samples were tested for each powder. The associated test results for the samples coated using nitrogen or helium as carrier gases are discussed separately in the following sections.

5.3.3.1 Bond Strength of the Cold Spray Coating Using Nitrogen as Carrier Gas

Figure 5-39 to Figure 5-41 depict the fracture surfaces of the two bond slugs after the bond strength testing for the samples coated with unaltered or milled hBN-Ni using nitrogen as carrier gas. As observed, for the samples coated with the unaltered particles, the failure mostly occurred at the interface between the coating layer and the substrate. The bare surfaces of the bond slugs are evident in Figure 5-39. This indicates an adhesive failure between the coating layer and aluminum 6061. For the samples coated with 1 hour milled particles, a mixture of failure types were observed; at the epoxy layer (Sample A) or through the coating layer, which
is indicative of cohesive failure (Samples B and C). Lastly, for 2 hour milled particles, failure occurred mostly within the coating layers between the coated particles. This is evident in Figure 5-41 where both bond slugs are covered with a layer of coating indicate a cohesive type failure.

Sample A (adhesive failure)  Sample B (adhesive failure)  Sample C (adhesive failure)

*Figure 5-39 Bond slugs after bonding test for unaltered hBN-Ni after cold spraying with nitrogen*
Sample A (failure in epoxy layer)  
Sample B (cohesive failure)  
Sample C (cohesive failure)

*Figure 5-40 Bond slugs after bonding test for 1 hour milled hBN-Ni after cold spraying with nitrogen*
Sample A (cohesive failure)  
Sample B (cohesive failure)  
Sample C (cohesive failure)  

Figure 5-41 Bond slugs after bonding test for 2 hour milled hBN-Ni after cold spraying with nitrogen

Bonding in cold spray forms via plastic deformation, and the resulting interlocking of particles through the collision of the coating powders with the substrate. Since aluminum 6061 is a relatively soft material, bonding between the first pass of the sprayed powders and substrate forms by plastic deformation of the nickel and the aluminum surface. This is evidenced in Figure 5-34 to Figure 5-36 in which impacting of the particles during cold spray resulted in undulation at the interface between the coating layer and the aluminum 6061 substrate. For the...
subsequent passes of particles, bonding was formed through plastic deformation of the encapsulating nickel in the coating powders. Figure 5-42 to Figure 5-44 show a close up view at the cross section of the coated samples with unaltered and milled particles using nitrogen as carrier gas. When unaltered powder was used, due to significantly high plastic deformation of the particles, a relatively uniform coating layer with a minimal amount of voids was generated. The bond failure occurred between coating layer and the aluminum 6061 surface (adhesion failure). However, with milling, the initial hardness of particles was increased and their capability to undergo plastic deformation decreased. As a result, relatively weak interlocking and bonding were formed between subsequent passes of sprayed powders due to insufficient plastic deformation of the composite nickel particles. Figure 5-43 and Figure 5-44 show porous coating layers with a significant amount of voids between the coated particles for 1 and 2 hour milled powder. As a result, bond failure occurred mostly within the coating layers and not at the interface between the coating and aluminum 6061 (cohesion failure). For the sample that showed failure in the epoxy (Sample A with 1 hour milled hBN-Ni layer shown in Figure 5-40), it is believed that epoxy penetrated through the thin and porous coating layer during the preparation of the samples before the bond strength test. Therefore epoxy failure occurred, rather than the adhesive/cohesive failure observed for the other samples.
Figure 5-42 A close up view with SEM for cross section of aluminum 6061 substrate coated with unaltered hBN-Ni, with nitrogen

Figure 5-43 A close up view with SEM for cross section of aluminum 6061 substrate coated with 1 hour milled hBN-Ni, with nitrogen
The results for the maximum stress levels that caused failure during bond strength tests for the different samples tested are shown in Table 5-1. Figure 5-45 also depicts these test results with their associated standard error bars. The bond strength for a test that was done using epoxy (with two uncoated samples) is included here for reference. A relatively small standard error was observed in the test results for the samples coated with unaltered particles. The bond strength for these samples, which mostly showed an adhesive type of failure, was close to the average value for this material (65.95 MPa).
Table 5-1 Bond strengths, cold spray with nitrogen

<table>
<thead>
<tr>
<th>Cold Sprayed Coatings</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Average Bond Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>84.85</td>
<td>65.80</td>
<td>79.13</td>
<td>76.59</td>
</tr>
<tr>
<td>Unaltered hBN-Ni with N₂</td>
<td>67.67</td>
<td>60.59</td>
<td>69.58</td>
<td>65.95</td>
</tr>
<tr>
<td>1 hr Milled hBN-Ni with N₂</td>
<td>74.07</td>
<td>69.20</td>
<td>14.98</td>
<td>52.75</td>
</tr>
<tr>
<td>2 hr Milled hBN-Ni with N₂</td>
<td>54.98</td>
<td>46.24</td>
<td>53.71</td>
<td>51.65</td>
</tr>
</tbody>
</table>

Figure 5-45 Bond strengths, cold spray with nitrogen

For the samples coated with 1 hour milled particles, although the average bond strength value (52.7 MPa) was found to be smaller than that for the unaltered particles, significant fluctuation was observed between the test results that resulted in a relatively large standard error (see Figure 5-45). This was due to the fact that insufficient plastic deformation of the hardened milled particles formed a deficient and porous coating layer on the aluminum surface. The large bond strength reported in Table 5-1 for Sample A of 1 hour milled particles (74.0 MPa) was closed to that of epoxy (76.6 MPa). The reason for this was because the failure
occurred in the epoxy layer, which, as explained earlier, penetrated through the porous coating layer and reach the aluminum surface (see Figure 5-40 A).

For the samples coated with 2 hour milled particles, the bonding test results showed small fluctuations, with a small standard error. The average bond strength for the 2 hour milled particles was found to be 51.7 MPa, which showed a reduction relative to unaltered particles. It should, again, be noted that the bond strength values obtained for the samples coated with unaltered powder represented the adhesion strength between the coating layer and the aluminum 6061 surface whereas the samples coated the 2 hour milled particles represent the cohesion strength between the sprayed particles. In that sense, the comparison was somewhat incomplete, because the cohesion strength for the unaltered particles, which was not measurable, may have been much larger than the adhesion strength that was reported in Table 5-1 and Figure 5-45 for this material.

Figure 5-46 compares the trends of variation as a result of milling in particle size, particle hardness, and average bond strength for samples coated with unaltered and milled hBN-Ni particles. The results for the samples coated with 24 hour milled particles are also included in this figure to give a broader picture for how milling can affect different properties of the coating powders. As a result of milling, the particle sizes were generally reduced, the hardness was increased, and the average bond strength for the resulting coating layer was reduced. The absolute rate of the variations for these parameters was quite similar, especially up to 2 hours of milling. That is, a more significant initial change was seen in all results after 1 hour milling, than the additional modification due to longer milling. Note that the results for average coating layer thickness and bond strength for the 24 hour milled particles were not measurable, so they were simply assumed to be equal to zero in Figure 5-46.
Figure 5-46 Comparison of particle size, average bond strength, and particle hardens for unaltered and milled hBN-Ni particles, cold sprayed with nitrogen

In a similar fashion, Figure 5-47 compares the trend of variations in particle hardness, and the average thickness and bond strength of coating layer for unaltered and milled hBN-Ni particles. Again, a similar trend was seen for these parameters. The most significant change in the average coating layer thickness occurred after 2 hours milling.
Figure 5-47 Comparison of average coating layer thickness, average bond strength, and particle hardens for unaltered and milled hBN-Ni particles, cold sprayed with nitrogen

5.3.3.2 ImageJ Analysis for the Cold Spray Coating Using Nitrogen as Carrier Gas

Image analysis was performed on the samples coated with unaltered and milled particles using nitrogen as carrier gas to better understand how the particles are deformed in cold spray. As explained in Section 3.8 the coated aluminum 6061 samples were sectioned, mounted in resin, and then polished to see the cross section of the coating layer. The images of the cross section of the samples were analyzed with ImageJ software Ver. 1.46r. ImageJ recognizes the boundaries of the coated particles and superimposes a circumscribing ellipse around each particle, and determines its aspect ratio. This ratio was equal to d1/d2, where d1 and d2 were the major and minor diameters of the circumscribing ellipse for each particle, respectively. The larger the aspect ratio, the more flattened the particles had become in the coating layer.
Table 5-2 compares these aspect ratios for the unaltered and milled particles after cold spray. Original, superimposed images and histograms of these particles are shown in Figure 5-48 to Figure 5-56. As seen, the average aspect ratio of unaltered hBN-Ni cold sprayed particles was larger than those for the milled ones. This indicated that the unaltered hBN-Ni particles deformed more significantly and became more flattened after impacting the substrate through cold spray. For the 1 and 2 hour milled hBN-Ni particles, ball milling increased the initial hardness of the deposited nickel and therefore reduced the deformability of the particles, resulting in smaller aspect ratios for the coated particles after cold spray. As discussed in the previous sections, ball milling resulted in smaller particle sizes. Champagne et al. (2007) and Bae et al. (2010) showed that smaller particles are accelerated faster than larger ones, and also become more flattened through cold spray coating. However, the results of image analysis in this section showed the opposite for the milled particles. This was due to the fact that milling also increased the initial hardness of the particles, and reduced their deformability.

**Table 5-2 Aspect ratio of the particles after coating aluminum 6061 substrate**

<table>
<thead>
<tr>
<th>Cold Sprayed Particles</th>
<th>Number of Particles</th>
<th>Average Aspect Ratio</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaltered hBN-Ni with Nitrogen</td>
<td>498</td>
<td>1.65</td>
<td>0.031</td>
</tr>
<tr>
<td>1 hr Milled hBN-Ni with Nitrogen</td>
<td>565</td>
<td>1.56</td>
<td>0.024</td>
</tr>
<tr>
<td>2 hr Milled hBN-Ni with Nitrogen</td>
<td>840</td>
<td>1.28</td>
<td>0.018</td>
</tr>
</tbody>
</table>
Figure 5-48 Optical microscopy image of unaltered hBN-Ni particles cold sprayed on aluminum 6061 substrate

Figure 5-49 Superimposed image for the unaltered hBN-Ni particles and their circumscribing ellipses
Figure 5-50 Aspect ratio histogram of unaltered hBN-Ni particles

Figure 5-51 Optical microscopy image of 1 hour milled hBN-Ni particles cold sprayed on aluminum 6061 substrate
Figure 5-52 Superimposed images for the 1 hour milled hBN-Ni particles and their circumscribing ellipses

Figure 5-53 Aspect ratio histogram of 1 hour milled hBN-Ni particles
Figure 5-54 SEM image of 2 hour milled hBN-Ni particles cold sprayed on aluminum 6061 substrate

Figure 5-55 Superimposed images for the 2 hour milled hBN-Ni particles and their circumscribing ellipses
Image analysis was also performed on the samples to measure the area percentage of pores in the coating layers. For each type of coating, five images from different locations on the cross section of the samples were taken and analyzed with ImageJ software. The software recognized the pores boundaries and superimposed a circumscribing ellipse around each one. The area percentage porosity was determined as the area of the ellipses upon the total area of the coating layer cross section. Figure 5-57 compares the average area percentage porosity for the samples coated with unaltered and milled particles. The error bars were also included in this figure to indicate the variability of the results, in the five images that were analyzed for each sample cross section. These results again confirmed the understanding that the unaltered hBN-Ni particles resulted in more uniform coating layer, through cold spray, on the surface of the aluminum substrate. For the 1 and 2 hour milled hBN-Ni particles, ball milling increased the initial hardness of the particles and reduced their deformability, which resulted in a larger amount of pores in the coating layers.
5.3.3.3 Bond Strength of the Cold Spray Coating Using Helium as Carrier Gas

Figure 5-58 to Figure 5-60 show the fractured surfaces of the two bond slugs after the bond strength testing for the samples coated with unaltered or milled hBN-Ni using helium as carrier gas. Table 5-3 compares the average bond strength values reported for unaltered and milled particles. These test results with their associated standard errors are also shown in Figure 5-61.
Sample A (cohesive failure)  
Sample B (cohesive failure)  
Sample C (failure in epoxy layer)

*Figure 5-58 Bond slugs after bonding test for unaltered hBN-Ni after cold spraying with helium*
Sample A (cohesive failure)  Sample B (cohesive failure)  Sample C (cohesive failure)

Figure 5-59 Bond slugs after bonding test for 1 hour milled hBN-Ni after cold spraying with helium
Figure 5-60 Bond slugs after bonding test for 2 hour milled hBN-Ni after cold spraying with helium
Table 5-3 Bond strengths, cold spray with helium

<table>
<thead>
<tr>
<th>Cold Sprayed Coatings</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Average Bond Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>84.85</td>
<td>65.8</td>
<td>79.13</td>
<td>76.59</td>
</tr>
<tr>
<td>Unaltered hBN-Ni with He</td>
<td>32.23</td>
<td>47.55</td>
<td>52.49</td>
<td>44.09</td>
</tr>
<tr>
<td>1 hr Milled hBN-Ni with He</td>
<td>13.95</td>
<td>11.75</td>
<td>13.11</td>
<td>12.94</td>
</tr>
<tr>
<td>2 hr Milled hBN-Ni with He</td>
<td>35.95</td>
<td>34.20</td>
<td>48.94</td>
<td>39.07</td>
</tr>
</tbody>
</table>

Figure 5-61 Bond strengths, cold spray with helium

When helium was used for the unaltered particles, as opposed to what was observed for the samples cold sprayed with nitrogen, various samples exhibited different types of failure (i.e. cohesive, adhesive and epoxy). Additionally, a relatively large fluctuation in the test results was observed. The average bond strength for these unaltered samples was found to be 44.0 MPa, which was smaller than the corresponding result obtained for the samples coated with nitrogen (66.0 MPa).
All samples coated with 1 hour milled particles failed within the coating layer corresponding to cohesive failure (Figure 5-59). Unexpectedly, these samples, showed a very low average bond strength value (13.0 MPa), even lower than that for 2 hour milled (40.0 MPa). For the 2 hour milled particles epoxy failure was visible at the fracture surface for all three samples tested (see Figure 5-60). According to ASTM C633 (ASTM 2013) the test procedure used in this study for measuring the bond strength is only valid when the coating thickness is greater than 380 µm. For a smaller coating thickness the epoxy, used for bonding the two bond slugs, tends to penetrate through the coating layers, which will then invalidate the results. For the samples coated with 2 hour milled particles the average coating thickness was shown in Figure 5-37 to be 96.20 µm. Therefore, during sample preparation, the epoxy may have penetrated through the thin coating layer on the aluminum 6061 samples. The bond between epoxy and aluminum 6061 failed at a higher stress than that with 1 hour milled particles.

Figure 5-62 shows a close up view, by SEM, of the cross section of the coated samples with unaltered and milled particles, using helium. It was evident that the coating layer for all samples coated with helium was problematic, where segregation and micro cracks between layers of coated particles were visible. These problems were more pronounced for the sample coated with milled particles. In general, helium, as a carrier gas, showed a relatively poor performance, compared to nitrogen, for cold spraying hBN-Ni particles on aluminum 6061. As explained, it is essential that the particles plastically deform during the collision with the substrate. Low mass density of helium caused the velocity of hBN-Ni particles to increase beyond the erosion velocity. Therefore, the contact time was not sufficient for these particles to deform plastically and form bonding. On the other hand, when nitrogen was used, it provided
the kinetic energy and contact time required for plastic deformation of the sprayed particles, and therefore, more efficient coating was resulted.

Figure 5-62 A close up view of cross section of aluminum 6061 substrate coated with unaltered hBN-Ni powders, with helium
Figure 5-63 A close up view of cross section of aluminum 6061 substrate coated with 1 hour milled hBN-Ni with helium

Figure 5-64 A close up view of cross section of aluminum 6061 substrate coated with 2 hour milled hBN-Ni with helium
Similar to what was done for coatings with nitrogen image analysis was also performed on the samples coated with helium to measure the area percentage of pores in the coating layers. Again, for each type of coating, five images from different locations on the cross section of the samples were analyzed with ImageJ software. Figure 5-65 compares the average area percentage porosity for the samples coated with unaltered and milled particles. As indicated, the amount of pores in these coating layers was generally larger than those for coatings with nitrogen (see Figure 5-57). Ball milling further increased the porosity of the coating layers.

![Figure 5-65 Area percentage porosity of coating layers with Helium](image)

**5.3.4 Hardness in Coating Layers**

Variation of Vickers hardness in the coating layers was examined perpendicular to the samples cross sections, and through the coating layer thickness, using the procedure described in Section 3.3.8. The associated test results for the samples coated using nitrogen or helium as carrier gas are discussed in the following sections.
5.3.4.1 Hardness in the Coating Layers, using Nitrogen as carrier gas

The Vickers hardness was determined for the samples coated with unaltered and 1 hour milled particles at four points through the coating layer. The first point was taken near the interface of coating with aluminum substrate, and the last one near the outside surface of coating. Two intermediate points were also taken at approximately one third locations through the layer. For the sample coated with 2 hour milled particles, since coating thickness was small hardness was only measured at two points: near the aluminum surface and near the outside surface of the coating. For each measurement point, hardness was determined at three different locations along the sample cross sections. The average hardness values for unaltered and milled particles are shown in Figure 5-66 to Figure 5-68. Based on the results, it is possible to understand how different passes of particles were hardened, due to plastic deformation and flattening in cold spray. As shown, unaltered particles were generally more hardened than the milled ones in the coating layers. The difference in hardness was more pronounced near the interface of coating with aluminum substrate. In addition, the longer the duration of milling, the smaller hardness values were resulted in the coatings. This happened because milling increased the initial hardness of the particles via work hardening of the nickel encapsulation, as well as reducing air pockets within particle agglomerations, and therefore reduced their deformability.

Another important effect that can be seen in these figures is that, the hardness values, especially for the milled particles showed an ascending trend through the coating layer thickness, by increasing distance from the interface of coating and substrate. This indicated that the first passes of the particles underwent smaller deformations than the subsequent passes. In fact, the first passes of the particles impacted on the surface of the soft aluminum substrates. Therefore, part of the kinetic energy of the particles was absorbed through plastic deformation
of the substrate (King et al. 2009b, Yin et al. 2011). For the milled particles, in particular, bonding between the first passes of the hardened particles with the aluminum substrate was primarily formed through deformation of the substrate. For the subsequent passes, however, particles were sprayed on the surface of the hardened coating layer resulted by the first passes, and therefore, deformed further. Since nitrogen was used as carrier gas for these samples, the contact time was sufficient for the particles to deform and bond.

![Graph showing hardness measurements for cold spray layer of unaltered hBN-Ni with nitrogen](image1)

*Figure 5-66 Average hardness measurements for cold spray layer of unaltered hBN-Ni, with nitrogen*

![Graph showing hardness measurements for cold spray layer of 1 hour milled hBN-Ni with nitrogen](image2)

*Figure 5-67 Average hardness measurements for cold spray layer of 1 hour milled hBN-Ni, with nitrogen*
5.3.4.2 Hardness in the Coating Layers, using Helium as carrier gas

The hardness was measured at four points through the thickness of coating layer for the sample coated with unaltered particles. For the samples coated with 1 and 2 hour milled particles, three and two measurement points were taken, respectively, since coating thickness was reduced as a result of milling. For each measurement point, hardness was determined at three different locations along the samples cross sections. The average hardness values for unaltered and milled particles are shown in Figure 5-69 to Figure 5-71. As shown, for the sample coated with unaltered particles different passes of sprayed particle deformed almost identically and gained similar hardness values (Figure 5-69). The hardness in the coating layer for this sample was larger than that with nitrogen (Figure 5-66). This was interesting, considering the fact that the resulting coating layer with helium was found to be thinner with smaller bond strength, compared to those with nitrogen. In fact, helium resulted in larger impact velocities for the particles, than nitrogen. As depicted in Figure 5-38, for larger particle sizes in the powder, the impact velocity with helium was very large, but still less than the erosion velocity. Therefore those particles bonded to the substrate by having significant plastic
deformations. However, for the smaller particle sizes in the powder the impact velocity was larger than the erosion velocity, so they bounced back after impact. As a result, although the coated particles were hardened further with helium, the resulting coating layer was thinner and more porous than the coating with nitrogen.

For the samples coated with milled particles using helium, as opposed to what observed for coating with nitrogen, the hardness values showed a descending trend through the coating layer thickness, by increasing distance from the interface of coating with the substrate. For the first passes of the sprayed milled particles, bonding was formed through deformation of soft aluminum substrate. For the subsequent passes, however, particles impacted on the surface of the formed coating layer resulted by the first passes. Yin et al. (2011) demonstrated that cold spray coating of copper particles on aluminum 6061 substrates, with impact velocity of 900 m/sec or larger, incurred large deformation on the substrate or the initially formed coating layer. Similarly, based on the test results in Figure 5-70 and Figure 5-71, excessive impact velocity of the initially hardened milled particles in the subsequent passes resulted in larger deformation of the formed coating layer, which further increased the hardness of this layer. However, the sprayed particles in the subsequent passes either bounced back or underwent insufficient plastic deformations after impact to the coating layer. Large segregations between the particles in the coating layers, away from the surface of aluminum, were evident in Figure 5-63 and Figure 5-64 for the samples coated with milled particles using helium. This resulted in a softer microstructure and lower hardness values in the coatings at these locations.
Figure 5-69 Average hardness measurements for cold spray layer of unaltered hBN-Ni, with helium

Figure 5-70 Average hardness measurements for cold spray layer of 1 hour milled hBN-Ni, with helium
A set of experimental parametric studies were completed in this chapter to prove the hypothesis developed in Section 4.3. This was accomplished by varying the initial ductility of the hBN-Ni particles and examining the particles and the coated layer before and after cold spray coating.

The results for the samples coated with unaltered and milled particles with nitrogen and helium carrier gas supported the hypothesis introduced in Section 4.3. That is, increasing the initial hardness in the particles and subsequently reducing their capability for having significant plastic deformation through cold spray deposition inhibited interlocking between the coated particles. This resulted in a porous and problematic coating layer on the surface of aluminum 6061 substrates. Note that the adverse effects of increasing the initial hardness in the particles were so high that they outweighed the possible improvements in the deposition efficiency, expected due to having smaller particles, which was also resulted by ball milling.

![Graph showing hardness measurements](image-url)
Chapter 6  Conclusions and Recommendations

6.1  Summary and Conclusions

Unlike conventional coating methods that are usually performed at high temperatures, the cold spray method is a low temperature process to apply coatings on different surfaces. This method can be used where conventional coatings are not applicable because of melting, evaporation, gas release, crystallization, de-bonding and oxidation of the coating materials, which often preclude coatings from bonding to the surfaces. In this research, the cold spray deposition method was used to apply a composite self-lubricating coating material, which was vulnerable to high temperatures, on aluminum 6061. The self-lubricating coating was composed of micro scale lubricant particles of hexagonal boron nitride encapsulated and built into a metallic matrix of nickel (hBN-Ni). The performance of this coating material on the aluminum substrates was initially studied by Stark (2010). The study demonstrated very promising attributes for the coating, such as low friction, and high wear resistance. In addition, the coating layer was shown to have unexpectedly high bond strength with the substrate. The main objective of the present study was to find the reason for the observed high coating bond strength.

First, the literature pertaining to cold spray coating, mechanism of the interaction of coating particles with different substrates, and the physical and chemical properties of the coating powders that affect the performance of coating was reviewed in Chapter 2. Next, the equipment and the experimental procedures used in this study for producing hBN-Ni coating particles, ball milling, cold spray deposition and characterization of the particles and coated surfaces in terms of hardness, density, porosity, material composition, friction, wear resistance, and bond strength were described in Chapter 3.
An initial study was completed in Chapter 4 to compare the performance of hBN-Ni coating which was found to exhibit a high bond strength, while coatings with as-received pure nickel had a much lower bond strength. Looking at the EDS patterns of the two coating powders, it was understood that hBN-Ni coatings contained phosphorus which was not seen in as-received pure nickel. This phosphorus element, which was introduced in the nickel encapsulation process, was first believed to be the reason for the high bond strength of hBN-Ni coatings. To investigate the effect of phosphorus, the as-received pure nickel particles were encapsulated with nickel (Ni-Ni), following the same procedure that was used for the production of hBN-Ni particles. The EDS results did indicate the existence of the phosphorus element in the Ni-Ni coating powder. However, using this material to cold spray to aluminum 6061, the coating was in general not successful as had been originally hoped. The samples were barely coated, with only isolated lines of coating formed on the surface. These findings indicate that the existence of phosphorus in hBN-Ni could not be the main cause for the high bond strength of this coating to aluminum substrates.

Next, the XRD patterns of the hBN-Ni and pure nickel particles were obtained to compare the grain size (i.e. crystallinity) of these two materials. According to these results, the encapsulating nickel generated through the electroless nickel plating process was found to be amorphous (or “near amorphous) and much softer than the as-received pure nickel, which had a crystalline microstructure.

It was then concluded that the high bond strength of hBN-Ni particles could be related to the initial ductility of the particles and the work hardening of the encapsulating nickel layer during cold spray. That is, the nickel encapsulating the hBN particles was initially very soft but had the potential to harden through the cold spray process. In addition, the encapsulated hBN
particles which are soft and have a layered structure, permitted even more deformation and hardening in the nickel. Due to the significant plastic deformation and lack of initial stiffness, the agglomerated hBN-Ni clusters were able to retain their deformed shape after impacting the substrate due to the lack of elastic recovery. While the resulting cold sprayed layer retained its highly deformed state, it also had a relatively high density, stiffness, and strength as a consequence of the work hardening of nickel. On the other hand, in the Ni-Ni particles, the encapsulated nickel was initially hard, so the possibility of having plastic deformation and subsequently forming a strong bond upon impacting the substrate was relatively low. These findings are summarized in Section 4.3, in the form of a hypothesis to explain the bonding mechanism of hBN-Ni particles to aluminum 6061.

In order to prove this hypothesis, the influence of the initial ductility of hBN-Ni particles on coating efficiency were examined by changing these attributes through work hardening using ball milling at various durations. In addition to increasing the initial hardness, which according to the aforementioned hypothesis was believed to be the main contributor to bond formation between the encapsulated particles and the substrate, ball milling is also known to result in smaller particles with more uniform size distributions. This effect was expected to cause the particles to gain larger impact velocities in the cold spray process, and as a result, form stronger bonds to the substrate. In other words, ball milling was expected to have a both positive and negative influence on the particles’ properties and their potential to form a strong bond with the substrate through cold spray. These influences were examined in Chapter 5 in the form of two case studies.

In Case-1, the performances of high and low-energy ball milling methods were investigated on hBN-Ni particles before cold spray. The main objective of this study was to
determine which ball milling method was best suited for the hBN-Ni particles to increase their initial hardness before coating. The most significant findings obtained from this study can be summarized as follows:

- When using high-energy milling (HEM) for 15 minutes, the mean size of hBN-Ni particles decreased from 30.80 µm to 9.80 µm. This method caused the composite clusters as well as individual hBN-Ni particles to fracture, such that some of the hBN particles were expelled from the nickel matrix and became exposed. Existence of bare and non-encapsulated hBN particles after HEM was confirmed by EDS. Moreover, the total surface area of the particles was higher than that for unaltered particles because of fracturing of the clusters and encapsulated particles. In addition, by using HEM the hardness of the particles was increased through work hardening by approximately 18%, compared with unaltered particles.

- By using low-energy milling (LEM) for 15 minutes the mean particle size of hBN-Ni particles decreased from 30.80 µm to 26.00 µm. This method was found to compact the agglomerates and eliminate the air pockets within the encapsulated particles rather than fracturing them. The surface area of the particles also decreased after releasing the air pockets during milling. By low-energy milling, the hardness of the particles increased by approximately 11%, compared with unaltered particles.

In Case-2 the influence of changing the initial hardness of hBN-Ni particles on bond strength after cold spray was investigated using ball milling for different durations. The results for the study in Case-1 showed that high-energy milling equipment, although significantly
increasing the hardness of the particles, destroyed the encapsulated particles such that the encapsulating nickel was broken and the hBN exuded. Therefore, in Case-2 only low-energy ball milling was used. The coating materials were examined before cold spray coating, in terms of size, and hardness. The most significant findings can be summarized as follows:

- In measuring the size of the particles after 1, 2, 3, 4, 5, 6, 12 and 24 hours of milling, the average particle size showed a descending trend with an increase in the duration of milling up to 2 hours. This trend slowed down after 2 hours and the average particle size remained almost constant with longer milling times.
- SEM images and EDS patterns of milled hBN-Ni particles showed that the agglomerates still existed after 1 and 2 hours of milling. These agglomerates were compacted, and remained almost unbroken. However, the associated results for 24 hour milled particles indicate that almost all agglomerates were fractured and occasionally bare hBN particles were exposed. This effect was similar to that observed for the high-energy milled particles in Case-1.
- The surface area of the particles decreased after 1 and 2 hours of milling. This was due to the fact that the original clusters contained entrapped air pockets, which were compacted during milling, and therefore resulted in reduction of the surface area. However, milling for 24 hours resulted in a larger surface area due to fracture of the original clusters.
- Milling generally caused the Vickers hardness of the particles to increase. This occurred due to work hardening of the encapsulant nickel, as well as eliminating air pockets entrapped inside the agglomerates. The rate of increase in the

129
hardness was relatively fast at the beginning, (up to 2 hours of milling), but slowed down afterward.

Unaltered and milled hBN-Ni particles were cold sprayed on aluminum 6061 samples using nitrogen or helium as carrier gases. The most significant findings can be summarized as follows:

- Milling the particles before coating resulted in reduction of the cold spray coating thickness on aluminum substrates. This effect was more pronounced for longer milling durations. For 24 hour milled particles, only the first pass of sprayed particles bonded to the substrate and the following passes rebounded after hitting the surface. The resulting coating layer was patchy and could not be reliably characterized.

- SEM images from cross sections of coating layers showed that when unaltered powder was used, due to the high plastic deformation of the particles, a thick monotonic coating layer with minimal amount of voids resulted on the substrate surface. However, when the particles were milled, their initial hardness now being higher, the capacity for plastic deformation was reduced. As a result, relatively deficient interlocking and bonding was found to be the case for subsequent passes of sprayed powders. This resulted in porous coating layers with a significant number of voids between the coated particles. This effect was more significant for longer milling durations.

- Image analysis was performed on cross sections of layers sprayed to aluminum substrates, using ImageJ software Ver. 1.46r. A larger amount of pores in the coating layers for milled particles was also confirmed by image analysis.
Moreover, the results indicate that the unaltered hBN-Ni particles, compared to the milled particles, deformed significantly and became more flattened with larger aspect ratios after impacting the substrate through cold spray. For the milled hBN-Ni particles, ball milling increased the initial hardness of the encapsulating nickel and therefore reduced the deformability of the particles. The aspect ratio of the flattened particles was found to be smaller for longer durations of milling.

- Helium as a carrier gas generally showed a relatively poor performance compared to nitrogen for hBN-Ni particles cold sprayed to aluminum 6061. The resulting layers, for all different powders using helium, had smaller thicknesses and more pores and segregation between the coated particles, compared with nitrogen.

Bonding tests were performed using cylindrical slugs coated with unaltered, 1, and 2 hour milled hBN-Ni particles, with nitrogen and helium as carrier gas. The test was repeated 3 times for each coating. The most important finding from the test results are summarized in the following:

- The bond failure for all samples coated with unaltered particles, using nitrogen as carrier gas, consistently occurred at the interface between the coating layer and the aluminum surface (adhesive failure). The bond strength for these samples was found to be very high with minimal variation and good repeatability of the test results for the 3 samples tested. However, when helium was used for coating with unaltered particles, cohesive failure was observed for all samples, and the bond strength values were lower than those with nitrogen.
• For the samples coated with 1 and 2 hour milled particles, using nitrogen or helium as carrier gas, different bond failure modes (cohesive failure, or failure in the epoxy layer) were observed for different samples tested. In fact, the failure occurred mostly within the coating layer and not at the interface between the coating layer and aluminum.

• When nitrogen was used as carrier gas, large fluctuations were observed in the bond strength test results for the coatings with 1 hour milled particles. For the substrates coated with 2 hour milled particles, however, the bond strength was observed to be consistently lower than those for the coatings with unaltered particles.

• When helium was used as carrier gas, the bond strength values of the coatings with 1 hour milled particles were found to be dramatically lower than those for unaltered particles. For the samples coated with 2 hour milled particles epoxy failure was observed for all three samples tested. The bond strength results were found to be lower than those for unaltered particles; however, they were higher than the bond strengths for the coatings with 1 hour milled particles. This was due to the epoxy failure.

Variation of Vickers hardness in the coating layers was examined perpendicular to the sample cross sections, at multiple points through the coating layers. This was done to investigate how different passes of particles were hardened, as a result of plastic deformation and flattening in the cold spray process. The most important test results are listed in the following:
Unaltered particles were generally more hardened than the milled ones in the cold sprayed layers. The longer the duration of milling, the lower the hardness in the sprayed layers, for all passes applied.

The hardness in the sprayed layers for the samples coated with unaltered particles was larger using helium than nitrogen. This was due to the high impact velocity that helium produces for the particle, which caused these particles to have significant plastic deformations in cold spray. The resulting coating layer with helium was, however, shown to be thinner with a larger amount of pores and smaller bond strength, compared to those for coating with nitrogen. In fact, for the smaller particle sizes in the powder the impact velocity with helium was larger than the erosion velocity, so they bounced back after impact. As a result, although the coated particles were hardened further when helium was used, the resulting coating layer was thinner and more porous than the coating with nitrogen.

Using nitrogen as carrier gas, the hardness values, especially for the milled particles, showed an ascending trend through the coating layer thickness when increasing the distance from the interface of coating and substrate. The first passes of particles impacting on the aluminum surface underwent smaller deformation. For the subsequent passes, however, particles were sprayed on the surface of an already hardened coating layer from previous passes, and deformed more.

Using helium as carrier gas for coatings with milled particles the hardness showed a descending trend through the coating layer thickness, with increasing
distance from the coating/substrate interface. For the first passes of the sprayed milled particles, bonding was formed through deformation of the soft aluminum substrate. Excessive impact velocity of the milled particles in the subsequent passes resulted in larger deformation of the initial layer(s), which further increased the hardness of the first layers. However, particles sprayed in later passes either bounced back or underwent insufficient plastic deformations upon impact. This resulted in a softer microstructure and lower hardness in the coatings away from the interface with the substrate.

6.2 Salient Points

hBN-Ni is a very special system, where the core (hBN) has a soft and deformable microstructure, and the encapsulating nickel is amorphous and initially ductile. The test results supported the proposed hypothesis for bonding mechanism of hBN-Ni parties with aluminum 6061 substrates in cold spray; namely, bonding as well as cold spray deposition efficiency primarily depends on the initial ductility of the cold sprayed particles. By increasing the initial hardness of the nickel in the milled particles, and therefore reducing their capability to have significant plastic deformation during cold spray, the coating layer thickness was reduced. Increasing the level of hardness of the particles by continuing ball milling for longer durations resulted in a more problematic coating layer with a large amount of pores and poor interlocking between the particles.

Aside from increasing the initial hardness, ball milling also resulted in a more uniform size distribution for the particles, with smaller particle sizes. The effect of reducing particle size was examined by many other researchers (e.g. Champagne et al. 2010, Bae et al. 2010) and was found to positively affect the efficiency of coating by increasing the impact velocity of the
particles. The present study conversely showed that although the milled particles had smaller sizes, resulted in poorer coatings with smaller thicknesses and larger amounts of pores in the cold sprayed layers. In other words the adverse effects of increasing the initial hardness in the milled particles were so high that they outweighed any possible improvements in the coatings expected from the reduced particle size.

6.3 Recommendations for Future Studies

This study investigated the effect of increasing initial hardness in hBN-Ni particles through ball milling. Results showed that unexpectedly high bond strength of those particles cold sprayed to aluminum was related to the initial ductility and potential hardenability of the deposited nickel. Based on this understanding the following should be investigated in future studies:

- For the bond strength tests, only 3 specimens were tested for each type of coating powder due to budget limitations and time constraints. Especially the production of ~400 g of nickel encapsulated hBN for each cold spray run proved to be time consuming and costly. More specimens need to be tested in the future because of the large scatter of some test results.

- More studies are required to investigate the effect of decreasing the initial ductility of the particles before cold spray on the coating performance. This can be done by performing heat treatment (i.e. annealing) to reduce residual stresses in the particles.

- Additional research is suggested to further investigate the performance of different carrier gases on the coating layers. In this study nitrogen was found to have a more promising performance than helium in cold spray coating of hBN-
Ni. The main reason for this performance can be investigated through additional experimental studies with other carrier gases or combinations thereof.

- For a better understanding of the cold spray process, additional experimental and numerical studies will be needed to find the optimum velocity, to which the particles should be accelerated with the carrier gases to form strong bonds to the substrates.

- Numerical studies are recommended to simulate the effect of particle hardness on plastic deformation of substrate and particles during cold spray.
References


3. ASTM G133-05 (ASTM 2010), Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear. West Conshohocken, PA.


Appendix: Additional Tables

Table A-1: Polishing procedure used for samples

<table>
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<th>Silicon Grind</th>
<th>Lubricant</th>
<th>Force</th>
<th>Direction</th>
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<td>5-10 N</td>
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<td>5-10 N</td>
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<td>Direction</td>
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<td>alcohol based lubricant</td>
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<td>Direction</td>
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Table A-2: Bond strengths, cold spray with nitrogen and helium

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<th>Diameter Ave (MPa)</th>
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<td>44.09</td>
<td>10.57</td>
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<td>Max Stress (ksi)</td>
<td>Stan. Dev</td>
<td>Diameter</td>
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CURRICULUM VITAE
Maryam Neshastehriz
neshastehriz@gmail.com
(814) 769-3522

EDUCATION

- PhD, Engineering Science and Mechanics, Pennsylvania State University, University Park, August 2014.
- M.Sc., Amirkabir University of Technology, Tehran-Iran, Fall 2007.
- B.Sc., Isfahan University of Technology, Isfahan-Iran, Fall 2004.

PUBLICATIONS AND PRESENTATIONS

- Papers

- Conference Presentations

AWARDS

- Best paper award in CERS 2013, for paper entitled: “Cold Spray Coating on Aluminum Substrates with Nickel Encapsulated hBN Lubricant Particles”.
- Best poster award in ESM Today 2013, for poster entitled: “Synthesis of Nickel-Encapsulated Particles for Deposition with Cold-Spray”.
- Second best poster award in ESM Today 2014 for poster entitled: “Microstructures of Ball Milled hBN-Ni Cold Sprayed onto an Aluminum Substrate”.