ENGINEERED SELF-LUBRICATING COATINGS

UTILIZING COLD SPRAY TECHNOLOGY

A Thesis in
Engineering Mechanics

by
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ABSTRACT

It is often beneficial to modify the surface of engineered components to gain desirable properties, such as improved wear resistance. One fabrication method is to apply a coating with these desirable properties. Self-lubricating coatings can improve the performance of contacting surfaces and extends a part’s lifetime by reducing the coefficient of friction and specific wear rate. In this study, self-lubricating coatings of hexagonal boron nitride particles in a nickel matrix were investigated and optimized to improve wear resistance.

These self-lubricating coatings were fabricated by high velocity particle consolidation (Cold Spray) of hexagonal boron nitride powder encapsulated by nickel and nickel-phosphorous alloys. The nickel encapsulation, via electroless nickel plating, gives the particles desirable properties for the cold spray process. In fact, this ductile nickel encapsulation protects the brittle boron nitride and allows particle deformation, which is critical for the success of cold spray deposition. The resulting nickel coating contains imbedded lubricant particles, which are released during intimate contact with a surface. The release of the lubricant particles reduces the interaction between mating materials and the potential for wear.

Hexagonal boron nitride particles have been successfully encapsulated through the electroless nickel deposition procedure resulting in powder of 20 micron mean particle size. The powder was successfully deposited by cold spray on aluminum 6061 substrates. The wear properties of the coatings were tested and compared to a pure nickel cold sprayed coating. The results showed that incorporating an optimal amount of
hexagonal boron nitride in the nickel coating will reduce the coefficient of friction and the wear rate. Coatings were tested via reciprocating ball-on-flat wear, sliding pin-on-disk wear, and fretting. Hexagonal boron nitride particles embedded in the coating were characterized through optical microscopy, scanning electron microscopy, energy dispersive x-ray spectroscopy, focused ion beam, micro hardness, and density.
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Chapter 1: Introduction

1.1 Purpose

It is often beneficial to modify the surface of engineered components to gain desirable properties from the material. Self-lubricating coatings can improve the performance of contacting surfaces and allow for an extended lifetime by reducing the coefficient of friction and increasing wear resistance. The purpose of this study was to investigate and optimize self-lubricating coatings that reduce wear between mechanical surfaces. Self-lubricating coatings were deposited by high velocity particle consolidation (Cold Spray) of hexagonal boron nitride encapsulated by nickel. Nickel encapsulation, via electroless Ni plating, gives the particles desirable properties for use with the cold spray process. The nickel protects the brittle boron nitride and allows particle deformation, both of which are critical to the success of cold spray coatings. Coatings of this kind have been shown to reduce the coefficient of friction and the surface wear.

1.2 Thesis Outline

Background information in the form of a literature review is found in Chapter 2. In this chapter, topics are described such as wear mechanics, lubrication, electroless nickel deposition, cold spray technology, and effects of phosphorous. Chapter 3 describes the experimental procedures that were following throughout this study, including electroless nickel encapsulation of hBN particles, deposition of cold spray coatings, and evaluations of coating properties. Chapter 4 describes all analyses of
powders and coatings and discusses the results of all coating tests. All conclusions are summarized in Chapter 5, as well as, recommendations for future work.
Chapter 2: Background

2.1 Wear Mechanics and Lubrication

2.1.1 Wear

Wear is the removal of material from solid surfaces as a result of one contacting surface moving relative to another. There are several general wear mechanisms: adhesive wear, abrasive wear, erosion, corrosion wear, and surface fatigue. Adhesive wear occurs when surfaces are metallurgically compatible. These surfaces may form bonds which can break outside the original interface, causing disruption and damage [1]. Furthermore, dislodged fragments within the interface can cause scratches or scuffs. Abrasive wear occurs when one surface is penetrated by a harder body during cutting actions, particles moving over a surface, or hard particles moving between two surfaces [2]. Material loss during surface contact with a fluid containing solid particles is defined as erosion. Corrosive wear occurs when chemical reactions alter the surface. The most common corrosive reaction is the formation of an oxide on the surface of a material. On undisturbed surfaces, oxidation is usually a self-limiting process. However, when surfaces are in contact the oxide layer can be shed and the reaction allowed to continue. Surface fatigue can occur when a surface is subjected to severe loads; for example, a ball rolling creates a concentration force applied to the surface, which may cause surface failure. [2]
Often wear is caused by a combination of mechanisms. Fretting wear results from small amplitude, high frequency, oscillatory slip motion between two solid surfaces in contact [3]. Fretting wear is a combination of abrasion, adhesion, and corrosion [2], which produces failure due to the production of debris material or the initiation and propagation of fatigue cracks. This small amplitude motion allows solid lubricants to remain in the immediate contact area, encouraging the success of the lubricant particles [4].

Wear is characterized, among other things, by the relationship between the two opposing properties of ductility and hardness [5]. A surface with a higher ductility will be allowed to plastically deform before fracturing. Wear can also be reduced by increasing the surface hardness which effectively reduces the ductility; however, a hard surface can still cause wear to the mating pair emphasizing the need for lubrication [2], [6].

The coefficient of friction is often used to measure the potential for wear on a surface. Electrostatic, capillary, and Van der Waals surface forces can significantly impact the friction of surfaces and wear properties [7]. Many assume that the coefficient of friction is dependent upon the surface roughness; however, this relationship is often weak because surfaces with minimal roughness may have a very high coefficient of friction due to the increased surface contact area while very rough surfaces may also have a high coefficient of friction due to the energy needed to overcome the asperities [8].
Lubrication

Lubricants are used to facilitate the freedom of relative motion between two surfaces. Lubricants are most commonly semi-solids or liquids but they may also be solids or gases. They are essential for increasing product lifetime by decreasing the coefficient of friction and the specific wear rate. All phases of lubricants share the properties of low shear strength and high compressive strength. These properties make the lubricant the weakest material within the interface, thereby decreasing the coefficient of friction. Lubricants can also form a monolayer on the surface of a material, which decreases the adhesion between two metallurgical compatible surfaces [9]. In extreme pressure applications, fatty acids are added to oil lubricants as a chemical contaminate to the metal surface that creates a protective layer after the oil has been squeezed out. [8] Solid lubricant particles can also be added to liquid or semi-solid lubricants to increase efficiency.

Solid lubricants can be used to provide durable lubrication in applications where liquids are not practical. Solid lubricants must be soft, shear easily, and be impervious to chemical or structural changes during the course of their application and throughout their lifetime as a lubricant [10]. Common solid lubricants are hexagonal boron nitride, molybdenum disulfide, and carbon-derived materials. Most solid lubricants have laminar structures with stacked atomic planes of loosely held van der Waals bonds. It is believed that shearing of those planes is assisted by dislocations in the crystalline structure [11]. Solid lubricants generally have a coefficient of friction between 0.002 and 0.2 depending on the application and the environment. [12]
Unlike oil or grease, solid lubricants have virtually no tendency to flow or creep. Therefore, they can be sustained for a longer time period and are less likely to contaminate their environment. During sliding motions, chemical interactions take place between the solid lubricant particle and the sliding surface, creating bonds which help to dissipate energy and hold the particle in place for a longer lasting effect [12]. Many solid lubricants are effective at extreme temperatures, in radioactive or reactive chemical environments, under high loads, at low speed, or under vibrations. In addition, solid lubricants have low volatility and, depending on the lubricant, can be used in a vacuum.

Despite these benefits, solid lubricants are not adequate for all environments due to the difficulty of replenishment and poor thermal conductivity. The most important concern with using solid lubricants with metals is the differences in thermal expansion, which may lead to clearance loss during temperature change. [13]

Many solid lubricants, such as graphite, molybdenum disulfide, and boron nitride are sensitive to their environments. For instance, graphite and boron nitride lose their lubricious properties in a vacuum, due to the lack of vapor particles that assist in the process; while molybdenum disulfide performs significantly better as a lubricant under dry conditions [14] [15]. Additives are sometimes used to increase the lubricious properties in unfavorable environments. For example, polytetrafluoroethylene, hydrophobic by nature, improves the properties of molybdenum disulfide in humid conditions and the addition of fluoride to graphite increases the lubricious properties by replacing the carbon bonds to create weaker bonds between atom planes. [7]

Lubricant particle size and orientation are important properties to consider for optimization. When solid lubricants are ground to a smaller particle size, the proportion
of exposed crystalline edges to laminar layers increases, which consequently increases the abrasion and wear. If laminar particles lose the plate-like shape, they are more likely to not lie flat, decreasing their efficiency as a lubricant particle [13], [16], [17]. The preferred particle size for lubrication purposes is between one and four microns. For adequate lubrication of these laminar structures, it is also important that atomic planes be positioned parallel to the surface to allow for maximum shear; otherwise, these solid particles may act as abrasives [13]. Hence, to choose the appropriate lubricant, it is important to understand the surfaces in which it will contact, the environment in which it will operate, and the type of application that it will be used for.

2.1.2.1 Hexagonal Boron Nitride

Hexagonal boron nitride (hBN) is a laminar structured lubricant very similar to graphite, and is sometimes referred to as "white graphite". Its two dimensional covalent bonds between boron and nitrogen, shown in Figure 2-1, create strong layers that are stacked and held together by weak Van der Waals forces. Graphite and hBN are both highly efficient lubricants; however graphite is a conductive material, whereas hBN is an insulator at room temperature [18]. The conductive nature of graphite results from p-bonding and p-antibonding bands that slightly overlap at the Brillouin-zone boundary, while hBN’s bands are well-separated. The crystallochemical features of boron nitride results in a Mohs hardness (HM) of approximately 290 for its cubic form and 1.65 in the hexagonal crystalline structure [19]. Hexagonal-BN is stable at temperatures up to approximately 1000°C, making it useful for many mechanical applications [12].
2.2 Electroless Nickel Encapsulation

Electroless plating is a process by which catalytic metals can be deposited onto a substrate by reducing a metal salt solution. The success of the deposition depends on the combination of many parameters including, pretreatments, composition of the plating bath, pH, temperature, compatibility of depositing metal with the substrate, particle size, and particle distribution [21], [22].

While there are many different compositions of electroless plating baths, all baths must contain at least the following: nickel ions, a reducing agent, a complexing agent, and a bath stabilizer. Good sources of nickel ions include nickel chloride or nickel sulfate. Reducing agents provide the source of electrons needed for the reaction [23]; hypophosphite is one of the strongest reducing agents and can be used in the form of}

Figure 2-1: Hexagonal boron nitride atomic structure [20]
sodium hypophosphite or sodium borohydride [24]. Complexing agents form a complex with the nickel and prevent excessive free nickel ion concentration, which stabilizes the solution and acts as a pH buffer. In alkaline hypophosphite baths, ammonium acts as a complexing agent [24]. Stabilizers, like sodium citrate, are added to the nickel plating bath to delay or prevent unwanted homogeneous reactions that may cause subsequent decomposition of the entire nickel solution. An increase in the concentration of stabilizers causes a decrease in the nickel deposition rate [25].

Pre-treatment of the substrate is important due to the sensitivity of the electroless procedure. Debris on the substrate must first be removed by washing in an acidic solution to prevent interference with the deposition process. This acid wash, usually nitric acid, will also create a hydrophilic effect that helps to disperse particles in the pre-treatment baths, better exposing the surfaces to deposition.

Further pre-treatments are necessary for non-catalytic surfaces including boron nitride and carbon derived materials. The pretreatment process can consist of a surface activation with tin ions followed by palladium ions. First, the lubricant particles are soaked in a tin chloride solution to deposit Sn\(^{2+}\) ions which sensitizes the surface. Afterwards, the lubricant particles are soaked in palladium chloride in which Pd\(^{2+}\) ions are reduced to Pd by Sn\(^{2+}\) ions, creating catalytic centers. These catalytic centers reduce the nickel ions to neutral nickel atoms during the plating process, which creates nucleation centers consisting of nickel islands. After a prolonged period of time, the catalytic centers will be covered, but nickel’s self-catalytic properties allow continuous nickel deposition until the concentration of nickel in the solution is no longer adequate. Figure 2-2 shows the pre-treatment and electroless nickel deposition process.
Two of the most important bath parameters for deposition which directly affect the coating properties, are temperature and pH. The coating thickness can be related to both the plating duration and the concentration of the nickel solution. [26], [27]

It has been shown in previous studies that when sodium hypophosphite is used in the nickel bath, phosphorus is also deposited on the surface [26]. In a study of Ni-P-Diamond composite coatings, a lower phosphorus level had minimal bonding integrity with the diamond particles when compared with higher phosphorous levels. Also, it was found that coatings with smaller (3-6 microns) diamond particles had a high wear resistance compared to those with larger (20-40 microns) diamond particles. In addition, larger diamond particles appeared to be held less firmly. It can be concluded that for
better bonding between the particle and nickel matrix, there should be an optimum ratio between the coating thickness and the particle size. [28]

2.3 Cold Spray Technology

Cold spray is a technology that forms a low porosity coating when solid-phase particles are accelerated by supersonic gas flow toward a substrate [29]. Cold spray was first developed in the mid-1980s at the Institute of Theoretical and Applied Mechanics of the Siberian Division of the Russian Academy of Science in Novosibirsk by studying particle in a supersonic wind tunnel. They discovered that at a particular velocity the particles adhered to the surface rather than abrading it [30], [31], [32].

It is essential that the particles plastically deform during the collision with the substrate to ensure bonding and the formation of a coating. A critical velocity, usually between 300 to 1200 m/s, must be met for proper attachment of the particles. Studies have shown that particle adhesion is not possible if the particles are traveling at a velocity less than the critical velocity [30], [29]. Conversely, erosion of the substrate surface or shattering of the particles can occur if the particles are traveling at a speed greater than the critical velocity.

2.3.1 Process Parameters

Compressed processing gas, usually nitrogen, helium, or air at pressures ranging between 1.4 - 3.4 MPa (200 - 500 psi), but typically around 1.7 MPa (250 psi), is heated
prior to the introduction of the particles [29]. One reason that the process gas is preheated is to soften the powder particles which increases their ductility and consequently reduces the critical velocity. The second reason for preheating is to increase the speed of sound in the process gas, illustrated by equation 2.1, where $\gamma$ is the ratio of the constant pressure and constant volume gas specific heats (approximately 1.4 for a diatomic gas, 1.67 for a monatomic gas), $R$ is the universal gas constant (8.314 J/mol-K), $T$ is the absolute temperature and $M$ is the gas molecular weight.

$$V_s = \sqrt{\frac{\gamma RT}{M}}$$

(2.1)

Shown in Figure 2-3 is the effect of temperature on commonly used process gases. It can be seen that helium, with a low molecular weight and high specific heat ratio, can obtain a greater speed of sound. While helium is the best candidate for a process gas, the use of nitrogen will result in sufficient coating density and adhesion for many applications, and is the preferred gas due to its lower cost [33].

Feedstock powder is introduced axially and centrally into the gas flow at the gun nozzle intake. The spray gun is typically fitted with a convergent-divergent de Laval nozzle. Particles are forced by the carrier gas into the convergent section of the nozzle; upon entering the divergent section the gas expansion accelerates the gas jet and particles [30], [34].
Cold spray technology has significant advantages compared to other deposition techniques. For instance, it allows rapid deposition for coatings that are tens of microns to several millimeters thick, as well as a wide range of metals, alloys, polymers, and some powder composite materials [33]. Due to the low processing temperature, deposition takes place without vaporization or melting, which avoids oxidation and allows the coating to retain the properties of the initial particle materials. The cold spray technique also increases the number of different materials that can be deposited, including those which are thermally sensitive [30], [33]. Figure 2-4 shows a comparison between process parameters of various thermal spray techniques and the advantages of cold spray.

**Figure 2-3:** Comparison between common process gases speed of sound as a function of temperature [33]
2.3.2 Bonding Mechanism

The bonding mechanisms of cold spray coatings are not well understood. However, it is thought that the high velocity impact disrupts the oxide layer and allows for intimate contact between the powder and substrate’s atomic structure under temporarily high interfacial pressures and temperatures [36], [37].

A particle traveling at its critical velocity will undergo plastic deformation and form a coating after impacting the substrate. A scanning electron micrograph reveals that a ring forms around the impacting particles [38]. Shown in Figure 2-5 are the profiles for stress and strain versus radial path distance. For the impact velocity of 300 m/s, an monotonic increase in stress as the particle approaches the interface is a result of hardening effects due to the high strains at the interface. A softening effect due to
adiabatic heating occurs when the particle velocity is increased to 900 m/s, which can dominate against the hardening effects seen at slower impact speed [38].

![Graph](image)

Figure 2-5: Calculated profiles of A) plastic strain and B) flow stress along the radial path for velocities of 300 and 900 m/s [38]

2.4 Self-lubricating Coating Studies

Self-lubricating coatings have been studied in recent history for their potential to reduce maintenance and extend the lifetime of mechanical compounds. Coatings have typically utilized moly disulfide (MoS₂) or graphite to gain lubricious properties. Coatings can be deposited via magnetron sputtering, vapor deposition, electroless plating, and electroplating, among other methods [39], [6].
It has been shown that electroless Ni-P coatings have excellent corrosion and wear resistance. Incorporation of lubricant particles into electroless coatings is important to protect the mating material from the hard electroless coating. Coatings incorporating nano-MoS$_2$ in a nickel matrix have been found to decrease corrosion resistance but significantly decrease the coefficient of friction when compared to electroless coatings without the lubricant nano-particle [40].

It has been shown in previous studies that the content of electroless Ni-P coatings are greatly influenced by the bath parameters including; temperature, pH, and concentration of solution chemicals. Electroless depositions from alkaline hypophosphite baths produce Ni-P alloys with a 3-15% phosphorous content. [24] The final coating content and morphology effects the wear resistant properties of the coatings. Generally, it is accepted that the microcrystalline, amorphous or a co-existence of the two phases can be obtained depending on phosphorus content [41]. Moreover, it has been shown that coatings which have been annealed after coating alter their crystalline structure and increase the wear resistance [21], [42], [43]. Coatings that were heat treated at 400°C produce deposits of Ni$_5$P$_2$, Ni$_2$P and NiP$_2$ as major compound constituents [21].

Electroless coatings have demonstrated a lower coefficient of friction at higher loads. The friction coefficient range has been shown to be 0.15-0.35 when tested under a 15-60 N loading condition [42]. Also coatings with a higher phosphorous content have been shown to exhibit higher coefficient of frictions when compared to coating with a lower phosphorous content when tested with a ramp apparatus [43].
2.4.1 Coatings Considerations

While developing a coating for a particular application, it is important to consider a variety of properties including thickness, hardness, and surface features. A thin soft coating on a hard substrate can create a shearing action and decrease the coefficient of friction and wear rate. In addition, a thick hard coating on a soft substrate will support the load of a mating surface and reduce wear [17].

Thermo-elastic properties are also important considerations for coatings. Differences in the coefficient of thermal expansion of the substrate and the coating composites cause thermal stresses in the coating upon temperature change. Thermal stresses can also be reduced by decreasing elastic modulus or optimizing the coating thickness to account for the thermal properties [17], [44].

2.5 Carbon Derived Materials

While, not investigated in this study, it is well known that many carbon derived materials have lubricious properties [45], [46], [15], [47]. Carbon nanotubes are described as a honeycomb structure that is rolled into cylinders and closed at each end [1]. Since carbon nanotubes (CNTs) were first discovered in 1991 by Iijima [48], they have been found to have super-strong mechanical properties, such as exceptionally high elastic modulus, large elastic strain and fracture stain sustaining capabilities [49], [50]. Their incredible tensile strength and low density has focused more attention on using CNTs as a structural reinforcement for materials and coatings [51], [52].
Ni-P-CNT composite coatings have been produced using electroless plating deposition on medium carbon steel substrate. The process lowers the coefficient of friction and increased the micro-hardness, thereby reducing the wear rate. Wear resistance showed a steady increase as a function of the CNT until a concentration of approximately 11%, at which point the accumulation of agglomeration of CNTs in the matrix increased the wear [53]. Similar results were recorded for samples of Ni-CNT composite electroless plated coatings on low carbon steel [54], [55].

CNT-Al composite coatings have successfully been created via the cold spray process. Although fragmentation of the CNTs took place during the high velocity impact, the CNTs improved the fracture toughness of the coating [56]. Impact fracture occurred by necking and cup-and-cone type fractures. Internal capping was formed, which indicates the tendency towards formation of more stable carbon onions [57].

Three essential obstacles exist that complicate the use of carbon nanotubes as a reinforcing additive, namely the dispersion of CNTs, the wettability of the CNTs surface, and the load transfer from the matrix to the CNTs. CNTs have a tendency to form aggregates due to their strong van der Waals interactions. These interactions can be overcome by the addition of a surfactant such as sodium dodecyl sulfate, to help separate the CNTs from each other and enhance the suspension stability of CNTs through steric hindrance. Ball milling may also help the dispersion of CNTs in the electroless bath by shortening, straightening, and forming more isolated tubes [53].
2.6 Post Process Treatments

Post process heat treatments are commonly used for coatings. For many composites, heat treatments will change the crystal structure from an amorphous to crystalline state [58]. In addition, it has been demonstrated that electroless nickel-plated carbon nanotube coatings that were heat treated for 2 hours at 673 K have a harder surface, a higher wear resistance, and a lower coefficient of friction compared to non-treated coatings. [54] Studies have also shown that heat treated electroless nickel surfaces with a high phosphorus content form fine Ni$_3$P precipitate and have better wear resistance than at lower phosphorous content [28], [59] It has also been indicated that the hardness of the Ni-P coatings degrades with excessive annealing due to grain coarsening [60].
Chapter 3: Experimental Procedure

3.1 Overview of Nickel Encapsulation: Preparation and Procedure

3.1.1 Introduction

All electroless deposition experiments used the same boron nitride powder preparation procedure, nickel solution chemicals, and equipment. However many experiments vary in chemical concentrations, electroless nickel deposition procedure, agitation techniques, temperature, and deposition time. These differences allow for unique deposition properties.

3.1.2 Equipment

All chemicals weighing more than 10 grams, including sodium hypophosphate, sodium citrate, and nickel (II) sulfate, were evaluated on a Mettler PJ6000 digital scale (0.0-6000.0g), while chemical measurements that required more precision, including those for the lubricant particles and the palladium (II) chloride, were assessed on a Mettler AE200 digital scale (0.0000-200.0000g).

Clean laboratory beakers, flasks, and graduated cylinders were used in all stages of nickel deposition. The size of the deposition bath glassware was dependent upon the experiment conducted and varied between a 500 ml beaker, a 1000 ml beaker, and a 4 L
Erlenmeyer flask. During solution preparation, the pH was measured using BDH-35312.607 pH strip indicators.

Solution agitation was achieved by using an ultrasonic unit, a mechanical stirrer, or a combination of both methods. The ultrasonic unit initially used was the Branson 5510; when larger quantities of powder were being produced the Branson 8570, was used. A Barnant Series 10 mechanical stirring unit was used to mechanically stir the nickel bath until it was replaced by the VWR VOS 16 (40-1200/min).

Powder filtration was required at various stages of processing. For this purpose a filtration unit was setup with Supor®200 0.2 µm membrane filter paper and a Welch 1405 vacuum pump. After it began to malfunction, this vacuum pump was replaced with a KNF Lab Filtration Pump. All powder was dried in a Lindber Blue M oven at temperatures between 80-90℃.

### 3.1.3 Cleaning Standard

Proper cleaning of all glassware, thermometers, and stirrers was important for the success and repeatability of the metal deposition. Failure to properly clean all exposed surfaces can result in significant deposition on the glass instead of on the substrate.

All glassware, thermometers, and stirring rods were cleaned by a two-step standard process. Cleaning Standard 1 was a basic solution prepared with five parts distilled water, one part 30% hydrogen peroxide, and one part 30% ammonium hydroxide, used to remove all organic contaminates. An appropriate amount of Cleaning Standard 1 was placed in the glassware, with all exposed sides covered. The thermometer and stirring rods were also placed in the glassware during cleaning. To
complete the process, the cleaning solution was heated to 60-70°C using a hot plate for at least 10 minutes. The cleaning solution was then removed and allowed to cool in a separate container. All glassware were then rinsed at least three times with distilled water. The procedure was then repeated using Cleaning Standard 2 to remove all metallic contaminates; Cleaning Standard 2 was an acidic solution of six parts distilled water, one part 30% hydrogen peroxide, and one part 30% hydrochloric acid. This solution was heated to 60-70°C for at least 10 minutes and the glassware was again rinsed with distilled water at least three times. Cleaning standard solutions were reused for several cleanings before discarding.

3.1.4 Powder Substrate Preparation

Proper lubricant powder preparation was necessary for the success of the electroless nickel deposition reaction. Firstly, the lubricant surface must be clean of all contaminates. Non-active surfaces, like boron nitride, must be pre-treated to create a catalytic surface and allow for nickel nucleation. This sensitization is done by depositing tin ions followed by palladium ions to the surface of the boron nitride. Often a bulk quantity of powder was pre-treated for the purpose of dividing it into several nickel encapsulation experiments.
3.1.4.1 Acid Wash

Nitric acid was used to clean contaminants from the surface of the lubricant particles and to create a hydrophilic surface favorable for deposition. To begin the process, the lubricant was placed in a beaker with a 5:1 70 % nitric acid to powder ratio and allowed to sit for at least 30 minutes. Next, filtration was necessary to remove the cleaned lubricant from the solution. To prevent damage to the filtration system, the solution was diluted by at least half with distilled water by pouring the acid-substrate solution into a clean beaker of dH₂O. To promote a faster filtration time, the powder was allowed to settle to the bottom of the beaker before the solution was slowly poured into a vacuum filtration system. The powder retained on the filter paper was rinsed at least three times with dH₂O then placed in the oven to dry overnight at approximately 80-90℃.

3.1.4.2 Tin Sensitization

Deposition of a catalytic layer of tin ions on the surface of the powder was required for the sensitization of that surface; therefore, the lubricant powder was bathed in a 0.044 M tin (II) chloride-0.12 M HCl solution. To prepare the solution, 9.928 g of stannous chloride dehydrate were dissolved in approximately 500 ml dH₂O, before 40 ml of 3 M hydrochloric acid were added. The solution was diluted with additional dH₂O to a total volume of 1000 ml. The solution, which has a working shelf-life of two weeks, was divided into aliquots for the various experiments.
The sensitization solution was warmed in a clean beaker on a hot plate to approximately 25°C prior to the addition of the lubricant. Agitation by mechanical stirring, ultrasonic vibration or a combination of both was used during the bath duration, which varied between 8 and 90 minutes for each experiment. The solution was then filtered with a vacuum filtration unit and the filtered powder was dried in an oven at 80-90°C before proceeding.

3.1.4.3 Palladium Activation

Tin ions on the lubricant surface provide deposition sites for palladium ions and create a catalytic surface ideal for nickel deposition. To achieve the catalytic surface, the tin-activated lubricant powder was bathed in 5.6 x 10^{-4} M palladium-0.12 M hydrochloric acid solution. The solution was prepared by first dissolving 0.0993 g palladium (II) chloride in approximately 500 ml of dH_2O. After the palladium chloride was dissolved, 40 ml of 3 M hydrochloric acid were added, and then the solution was diluted with dH_2O to a final volume of 1000 ml. When necessary, the solution was heated slightly to aid in the dissolution of the palladium chloride. The resulting solution, which had a shelf-life of two weeks, was divided into aliquots for use in the various experiments.

To bathe the tin activated lubricant powder, the palladium chloride solution was warmed to approximately 25°C in a clean beaker on a hot plate. The powder was placed in the solution and agitated by mechanical stirring, ultrasonic vibration, or a combination of both. Bath duration varied between 8 and 90 minutes per experiment. After the
appropriate bath duration the powder was filtered using a vacuum filtration unit. Afterwards, the filtered powder was placed in an oven at 80-90℃ until completely dry.

3.1.5 Electroless Nickel Encapsulation

All electroless deposition experiments use the same basic nickel solution chemicals, but the chemical concentrations, procedure, agitations techniques, temperature and deposition times were varied. The majority of the electroless nickel deposition experiments evaluated in this study can be divided into two main categories: one-solution deposition methods and two-solution deposition methods. One-solution deposition methods were explored initially but yielded minimal nickel deposition. Two-solution deposition methods were investigated to attempt to create thicker nickel coatings. Two solutions were necessary due to the size limitations of the laboratory scale deposition baths and the excessive reactivity of the concentrated nickel deposition solution.

3.1.5.1 One-solution Deposition Methods

Initially, one-solution deposition experiments used small bath volumes of 315 mL or 945 mL. Each bath solutions consisted of 0.08 M nickel sulfate hexahydrate, 0.20 M sodium hypophosphite monohydrate, and 0.08 M sodium citrate dehydrate. When thicker nickel encapsulation was desired, a 3 L bath volume was used with a bath solution of 0.16 M nickel sulfate hexahydrate, 0.40 M sodium hypophosphite monohydrate, and 0.16 M sodium citrate dehydrate. Each deposition solution was prepared by measuring the required quantities of nickel sulfate hexahydrate, sodium hypophosphite monohydrate,
and sodium citrate dehydrate and placing them in either a beaker or an Erlenmeyer flask with warmed dH₂O to the appropriate concentration. The pH of the solution was then increased to approximately 10 S.U. by adding ammonium hydroxide. The solution was agitation immediately after the desired amount of treated hBN was added to the deposition solution. The solution was monitored every ten minutes visually and with a thermometer. A digital timer was used to record the deposition time for each experiment. The amount of time required for the solution to reach an appropriate temperature and to react was unique for each experiment. After encapsulation was complete, the powder was filtered using a vacuum filtration system and dried overnight in an oven at 80-90°C.

3.1.5.2 Two-solution Deposition Methods

Two-solution deposition methods were used when a thicker nickel coating was desired. Moreover, this process was also required due to the reactivity of the solution at that concentration and the laboratory scale limitations to volume. Two-solution deposition methods began with a warmed bath containing approximately 0.19 M nickel sulfate hexahydrate, 0.48 M sodium hypophosphite monohydrate, and 0.19 M sodium citrate dehydrate in a 4 L Erlenmeyer flask. The solution pH was raised to approximately 10 S.U. by adding ammonium hydroxide. Next, the Erlenmeyer flask was placed in a warmed ultrasonic bath. A polypropylene dual propeller stirring rod attached to a mechanical stirring motor was placed in the solution. Using a digital scale, the treated hBN was weighed in a plastic weigh boat and then added to the deposition bath. The weigh boat was rinsed with dH₂O to ensure that all of the powder was added to the
solution. A digital timer was set and the temperature was recorded periodically throughout the deposition process.

After the start of the nickel deposition reaction was observed, the second solution was prepared. The second more concentrated solution consisted of 2.00 M sodium hypophosphite monohydrate and 0.80 M nickel sulfate hexahydrate. It was not necessary to add the sodium citrate dehydrate stabilizer to the second solution due to the excess of stabilizer in the first solution. The pH of this second solution was raised to 10 S.U. by the addition of ammonium hydroxide. After the second solution was prepared, it was slowly added to the first solution in 100 mL aliquots at 10 minute intervals. At all times, the bath was closely monitored to ensure that the desired reaction occurred after each aliquot of solution was added. This process continued for 60 minutes, at which point all of the second solution had been added. The deposition was allowed to continue overnight until no further reaction could be observed.

3.2 Individual Nickel Encapsulation Experiments

3.2.1 Activation of hexagonal boron nitride

A bulk amount of hBN was activated for the purpose of the experiments to follow. The procedure stated in Section 3.1.4 was used for the activation of 16 g of hBN by the specifications in Table 3-1.
### Table 3-1: Experiment 1 specifications

<table>
<thead>
<tr>
<th></th>
<th>Solution</th>
<th>Duration</th>
<th>Agitation</th>
<th>Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Wash</td>
<td>450 mL</td>
<td>4 hr 30 mins</td>
<td>none</td>
<td>Room</td>
</tr>
<tr>
<td>Tin Sensitization</td>
<td>1000 mL</td>
<td>31 mins</td>
<td>Ultrasonic</td>
<td>26.0</td>
</tr>
<tr>
<td>Palladium Activation</td>
<td>1000 mL</td>
<td>10 mins</td>
<td>Ultrasonic</td>
<td>24.1</td>
</tr>
</tbody>
</table>

The success of this first activation experiment led to similar activations of hBN when more lubricant was needed for encapsulation experiments.

#### 3.2.2 Experiment 1: Small Bath Volume

The first electroless nickel encapsulation experiment was based on previous hBN encapsulation research done at Penn State using 315 mL of electroless nickel solution and encapsulated 20 micron hBN [61], [62], [63]. Due to the smaller particle size of the current hBN and consequently the larger surface area, the recipe was tripled.

A 945 mL solution was in a 4 L Erlenmeyer flask was created consisting of 19.88 g of nickel sulfate hexahydrate, 20.03 g of sodium hypophosphate monohydrate and 22.23 g of sodium citrate dehydrate in distilled water. Approximately 150 drops of ammonium hydroxide was added from a disposable pipette to increase the solution pH to between 9.1 and 9.5.

The Erlenmeyer flask was then placed in the heated ultrasonic bath. The 5.04 g of hBN was added to the solution and stirred until powder was completely dispersed. The solution was allowed to sit in the bath for 3 hours. After the completion of the reaction, the solution was filtered using the vacuum filtration unit and placed in an oven overnight to dry.
3.2.3 Experiment 2: First Deposition Using Hot Plate

A significantly greater solution to hBN ratio was used in the second experiment to allow for more nickel deposition on the particles. A 4 L Erlenmeyer flask was cleaned using the cleaning standard solutions 1 and 2, then 126.3 g of nickel sulfate hexahydrate, 126.8 g of sodium hypophosphate monohydrate, and 141.1 g of sodium citrate dehydrate were added to the flask. Distilled water was added to create a total solution volume of 3000 mL. As in previous experiments, the pH of the nickel solution was raised to 10 S.U. by adding ammonium hydroxide. Next, 0.1 g of treated hBN was added to the bath and the flask was placed in a 19°C ultrasonic vibrating bath. The solution was then mechanically stirred and heated.

3.2.4 Experiment 3: Second Deposition Using Hot Plate

Experiment 2, described in 3.2.3 was moved to a hot plate to aid in the solution heating process; however, during the transition from the ultrasonic bath to the hot plate, the stirring rod was not placed back into the Erlenmeyer flask during the critical beginning stages of the reaction. The current experimental procedure was identical to the previous, in Section 3.2.3, except that the stirring rod was transferred to the hot plate with the Erlenmeyer flask and was utilized when the reaction began. This agitation is important for the break up and separation of the hBN particles during deposition and preventing agglomerates of hBN particles being encapsulated.
3.2.5 Experiment 4: Deposition Leading to Series A

Previous one-solution deposition methods successfully encapsulated hBN particles with a thin layer of nickel; however it was important to increase this thickness of the layer. This experiment utilized the two-solution deposition method in an attempt to deposit a thicker nickel coating.

In the first step of the experiment, 126.3 g nickel sulfate hexahydrate, 126.8 g sodium hypophosphite monohydrate, 141.1 g sodium citrate dehydrate, and 2250 mL distilled water were combined in a 4 L Erlenmeyer flask. The solution pH was increased to approximately 10 S.U. by adding 55 mL of 30% ammonium hydroxide. The Erlenmeyer flask was placed in an ultrasonic bath and a polypropylene dual propeller stirring rod attached to a mechanical stirring motor was inserted to agitate the solution. A digital scale and plastic weight boat were used to weigh 0.1 g of treated hBN powder. The treated powder was added to the deposition bath and the weigh boat was rinsed with dH₂O to ensure that all of the powder was transferred to the flask. A digital timer was set and the temperature was recorded periodically throughout the deposition period.

After the observation of the nickel deposition reaction, the second solution was prepared. The second solution was more concentrated, and consisted of 126.8 g sodium hypophosphite monohydrate and 126.3 g nickel sulfate hexahydrate in 400 mL of distilled water. The pH of this solution was increased by the addition of 95 mL of 30% ammonium hydroxide. Once the second solution was prepared, it was slowly added to the first solution in 100 mL increments at 10 minute intervals. The bath was closely monitored to ensure that the reaction was occurring after each increment of solution was
added. This process continued for 60 minutes, at which point all of the second solution had been added to the first. Deposition was allowed to continue overnight until no further reaction could be seen, then the solution was filtered and the powder was dried in an oven overnight.

3.2.6 **Series A Feedstock Cold Spray Powder**

The success of the first two-solution deposition method, described in Section 3.2.5, created a need for a bulk supply of this powder for cold spray. Thirty-two batches of this powder prepared using the procedure described in 3.2.5 were combined and labeled as Series A feedstock cold spray powder. During the production of this bulk supply, pre-heating modifications were made to the procedure to reduce the processing time. For example, the distilled water in the 4 L Erlenmeyer flask was heated to 55°C prior to adding any solid chemicals and the ultrasonic bath was heated to 65°C prior to adding the flask.

Each batch was filtered in the vacuum filtration system and placed in an oven overnight. The batches were then brushed through a 425 micron sieve to eliminate any large contaminate particles, as well as, undesirably large particles that had formed on the stirring rod. Finally, the batches were mixed together in a polypropylene jar on a rotating mixer for 5 minutes prior to cold spray.

3.2.7 **Experiment 4: Deposition Leading to Series B**
After the success of the two-solution deposition method used in Series A feedstock powder, the procedure was modified to attempt to create a composite powder with a higher concentration of hBN. In this experiment, 1.0 g of hBN was added to the bath instead of 0.1 g. This was the only deviation from the previous experiment in Section 3.2.5.

3.2.8 Series B Feedstock Cold Spray Powder

After successfully increasing the lubricant content in experiment 4, described in section 3.2.7, a bulk supply of cold spray powder with this composition was created. Series B cold spray powder is a combination of 19 batches of the powder produced using the procedure described in 3.2.7. Each batch was brushed through a 425 micron sieve to eliminate any large contaminate particles and undesirably large particles. The powder was mixed on a rotating system for 5 minutes prior to use in the cold spray equipment.

3.2.9 Series A+B Feedstock Cold Spray Powder

After Series A and Series B were independently tested, a composite powder combining both was prepared. As discussed later, this exercise proved useful for a third comparison of wear data. Series A+B was created by mixing 55 wt. % Series A with 45 wt. % to Series B in a roller mixer for five minutes.
3.3 Characterization of Raw Boron Nitride, Cold Spray Feedstock Powders, and Cold Spray Coatings

All raw boron nitride, electroless nickel encapsulated powder, and cold sprayed coatings were characterized using a variety of methods including optical and scanning electron microscopy, energy dispersive x-ray spectroscopy, focused ion beam, particle size analysis, density, and Vickers hardness.

3.3.1 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

A scanning electron microscope (SEM) was used to obtain visual images and energy dispersive x-ray spectrums to characterize the raw boron nitride and the electroless nickel encapsulated boron nitride. To prepare the samples for analysis, a small amount of powder was placed on a disk of carbon tape and lightly tapped to remove loose powder. To analyze the boron nitride, a nonconductive material, it was necessary to sputter a thin layer of gold on the surface of the powder before analyzing it.

To analyze the nickel encapsulated boron nitride powder, it was useful to have the cross section of the powder so that the boron nitride core was exposed. The powder was prepared to be viewed with the SEM by mounting, grounding, polishing, and sputtering with gold. A cold epoxy mounting material was used to position the powder. First the powder was placed in the 2.54 cm (1 inch) mold then a small amount of the epoxy was added and stirred to create a thick paste. The mold was then filled to the top with the remainder of the epoxy resin. A vacuum was used to expel any air bubbles that had developed in the mount; the mounts were allowed to harden for 24 hours. Plane grinding
was performed to expose the cores of the powder by using 800, 1200, and 2400 grit silicon carbide paper. The grinding was performed by hand using light pressure and water for lubrication. Samples were then polished using a Struers RotoPol-22 and RotoForce-4 assembly auto-polisher with a five sample holder. Appendix A - Table A-1 shows the polishing recipe used to obtain a mirror finish. Images were obtained using a Joel 6700F Field Emission SEM, FEI Philips XL-20 ESEM, and Hitachi S-3500N SEM at various working distances and accelerating voltages.

3.3.2 Focused Ion Beam

As an alternative to mechanical grinding and polishing procedures, a focused Ion Beam equipped with a Quanta 3D 200 SEM was used in an attempt to expose the core of the nickel encapsulated boron nitride. The goal was to expose the core without the risk of dislodging the boron nitride particles.

All equipment was operated with help from the Materials Characterization Lab staff at Penn State. Initially, a strip of platinum was locally deposited via a gas injection system (GIS) on the surface of a single particle of nickel encapsulated powder; the 20 micron strip was used to focus an ion beam. Next, material was selectively removed by controlling the beam size, the location, and the current density. This sputter removal of material created a gully that was precise and had a polished smooth finish. Images were captured with an in situ scanning electron microscope (SEM).
3.3.3 Particle Size Analysis

The particle size of all boron nitride and feedstock powders was measured using a Horiba LA950; this equipment used laser diffraction to determine the particle size distribution. Both water and isopropanol were used as dispersants for comparison. Three analyses were performed for each sample and the mean value was calculated and reported.

3.3.4 Density

The density of the feedstock powders was measured with a multi-pycnometer. This equipment measures the volume of a sample by placing a known amount of nitrogen from a reference chamber into a chamber containing the sample. The recorded measurement is the pressure difference due to the gas displacement. By weighing the sample prior to measuring the volume, the density can thus be calculated. A 135 cc chamber was used for the feedstock powder. All tests were calibrated at least six times before recording volume measurements.

3.3.5 Hardness

The hardness of each cold spray coating was measured using a Leco Hardness Tester. Samples were mounted in cold epoxy, ground, and polished according to the polishing recipe in Appendix A. Measurements were taken perpendicular to the coating
surface at approximately 500 microns and 1000 microns from the surface, as well as perpendicular to the cross section of the coating. A Vickers Microhardness Indenter at 200 gf load was used for all indentations. A Leco Video Line Micrometer (VL-101) was used to measure the length of the diagonal of the indentation and to calculate the hardness.

### 3.4 Overview of High Velocity Particle Consolidation (Cold Spray) Procedure

All High Velocity Particle Consolidation (HVPC) or Cold Spray trials were performed at the Applied Research Laboratory at the Pennsylvania State University. The cold spray equipment was operated in an acoustic room supplied by Industrial Acoustics Company. Substrates were held in a vise located in a Sulzer Mecto Spray Hood with a dust collection system. The cold spray unit was equipped with an ABB, IRB2400 inverted robot that is programmed to move across the substrate while spraying. Figure 3-1 is a photograph of the automated robotic arm, vise, and ventilation system.

Most cold spray trials were performed with nitrogen as the main process gas, though some sprays used helium. The cold spray system was equipped with a dual inlet connection for both carrier gases. The gas was heated to operational temperatures of up to 500°C before the powder was introduced. The feedstock powder was placed in a heated cylindrical hopper that can be operated at up to 500-psi of pressure fitted with a Praxair powder feeder. The powder flow was integrated into a data acquisition and control system, which can monitor and adjust parameters such as the feed rate and wheel speed. A 153 mm tungsten carbide De-Laval type nozzle with a 3 mm throat was used
for all sprays. In addition, a 240-hole powder feed wheel at various powder feed rates was used within the hopper to facilitate the powder feed. Figure 3-2 shows the cold spray system schematic.

Figure 3-1: Photograph of cold spray robot and ventilation hood

Figure 3-2: Cold Spray Schematic [64]
Up to three 2.54 x 2.54 cm substrates could be sprayed at one time. The robotic arm was programmed to spray at an offset distance of 1.27 cm, a vertical speed of approximately 100 mm/second, and a horizontal spray step of 1 mm. Parameters such as the wheel speed and feed rate were adjusted depending on the flow-ability of the spraying powder.

### 3.5 Cold Spray Process Parameters for Individual Sprays

For comparison purposes, all experiments were evaluated against pure nickel powder in addition to the experimental powders. All coatings were sprayed on aluminum 6061 samples of various shapes and sizes, including thin and thick 2.54 x 2.54 cm substrates cut from a stock bar, 2.54 x 5.08 x 2.54 cm substrates, and 2.54 cm round bond slugs. All substrates were grit blasted using 16 grit alumina oxide at 0.86MPa (125psi) and a 45° angle, before being cleaned in an ultrasonic bath of ethanol for 30 minutes. Before spraying, the substrates were measured for properties including, thickness, height, width, weight, and surface roughness. Table 3-2 expresses the parameters for a variety of cold spray trials.
### Table 3-2: Parameters for a variety of cold spray trials

<table>
<thead>
<tr>
<th>Powder</th>
<th>Substrate Al 6061 (cm)</th>
<th>Carrier Gas</th>
<th>Substrate Roughness (micro-inch)</th>
<th>Gas Temp</th>
<th>Powder Feed Rate (Calculated Ave)</th>
<th>Powder Vibrator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2.54 x 2.54 x 0.64</td>
<td>N₂</td>
<td>&gt;249 (avg)</td>
<td>480 °C</td>
<td>2 rpm, 16 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>Ni</td>
<td>2.54 x 2.54 x 0.64</td>
<td>N₂</td>
<td>&gt;239 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 19.4 g/min</td>
<td>138 kPa</td>
</tr>
<tr>
<td>Ni</td>
<td>2.54 x 2.54 x 0.32</td>
<td>N₂</td>
<td>&gt;213 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 26 g/min</td>
<td>138 kPa</td>
</tr>
<tr>
<td>Ni</td>
<td>2.54 x 5.08 x 2.54</td>
<td>N₂</td>
<td>&gt;250 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 28 g/min</td>
<td>138 kPa</td>
</tr>
<tr>
<td>Ni</td>
<td>6-2.54 cm Slugs</td>
<td>N₂</td>
<td>&gt;239 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 19.4 g/min</td>
<td>138 kPa</td>
</tr>
<tr>
<td>A</td>
<td>2.54 x 2.54 x 0.64</td>
<td>N₂</td>
<td>&gt;247 (avg)</td>
<td>480 °C</td>
<td>2 rpm, 10 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>A</td>
<td>2.54 x 2.54 x 0.64</td>
<td>N₂</td>
<td>&gt;242 (avg)</td>
<td>480 °C</td>
<td>2 rpm, 6.6 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>A</td>
<td>2.54 x 2.54 x 0.64</td>
<td>N₂</td>
<td>&gt;236 (avg)</td>
<td>480 °C</td>
<td>2 rpm, 9.9 g/min</td>
<td>0 kPa</td>
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<tr>
<td>A</td>
<td>2.54 x 5.08 x 2.54</td>
<td>N₂</td>
<td>unknown</td>
<td>480 °C</td>
<td>4 rpm, 14 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>A</td>
<td>6-2.54 cm Slugs</td>
<td>N₂</td>
<td>&gt;240 (avg)</td>
<td>480 °C</td>
<td>2 rpm, 6.6 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>B</td>
<td>2.54 x 2.54 x 0.32</td>
<td>N₂</td>
<td>&gt;250 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 11 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>B</td>
<td>2.54 x 5.08 x 2.54</td>
<td>N₂</td>
<td>&gt;250 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 11 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>B</td>
<td>6-2.54 cm Slugs</td>
<td>N₂</td>
<td>&gt;250 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 11 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>A+B</td>
<td>2.54 x 2.54 x 0.32</td>
<td>N₂</td>
<td>&gt;250 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 10 g/min</td>
<td>0 kPa</td>
</tr>
<tr>
<td>A+B</td>
<td>2.54 x 5.08 x 2.54</td>
<td>N₂</td>
<td>&gt;250 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 10 g/min</td>
<td>0 kPa</td>
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<tr>
<td>A+B</td>
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<td>N₂</td>
<td>&gt;250 (avg)</td>
<td>480 °C</td>
<td>4 rpm, 10 g/min</td>
<td>0 kPa</td>
</tr>
</tbody>
</table>

### 3.5.1 Process Parameters for Layered Coating

A layered coating may be desirable for particular applications. By varying the microstructure through the hBN content, qualities of more than one coating can be utilized. This experiment was performed to ensure that a layered coating of nickel and boron nitride was possible.

A layered coating, an aluminum 6061 2.54 x 2.54 substrate was obtained by first grit blasted and cleaned. Then, a cold spray coating of nickel was applied at a thickness...
of 762 microns (0.03 inch). After this first layer was deposited, a second coating of Series A powder was sprayed at a thickness of 508 microns (0.02 inch). A cross section of the coatings was analyzed optically.

3.5.2 Process Parameters for Repairing a Wear Scar

In addition to the cold spray trails listed in Section 3.5, an additional experiment was designed to repair a wear scar that was created via a ball-on-flat reciprocating arm (see section 3.6). The specimen was a 2.032 mm (0.08 inch) thick cold spray coating of Series A powder with a wear scar. The specimen was cleaned prior to repair by soaking in an ultrasonic bath of ethanol for 5 minutes. To demonstrate the effect of repairing the damage, half of the scar was masked with an aluminum sheet during spraying. Nitrogen was used as the main process gas for the Series A feedstock powder. A coating was then sprayed at a thickness of 737 microns (0.029 inch) and the aluminum mask was removed. The repaired coating was then ground to a uniform level of the original coating to showcase the elimination of the damage.

3.6 Ball-on-Flat Reciprocating Wear

Coatings with thicknesses of at least 1.016 mm (0.040 inch) were tested for reciprocating wear according to the ASTM G-133 standard for Linearly Reciprocating Ball-on-Flat Sliding Wear. The reciprocating test equipment used was a Plint High Frequency Friction Machine connected to a WavBook data acquisition system. The data
was viewed with WavView software and analyzed with a custom algorithm, as well as Microsoft Excel.

A fixture was machined to properly hold the 2.54 x 2.54 cm samples. However in cases where the coating thickness was larger, a precision saw was used to slice a sufficient amount of substrate off the back of the sample to allow proper fit into the fixture. The fixture was placed in a stage bowl equipped with a force transducer to record the friction force. An oscillating arm fixed with a ball anchor, was set to a sliding distance of 10 mm. Figure 3-3 shows the system schematic for the ball-on-flat reciprocating wear test.

![Figure 3-3: Ball-on-Flat reciprocating wear system schematic [65]](image)

The 302 stainless steel ball specimen measured 7.94 mm (5/16 inch) in diameter. Each specimen, flat and ball, was first cleaned by soaking in an ultrasonic bath of acetone for two minutes, and then allowed to dry. Each specimen was then soaked in ethanol for two minutes and also allowed to dry. Upon placing the flat specimen in the appropriate
fixture and the ball on the end of the oscillating drive, the specimens were cleaned once more by rubbing with acetone, and then ethanol, followed by air drying. All tests were performed without oil lubrication and at room temperature. A normal force of 24 N was applied to the oscillating arm for the 17 minute test duration. The oscillation frequency was 5.0 Hz. The voltage from the friction force transducer was recorded by the data acquisition software at 250-500 Hz to ensure an adequate representation of the data.

### 3.6.1 Determining the Coefficient of Friction

The coefficient of friction allows for a simple comparison between coating properties. The data from the WavView Data Acquisition software was converted from voltage to force by using the appropriate conversions. The data was then analyzed by applying the root-mean-squared of the force for each second. This accounted for the compression and tension of the friction force transducer during forward and backward sliding. The coefficient of friction for each second of the duration of the test was calculated by dividing the friction force (F) by the normal load (N), as indicated by equation 3.1.

\[
\mu = \frac{F}{N} \tag{3.1}
\]

The average coefficient of friction for each minute was calculated and the trends were compared. Typically, the first three minutes of data were neglected due to a wear-in period.
3.7 Fretting Wear

Wear under fretting conditions was also evaluated using the Plint High Frequency Friction Machine connected to a WavBook data acquisition system. The data was viewed with WavView software and analyzed with a custom program, as well as Microsoft Excel.

Pure nickel and the series A cold sprayed coatings were evaluated for fretting wear. Tests were run at an oscillating frequency of 45.0 Hz and a sliding distance of approximately 50 microns for 12 hours and 30 minutes. A normal load of 150 N was applied to a ball specimen placed on the coating surface. The coatings were soaked in ethanol for two minutes and dried prior to testing, though no other surface modifications were performed. Friction transducer recordings were taken at a frequency of 250 Hz for 10 minutes at four time points throughout the test duration.

3.8 Pin-on-Disk Sliding Wear

A pin-on-disk assembly was used to measure sliding wear of cold sprayed coatings. The assembly consisted of a disk specimen on an axially rotating shaft attached to a variable motor. Each pin was attached to a pneumatic system of variable pressure. Figure 3-4 shows the pin-on-disk assembly where the left image shows the pin retracted and the right image shows the pneumatically engaged pin. The pin assembly height was adjustable to move the wear track and utilize the entire area of the disk for multiple tests.
Pin samples were prepared by first cold spraying a coating on a 2.54 x 5.08 x 2.54 cm aluminum 6061 substrate. The coating was then surface ground to eliminate surface pits and defects and to obtain a uniform surface roughness between samples. Then, a wire electrical discharge machine (EDM) was used to create 6.35 mm (0.25 inch) diameter pins, as seen in Figure 3-5. Before testing, the pins were then soaked in ethanol for at least 2 minutes before beginning testing. The pin was measured for weight, diameter, and length.
The disk specimen was 1020 carbonized steel of an average hardness of 60 HRC and can be seen in Figure 3-6. The surface was prepared in a lathe by cutting approximately 1.27 cm (0.05 inch) off the surface to clear it of inconsistencies and contaminates from previous sliding wear experiments.

![Figure 3-6: Disk specimen for pin-on-disk sliding wear mounted on lath for surface preparation](image)

Tests were performed at a constant sliding speed by varying the rotational speed of the disk as a function of the wear track radial position. A strobe light of variable frequency was used to visibly set the appropriate rotational speed.

A load of approximately 4.53 kg (10 lbs) was applied to the pin; this load was measured with a load cell at the pin contact area prior to testing samples. Each sample was tested at a unique radial position on the disk to prevent contamination of samples.
The pneumatically engaged pin was manually held within a few millimeters of the rotating disk before being released and beginning the test. This technique improved the accuracy of the timed release by reducing the engaging duration as well as decreased the impact force. The pin was allowed to contact the disk for a set duration before disengagement. The pin was then removed, weighed, and the length measured in three radial locations. The test continued until a set cumulative sliding distance was achieved or wear had penetrated to substrate.

### 3.9 Bond Testing

The adhesive strength of each coating was measured by following ASTM-C633-1: Standard Test Method for Adhesion or Cohesion Strength of Thermal Spray Coatings. Cylindrical bond slugs of Al 6061 were used for all tests. Bond slugs measured approximately 3.56 cm (1.4 inches) long and had a diameter of 2.54 cm. Each bonding test used sets of six samples.

Bond slugs were prepared by grit blasting using 16 grit Al₂O₃, at 125 psi at a 45° angle. Each bond slug was then cleaned by soaking in an ultrasonic bath of ethanol for 30 minutes. A custom fixture was used to hold the bond slugs during cold spray to ensure equal coating on each bonding surface. The length of the bond slug before and after coating was measured at four independent positions and averaged. Using this data, the average coating thickness for each slug was also calculated. Coatings greater than 762 microns (0.030 inch) were obtained for each test series. The coatings were then surface ground to the desired thickness of 508 microns (0.02 inch). Digital images were
taken before and after surface grinding to document the uniformity of the surface preparation.

Next, each coated bond slug, as well as a mating slug of the same size was lightly grit blasted with Trin Blast -16 at 40 psi and a 45° angle. All slugs were cleaned a final time by soaking in an ultrasonic ethanol bath for 5 minutes. Bond slugs were mated by placing a sheet of Cytec Engineered Materials FM1000 adhesive film between the coating and the adjoining slug. The slugs were then placed in a custom fixture that utilized a spring to maintain compression. The entire fixture was placed into the oven for 4 hours at 204°C. Before the bond slugs were released from the fixture, the oven was then shut off and allowed to cool overnight. The slugs were examined to ensure that the mating was successful.

Testing was performed at room temperature on a 584 Instron Tensile Machine. All tests were performed at a displacement army of 1.27cm/min (0.05 in/min); the maximum tensile strength was obtained and the type of failure was examined. Photographs were also taken to document the failure mechanism for each tensile test.
4.1 Electroless Nickel Encapsulation

4.1.1 Characterization of Boron Nitride

As already discussed, hexagonal boron nitride (hBN) was used as the solid lubricant for the self-lubricating coatings in this study and was supplied by Atlantic Equipment Engineers. Figure 4-1 shows an SEM image of the as-received hBN. Hexagonal boron nitride particles are small disk-like laminar structures with a bi-modal particle size of 0.17 and 6.72 microns as seen in Figure 4-2. The XRD spectrum, shown in Figure 4-3 verifies that the as-received lubricant powder is hexagonal boron nitride with no detectable or limited or impurities.
Figure 4-1: SEM image of as-received hBN showing laminar structure

Figure 4-2: Particle size distribution of as-received hBN showing a bi-modal distribution with means at 0.17 and 6.72 microns
4.1.2 Powder Preparation

4.1.2.1 Acid Wash

All boron nitride powder was washed in a room temperature 70% nitric acid bath at a ratio of 5:1 acid to powder for 30 minutes before any other electroless deposition preparation. Powder was placed in a beaker with a 5:1 acid to powder ratio at room temperature for at least 30 minutes. To protect the filtration unit, the acid was then diluted with distilled water and filtered. For comparative purposes, an EDS of as received hBN and the acid washed hBN was performed. Quantitatively, there was no significant change in the composition of the hBN after the nitric acid wash. However, the acid wash was continued for the cleaning and hydrophilic benefits.

Figure 4-3: XRD spectrum of as received hBN
4.1.2.2 Tin Sensitization

Tin sensitization was performed on all hBN according to the procedure described in Section 3.1.4.2. The lubricant powder was allowed to soak with stirring or ultrasonic agitation for 8-90 minutes. During this treatment, the solution had a milky, light yellow color due to the particles in suspension. Throughout the bath treatment, no visual reaction was observed. The solution was then filtered using a vacuum filtration unit and the filtrate was discarded. Due to the suspension properties of the tin treated powder, the filtration process was very time consuming. Fortunately, the filtration time was significantly reduced by allowing the powder to settle to the bottom of the beaker, then filtering the top liquid before the settled powder. During the process, the filter paper was always replaced when needed. It should be noted that the tin-treated lubricant particles retained on the filter paper had a cream light almond tan color.

4.1.2.3 Palladium Activation

After the tin-activated hBN was filtered and dried, it was soaked in palladium activation solution according to the procedure described in Section 3.1.4.3. The lubricant powder was then allowed to soak with ultrasonic agitation for 8-90 minutes. The solution was then filtered in the vacuum filtration unit. An EDS of the tin and palladium activated hBN, shown in showed Figure 4-4, indicated palladium ions and trace amounts of tin ions were present.
4.1.3 One-solution Deposition Methods

4.1.3.1 Experiment 1: Small Bath Volume

Previous studies at Penn State had shown that electroless nickel encapsulation of 20-30 micron hBN particles was possible and a molar recipe was established [61], [62]. The goal of the first electroless nickel encapsulation experiments in this study was to demonstrate that encapsulation was indeed possible by using the same recipe from the previous work, only using hBN particles that are less than 6 microns. Using the procedure detailed in Section 3.2.2, a small bath volume of 945 mL was used for this initial experiment. The solution was allowed to heat in the ultrasonic bath to temperature of approximately 45°C. The reaction was visually observed by the change in solution appearance from a dark green and transparent to green-gray and opaque. Hydrogen release, in the form of small bubbles, was also observed. The reaction was then allowed
to proceed for three hours. After filtration and drying in an oven overnight, a sample was mounted on carbon tape and examined by SEM. The SEM images in Figure 4-5 show the nickel nucleation on the hBN after the three hours of deposition. The results of insufficient nickel encapsulation indicate that three hours is inadequate time for deposition. In addition, due to the increase in surface area because of the smaller particle size, the nickel content of the bath had to be increased to facilitate sufficient encapsulation.
Figure 4-5: Electroless nickel nucleation on activated hBN after three hours of deposition
4.1.3.2 Experiment 2: Deposition 1 Using Hot Plate

The purpose of this experiment was to improve the nickel encapsulation by significantly increasing the solution to hBN ratio thus allowing for more nickel deposition on the lubricant particles. Again, the solution was prepared as described in Section 3.2.3. The solution was then allowed to warm in an ultrasonic bath for approximately four hours, at which point the temperature had reached a steady state maximum. Unfortunately, a reaction was not observed; the solution remained a dark green color with little to no hydrogen release. At that point, it was decided that the heater within the ultrasonic unit was not sufficiently powerful enough to warm the solution to the appropriate temperature required for the reaction. For this reason, the Erlenmeyer flask was taken out of the ultrasonic bath to a hot plate with the temperature control set on medium. During and after the transition from the ultrasonic bath to the hot plate, the stirring rod was not placed back into the solution.

Within seconds of the flask being placed on the hot plate, the temperature of the solution reached 65 ℃ and the reaction was observed. At first observations, numerous small bubbles were noted. Within a few minutes, the solution turned to an opaque dark grey-green color, began to foam, and the temperature increased rapidly. Hence, the reaction appeared to start suddenly and progressed quickly. The temperature as a function of duration of the nickel deposition bath is depicted in Figure 4-6.
Figure 4-6: Temperature record during nickel deposition of experiment 2

The solution was then left overnight for a total of 17 hours and 30 minutes at which point no further reactions were seen. Moreover, nickel was not observed in the filtrate from this solution, suggesting that all particles were larger than the 0.2 µm filter paper. The total weight gain due to the encapsulation of the lubricant powder was 17 g.

A sample of the powder was mounted on a carbon taped post and placed in the SEM for imaging. Figure 4-7A and Figure 4-4B show nickel encapsulated hBN powder. The nickel coating was primarily decorative in nature due to the quick progress of the reaction. The nickel nucleation and deposition progression is visible by studying the shapes of the particles.
Figure 4-7: SEM image of nickel encapsulated hBN powder from experiment 2 at A) far field and B) magnified
The EDS results for this powder can be seen in Figure 4-8. No detectable amounts of BN were observed at various points on the sample; however, due to their low and similar atomic numbers it is difficult to detect either B or N when they are in the presence of a heavy metal like nickel. Carbon from the mounting medium, oxygen from oxide formation, and phosphorous from nickel-phosphorous that formed during the nickel plating process were also observed.

![EDS graph showing Ni, C, O, and P peaks]

**Figure 4-8: EDS of electroless nickel encapsulated particles for experiment 2**

A sample of the powder was mounted in cold epoxy, ground, and polished according to the recipe in Table A-1 in Appendix A and was examined under an optical microscope. Figure 4-9a shows the sample at a magnification of 200x where both small particles and large agglomerates were visible. Figure 4-9b and c, taken at a magnification of 1000x, show individual hBN particles encapsulated by nickel in both single particle and agglomerate form.

Agglomerate particles appeared to have a 4.5 micron thick nickel coating, while the individual particles were encapsulated by approximately 0.8 microns of nickel. This
is suspected to be due to the increased visibility of the nickel ions in solution for the large agglomerates of particles. Unfortunately, these particles are undesirable due to the lack of uniformity and potential of fracture and other complications during cold spray. Further experiments were designed to decrease the number of agglomerates of lubricant particles.
Figure 4-9: Optical image of nickel encapsulated hBN from experiment 2 at 200x (A) and 1000x (B & C)
4.1.3.3 Experiment 3: Deposition 2 Using Hot Plate

Experiment 2 showed significant agglomerates due to the lack of agitation during the nickel deposition. In order to avoid this problem, the current study (Experiment 3) used constant agitation from the stirring unit throughout the entire deposition process. The deposition bath process began in an ultrasonic unit with heating in addition to vibrational and mechanical agitation. After four hours without a reaction, the flask was placed on a hot plate to further increase the temperature. Within a few seconds after moving the flask to the hot plate, the solution began to react; the solution immediately turned a dark green-grey color and bubbled vigorously. At this point, the solution was agitated with a stirring unit only. The solution was left overnight with the heat at a low temperature and the stirring on. The following day, no reaction was visible and the resulting powder was filtered and placed in an oven to dry overnight.

During the process, much of the nickel was deposited on the bottom of the flask instead of being suspended in solution. Loosely fixed powder had to be scraped off the bottom of the flask before it could be filtered. The deposition on the bottom of the flask was attributed to two factors. The first was the difference in temperature between the glass surface in contact with the hot plate and bulk of the solution. Since the reaction was temperature sensitive, it was preferential to the hot glass. The second explanation as to why the nickel was attracted to the bottom of the flask was the nickel magnetic attraction to the strip in the hot plate.

The powder was then mounted, ground, polished, and viewed by optical imaging. Figure 4-10 shows an optical image of this sample at 1000x magnification. The image
represents the bulk of the sample in which all hBN particles were sufficiently coated with nickel. After each hBN was coated with nickel small agglomerates of these coated particles formed. The mean nickel thickness at 15 points on the particles was 0.94 microns.

![Optical image of experiment 3 at x1000. Represents the bulk of the sampled powder.](image)

Figure 4-10: Optical image of experiment 3 at x1000. Represents the bulk of the sampled powder.

Figure 4-11 illustrates the few large agglomerate particles that were present in the sample. These particles clearly began as agglomerates of hBN in which individual particles were unable to be coated. This results in very large particles with a thick nickel coating. Only a few of these particles were observed within the sample and did not represent the bulk of the powder.
In Experiment 3, the nickel encapsulation of the hBN powder was considered successful. Only small adjustments were required to break up the large agglomerates of hBN before the lubricant powder was placed into the deposition flask. These adjustments include adding a few drops of distilled water to the weighed hBN before adding it to the deposition bath and manually breaking up the agglomerates with a spoon. Additionally, in previous experiments, when the flask was taken out of the water bath and placed on a hot plate, the heat was isolated to only the bottom of the flask. The desire for more uniform heating was achieved with an immersion heater which compensated for the limitations of the ultrasonic heater. This allowed the flask to be kept in the bath for the entire duration of the deposition for further experiments.
4.1.4 Two-solution Deposition Methods

4.1.4.1 Experiment 4: Deposition Leading to Series A

Previous experiments demonstrated it is possible to encapsulate hBN with a thin nickel coating of approximately 1 micron. A two solution deposition process was designed to achieve a thicker nickel encapsulation. As described in Section 3.2.5, the two solution deposition method began with a solution containing concentrations similar to those used in the one solution deposition method. In the two solution method, a second solution of much higher concentrations was slowly added to the first solution after it reacted.

Figure 4-12 and Figure 4-13 show SEM images of the cross-section of the nickel encapsulated hBN produced in Experiment 4. Figure 4-12, at 8,000x magnification, shows the hBN encapsulated by nickel; the average nickel coating thickness was between 2-5 microns. The particles also have many pores that were formed by individually coated particles that agglomerate after the deposition had started. Figure 4-13 shows the same cross-sectioned powder sample at a much lower magnification where the irregular shape of the particles is obvious. Figure 4-14 shows an SEM image of the whole powder particles in which the rough and irregular surface characteristics of the nickel deposition are visible.
Figure 4-12: SEM cross-section image at x8000 of encapsulated hBN in experiment 4

Figure 4-13: SEM cross-section image at x800 of encapsulated hBN in experiment 4
Results from the particle size analysis, shown in Figure 4-15, revealed a narrow size distribution with the average diameter of 19.9 microns. The two-solution deposition method yielded better encapsulation of boron nitride particles with nickel than the one solution method. This procedure was used to produce the Series A feedstock cold spray powder.
Figure 4-15: Particle size analysis of experiment 4

EDS mapping was performed on a single particle of encapsulated hBN from Experiment 4. The results from the EDS are shown in Figure 4-16. The upper left image shows the SEM image of the section used for mapping and the hBN particles are visible. The lower left image shows the results of the nickel content. As expected, nickel was not detected as readily in the areas where the hBN was present. The upper right image shows the phosphorous content of the particle. Phosphorous is dispersed throughout the sample; however, it is more concentrated in the region on the hBN. This is evidence that the phosphorus content of the initial depositions is greater than that of the deposition later in the process.
Figure 4-16: EDS mapping of the cross section of a hBN encapsulated particle from experiment 4. A) SEM image, B) Phosphorous map, C) Nickel map

4.1.4.2 Experiment 5: Deposition Leading to Series B

Experiment 5 was the first trial for powders with a higher content of lubricant particles. In this study, the amount of hBN added to the bath solution was increased, resulting in a higher percentage of hBN in the powder. The resulting increase in the surface area of hBN consequently decreased the thickness of the nickel coating. The increase in surface area also had an effect on the mechanics of the electroless nickel reduction reaction allowing the nickel in solution to be reduced at a lower temperature.
Figure 4-17 shows the cross section of a sample from this experiment that was mounted in clear epoxy, ground, and polished according to the procedure in Appendix A. In this image it is apparent that the hBN was completely encapsulated by nickel with an average coating thickness of 0.6 microns. Particles of nickel-encapsulated hBN agglomerated after deposition had begun, resulting in powder particles that contained many encapsulated hBN particles.

Figure 4-17: SEM image of the cross section of experiment 5
4.2 Characterization of powders for cold spray

4.2.1 High-Density Nickel Powder for Baseline

Novamet, high density nickel powder was used to fabricate a cold spray coating and used as a baseline comparison for all cold spray coatings. This semi-smooth spherical powder was produced from the thermal deposition of nickel carbonyl by the manufacturer.

Figure 4-18 shows an SEM image of the nickel powder used for the cold spray coatings. The EDS in

Figure 4-19 shows that that this nickel powder had few impurities. The nickel powder had an average particle size of 19.7 microns and a density of 8.438 g/cc.

Figure 4-18: SEM image of Novamet high density nickel powder used as baseline for cold spray trials and wear tests
4.2.2  Series A Feedstock Cold Spray Powder

Thirty-two batches of Series A cold spray powder were produced as described in Section 3.2.6, containing approximately 1% (by volume) of hBN. Powder density, as measured with a multi-pycnometer, was found to be 7.924 g/cc. In addition, the powder measured at a mean particle size of 24.6 microns with the distribution shown in Figure 4-20. This wide distribution was not surprising due to the fabrication technique and could be narrowed by using a larger electroless nickel bath volume. However, a wide distribution of particles may aid in the flow-ability and deposition during cold spray.
Figure 4-20: Particle size distribution of Series A cold spray powder

Figure 4-21 shows an EDS of Series A cold sprayed powder. Series A contains 13.35 wt.% phosphorous, a trace amount of oxide, the remainder consisted of nickel at the points tested. A XRD spectrum of the sample showed that the constituents present were both in an amorphous and crystalline state. Figure 4-22 is an SEM image of the cross section of Series A cold spray feedstock powder, which shows hBN is present in the nickel matrix at a small quantity.

<table>
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<th>Element</th>
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<th>Atomic %</th>
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<tbody>
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</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>

Figure 4-21: EDS analysis of Series A cold sprayed powder
The focused ion beam (FIB) was used to dig a trench in a single particle of powder then polish the surface to expose the boron nitride cores. Figure 4-23 shows the core of a single Series A particle. From this figure, it is evident that the porosity within the powder is significant. The higher magnification portion of the photo shows the imbedded boron nitride, which appears dark due to its low atomic number. This method for exposing the core of the particles gave insightful information on the particle porosity and hBN content of a particle. However, only a single particle core could be exposed at one time and was too time consuming to give a good representation of the bulk powder.
Figure 4-23: FIB image of a single Series A particle with the core exposed
4.2.3 Series B Feedstock Cold Spray Powder

Series B cold spray powder, consisted of 19 batches of 10% (by volume) hBN, was produced as described in Section. The powder measured at a mean particle size of 21.2 microns with the distribution shown in Figure 4-24. Figure 4-25 shows the EDS spectrum of Series B feedstock powder. The phosphorous content is approximately 5.27% (by weight), which is much lower than Series A powder. This difference can be accounted for the change in the reaction mechanics at lower reacting temperatures.

![Series B Particle Size Analysis](image)

**Figure 4-24:** Particle size analysis for Series B cold spray feedstock powder showing and average size of 21.2 microns
Figure 4-25: EDS spectrum of Series B feedstock cold spray powder

Figure 4-26 is a cross sectional image of Series B powder that had been mounted, ground, and polished. As can be seen, the amount of hBN within the nickel matrix is significantly more than that of Series A, shown in Figure 4-22.

Figure 4-26: SEM image of the cross section of Series B cold spray feedstock powder
4.2.4 Series A + B Feedstock Cold Spray Powder

Series A+B was created by mixing 55 wt.% Series A with 45 wt.% of Series B cold spray feedstock powders; Figure 4-28 is an SEM image of the cross section of this composite coating. Series A and Series B particles can be distinguished by the hBN content.
4.3 Cold Spray Coating Characterization

4.3.1 Scanning Electron Microscopy

4.3.1.1 Pure Nickel Cold Sprayed Coatings

Pure nickel cold spray coatings were produced from spherical carbonyl nickel particles on aluminum 6061 substrates by using nitrogen as the main process gas. The resulting coatings had a uniform surface with few pores. Figure 4-29 depicts the cross section of the pure nickel coatings which has minimal cold spray defects. As discussed earlier, this cold sprayed coating was used as a baseline for wear comparisons.
4.3.1.2 Series A Coatings

Cold spray coatings of Series A electroless encapsulated hBN particles were successfully deposited on aluminum 6061 substrates by the independent use of both nitrogen and helium. Figure 4-30 depicts a successful coating of Series A powder at a thickness of 1.524 mm (0.060 inch).
Figure 4-30: Series A (electroless nickel encapsulated hBN) cold sprayed coating on an aluminum substrate

Figure 4-31 shows an SEM image of the cross section of the Series A cold sprayed coating with the spray direction and aluminum substrate noted. As can be seen from this image the Series A cold spray coating is much more porous than the pure nickel cold spray coating. Figure 4-32 shows a higher magnification of the same coating with the hBN particles indicated. The pores present in the figure were most likely caused by the cold spray process or by the fallout of hBN particles during sample preparation. A focused ion beam (FIB) was used to mill a trench and image the cross section to prevent hBN particles from being dislodged during polishing. Figure 4-33 illustrates that using the FIB can expose the hBN core.
Figure 4-31: SEM image of the cross section of Series A cold sprayed coating

Figure 4-32: SEM of the cross section of series A cold spray coating
4.3.1.3 Series B Coatings

Series B feedstock powder was successfully deposited on aluminum 6061 substrates by using nitrogen as the carrier gas. Throughout the cold spray process, a noticeable amount of hBN debris was observed on the surrounding fixture. This indicates that some of the hBN powder fractured and broke out of the nickel matrix upon impact. However, from Figure 4-34 it can be seen that Series B cold spray coatings contain a significantly higher concentration than those created with Series A feedstock powder.
Figure 4-34: SEM image of the cross section of Series B cold sprayed coating
4.3.1.4 Series A + B Coatings

Series A+B feedstock powder, consisting of 55% Series A and 45% Series B, was successfully deposited via cold spray on aluminum 6061 substrates with nitrogen as the main process gas. Figure 4-35 shows a cross section cut of this coating; this figure verifies the trends set by Series A and Series B cold sprayed coatings and reflects the approximately expected 5% (by volume) hBN composition in the coating.
Figure 4-35: SEM image of the cross section of Series A+B cold sprayed coating
4.3.2 Vickers Hardness

The hardness of the coatings was examined at the cross section and normal to the surface. In addition, the aluminum 6061 substrate was also tested at the cross section. All samples were mounted in epoxy, ground, and polished prior to testing. Hardness measurements were taken with a 200 lb load and a Vickers indenter. Figure 4-36 shows the hardness measurements at the cross section of the coating while Figure 4-37 exhibits the hardness measurements taken normal to the coating surface. Hardness remained uniform regardless of the angle of incident of the indenter.

The hardness measurements may give insight into the wear resistance of the coatings. Series A coatings show at a higher Vickers hardness compared to Series B coatings. This is suspected to be caused by the decrease in the nickel-phosphorous alloy content of the Series B coatings.

![Figure 4-36: Hardness measurements taken at the cross section of each coating or Substrate](image-url)
4.3.3 Bond Strength

The bond strength of the five different coatings was also evaluated. Six samples were performed for each test according to the procedure in Section 3.9, in addition to two tests to evaluate the epoxy strength. A tensile bond strength test was used to measure the cohesive/adhesive strength of the coatings to the aluminum substrate. If the bond fails at the substrate-coating interface the measurement is the adhesive strength; otherwise it is considered the cohesive strength.

Photographs were taken to document each stage of the testing. Figure 4-38 A shows an as-sprayed bond slug surface, B the same surface ground to a coating thickness of approximately 0.508mm (0.020 inch), and C the coated slug mated to an uncoated slug with FM1000 film epoxy.
Tests were performed on two separate days with identical preparation methods, test parameters, and test equipment. Initially, two samples of the FM1000 epoxy on uncoated bond slugs were tested and yielded an average bond strength of 69.82 MPa. Cold spray coated pure nickel coatings had the lowest average bond strength at 21.91 MPa with a cohesive failure through the coating. As expected, the coating consisting of a pure nickel pre-coat and a Series A second coat had a similarly low bond strength of 24.19 MPa. This coating appeared to have cohesive failure through the pure nickel layer. Figure 4-39 shows the cohesive failure of these two specimens.

Series A coatings had the best bond strength with an average of 71.67 MPa. For three of the series A samples, the coating tore during the test, two samples had adhesive failure, and one sample failed at the epoxy. Images from all three of these failure modes can be seen in Figure 4-40 A, B and C.

Series B had the lowest bond strength of the boron nitride encapsulated coatings at 28.79 MPa with cohesive failure. Coatings created by mixing Series A and Series B cold spray powders produced bond strength of 43.05 MPa with cohesive failure. Figure 4-41 shows the cohesive failure of both of these specimens.
Figure 4-39 A, B: Cohesive bond failure for A) Pure nickel, B) Pure nickel pre-coat with Series A second coat
Figure 4-40: Bonding test results for Series A cold sprayed coatings A) adhesive failure, B) cohesive failure, C) epoxy failure
Figure 4-41: Cohesive bond failure of A) Series B coating, B) Series A + B coating

Figure 4-42: Average bond strength data for cold spray coatings and epoxy resin
A summary of the bond strength results is shown in Figure 4-42 and a complete table of the data can be found in Tables A-2 and A-3 of Appendix A. From Figure 4-42 it can clearly be seen that the amount of boron nitride is inversely related to the cohesive strength due to the corresponding decrease of nickel and nickel-phosphorous alloys. Pure nickel samples had the lowest cohesive strength compared to the boron nitride encapsulated samples. This is the result of differences within feedstock powder composition, size, and morphology.

Figure 4-43 shows the relationship between the bond strength and the hardness of the cold sprayed coatings. The results show that the harder coatings had higher bond strength measurements.

![Bond Strength Versus Hardness Normal to Coating Surface](image)

**Figure 4-43:** Bond strength versus coating hardness measured normal to the coating surface
4.3.4 Layered Cold Spray Coating

A layered coating was produced to demonstrate the ability to create such properties using the cold spray process. An aluminum 6061 substrate was first coated in a 762 microns (0.03 inch) thick coating of nickel, followed by a 508 microns (0.02 inch) thick coating of series A powder with approximately 1% hBN.

Figure 4-44: Functionally layered cold spray coating of nickel and Ni-hBN

Figure 4-44 shows an image of the layered cold spray coating. On the surface, it appears to be similar to the earlier homogeneous coatings with minimal coating flaws. Figure 4-45 shows an optical image of the cross section of the coating, where the substrate, nickel, and Ni-hBN layers can each be clearly be distinguished.
4.4 Wear Testing of Cold Spray Coatings

4.4.1 Ball on Flat Reciprocating Wear

Ball-on-flat sliding wear tests were performed on all coating types, as described in Section 3.6. At least three samples of each coating were tested at 24 N of normal force for 17 minutes. To avoid contamination of the coatings, surface grinding was not performed. The first five minutes of testing were not included in the data sets due to a wear-in period. Once the ball was seated in the coating, measurements more accurately reflected the friction force and usually linear wear process.
Pure nickel coatings exhibited a wide variation in the coefficient of friction results, as well as, data trends. Figure 4-46 shows the trend lines for seven ball-on-flat reciprocating wear tests.

![Average Coefficient of Friction Data for Pure Nickel Coatings](image)

**Figure 4-46: Average coefficient of friction data for seven pure nickel coating samples with error bars**

The variation in the coefficient of friction measured for the pure nickel coatings is due to the significant wear that occurred during the tests; the results shown in Figure 4-46, reveals a wide distribution of data for each pure nickel sample tested. By analyzing the wear scar the wear mechanism can be determined. When material is pushed out of the way of the ball, due to a plowing effect, the coefficient of friction will either maintain a steady value or can decrease with further testing due to the establishment of wear-in track and a smooth surface of contact. However, when material is not plowed completely
out of the way, material will build into mounds on the sliding surface in the wear scar. Figure 4-47 shows a photograph of the nickel coating reciprocating wear scar with mounds of nickel buildup. The asperities cause inconsistencies in the friction measurements and an overall increase in the coefficient of friction.

![Figure 4-47: Photograph of nickel coating reciprocating wear scar, showing mounds of nickel buildup](image)

Series A cold spray coatings showed a decrease in both wear and the coefficient of friction when compared to the pure nickel samples. Figure 4-48 shows a comparison between the coefficient of friction data of pure nickel versus series A cold sprayed coatings; the data has been averaged per minute and graphed accordingly. The shaded regions represent all data sets from each test and the line represents the average of that data. Figure 4-49 shows a photograph of the size difference in the wear scars between the series A and the pure nickel cold sprayed coatings.
Figure 4-48: Comparison between the average COF averaged for each minute for pure nickel and series A cold spayed coatings

Figure 4-49: Wear scar from series A (left) and pure nickel (right)

Series B cold spray coatings, with approximately 10 vol.% hBN had a higher coefficient of friction than either Series A or Series A + B and Series A + B had a higher coefficient of friction than Series A. Figure 4-50 shows the trend lines from three friction
tests for each cold sprayed coating. It can be seen that there was overlap in friction trends between types of coatings; however, the is clear that as the amount of hBN increases the coefficient of friction increases as well. This is suspected to be due to the decrease in the hardness and the nickel-phosphorous alloy content. Figure 4-51 shows the average of all coefficient of friction data for each cold sprayed coating type.

Figure 4-50: Comparison of friction trends for individual Ni-hBN cold spray samples
Figure 4-51: Average coefficient of friction for all tests reciprocating wear tests

The wear scars’ length and width were measured using a digital caliper before the volume was estimated. Figure 4-52 is a comparison between the wear scar tracks from largest to smallest and Table 4-1 shows the estimated wear scar volume, measured with a digital caliper.

Figure 4-52: Wear scar tracks for cold sprayed coatings
Table 4-1: Wear scar volume measurements for ball-on-flat reciprocating wear test

<table>
<thead>
<tr>
<th></th>
<th>Average Scar Volume (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>587</td>
</tr>
<tr>
<td>Series A</td>
<td>442</td>
</tr>
<tr>
<td>Series B</td>
<td>550</td>
</tr>
<tr>
<td>Series A+B</td>
<td>448</td>
</tr>
</tbody>
</table>

The results show that the Series A cold spray coatings clearly exhibits the best wear resistance properties, both by the measurement of volume of its wear scar and the reduction of the coefficient of friction. It is believed that the improved wear resistance is due to the presence of the boron nitride, the quantity of nickel and nickel-phosphorous alloys, and the coating hardness. Series A+B exhibited the second best wear resistant properties due to its contribution of Series A feedstock powder. Series B coatings are only slightly better than the pure nickel baseline, which may be due to the decreased adhesion and phosphorous content.

4.4.2 Pin on Disk Sliding Wear

Preliminary data was collected using the pin-on-disk sliding wear assembly described in Section 3.8; three samples of each coating type were tested. All samples were run at an approximate normal pressure of 1.65 KPa and a sampling duration of 5 seconds. The pure nickel and Series B cold spray coatings experienced significant sliding wear during the tests, while Series A and Series A+B showed minimal wear. For this reason, the pure nickel and Series B cold spray coatings were run at a sliding speed of 2.13 m/s and the Series A and Series A+B cold spray coatings were run at 4.39 m/s.
Two of the three pure nickel samples tested wore at a rate of approximately $9.5 \times 10^{-5}$ cc/m, while the third wore at a rate of $0.3 \times 10^{-5}$ cc/m. The data inconsistency indicates that the current test methods and/or equipment setup are not ideal for evaluating wear of this coating. However, subsequent data showed that the Series A and the Series A+B coatings wore consistently at relatively low rates compared to the other coatings, thus allowing for a qualitative analysis between coatings.

Figure 4-53, Figure 4-54, and Figure 4-55 graphically show the wear rate of the pure nickel, Series B, and Series A+B cold spray coatings respectively. Data points that are marked as a cross represent wear that did not completely cover the surface of the pin and was considered the wear-in period. As is standard practices, the wear-in data was not included for the calculation of the steady-state wear rates. As can be seen from these graphs, wear-in durations and wear rates differ for each coating type as well as between samples of the same coating type, due to the variability in both the cold spray coatings and the system setup.
Figure 4-53: Pure nickel cold sprayed coating wear rates for pin-on-disk sliding wear. Cross data points represent a wear-in period in which the entire pin surface was not completely in contact and was not used to calculate the wear rate.

Figure 4-54: Series B cold sprayed coating wear rates for pin-on-disk sliding wear. Cross data points represent a wear-in period in which the entire pin surface was not completely in contact and was not used to calculate the wear rate.
Figure 4-55: Series A+B cold sprayed coating wear rates for pin-on-disk sliding wear. Cross data points represent a wear-in period in which the entire pin surface was not completely in contact and was not used to calculate the wear rate.

Table 4-2 shows the numerical wear rate data for each sample. The data shows that Series B cold spray coatings had the highest wear rate at 16.33x10^{-5} cc/m. Nickel coatings also had a significant wear rate of 6.43x10^{-5} cc/m. In contrast, Series A+B and Series A showed the best sliding wear resistance with average wear rates of 0.11x10^{-5} cc/m and 0.03x10^{-5} cc/m respectively.

Table 4-2: Pin-on-disk sliding wear rate summary

<table>
<thead>
<tr>
<th>Sliding Wear Rates (x10^{-5} cc/m)</th>
<th>Series B</th>
<th>Nickel</th>
<th>Series A+B</th>
<th>Series A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>16.33</td>
<td>6.43</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>Stdev</td>
<td>6.35</td>
<td>5.34</td>
<td>0.08</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Minimal volume loss occurred on Series A coatings and can be seen in Figure 4-56. Unlike the other coatings, complete wear of the pin surface did not occur with Series A samples indicating that the sliding wear parameters were not aggressive enough for this coating. In an attempt to increase the wear of these coatings, a third sample of Series A was tested at a variety of parameters. The results are listed in Table 4-3 and show that even at 20 second sampling durations and speeds as high as 6.58 m/s, minimal wear occurred.

**Figure 4-56:** Series A cold sprayed coating wear rates for pin-on-disk sliding wear (complete pin wear was never obtained)
Table 4-3: Series A various parameter results

<table>
<thead>
<tr>
<th>Rotational Speed (m/s)</th>
<th>Sampling Duration (s)</th>
<th>Cumulative Distance Traveled (m)</th>
<th>Wear Rate (x10^{-5} cc/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.13</td>
<td>5</td>
<td>153.6</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>219.5</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>318.2</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>449.9</td>
<td>0.10</td>
</tr>
<tr>
<td>4.39</td>
<td>10</td>
<td>581.6</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>844.9</td>
<td>0.03</td>
</tr>
<tr>
<td>6.58</td>
<td>10</td>
<td>1042.4</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1437.4</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Based on the data collected, Series A cold sprayed coatings clearly demonstrated superior wear resistance. However, cracks perpendicular to the sliding wear tracks appeared in the surface of these coatings after a minimal sliding distance. The cracks were suspect to be due to the residual stresses in the coating surface resulting from the cold spray process but may also be caused by the thermal stresses during testing. These cracks can be seen in Figure 4-57 and Figure 4-58.

Figure 4-57: Series A cold sprayed coating sliding wear pin after testing
4.4.3 Fretting Wear

Fretting wear was also investigated for applications of small amplitude vibrations may be an issue. The procedure from Section 3.7 was followed to obtain the results. Series A and pure nickel were evaluated for fretting as these coatings represented the least and greatest wear resistance. The mating ball was oscillated on a cold sprayed coating at a distance of 50 microns at a frequency of 45 Hz. A normal force of 150 N was applied to the ball specimen for the duration of 2 million oscillating cycles. The friction force was measured for 10 minute periods at the hours of 1, 5, 9, and 12 of the test and the results are shown in Figure 4-59. The friction results do not indicate clear trends to help compare the Series A with the pure nickel coating. Figure 4-60 shows
optical images of the fretting wear scars; fretting damage to both coatings was minimal. Wear scars measurements also supported this finding and indicate that there was not a significant difference between the coatings at the fretting parameters used.

Figure 4-59: Friction results for fretting wear on Series A and pure nickel cold sprayed coatings
Figure 4-60: Fretting wear scars for A) Series A and B) pure nickel cold sprayed coatings
4.4.4 Reparability of Wear Scar

Reparability is an important feature for practical applications of self-lubricating coatings. For demonstration purposes, half of a reciprocating wear scar was repaired with Series A feedstock powder. The progression of the repair is documented in Figure 4-61.

Figure 4-61A shows the original scar of the Series A cold spray coating. The left half of the scar was masked with a metal plate while the right portion was repaired by cold spraying that portion of the scar to a thickness greater than the scar depth, as seen in Figure 4-61B. The repaired section of the coating was then ground to the level of the original coating seen in Figure 4-61C. This successfully demonstrates the potential for repairing worn surfaces using the self-lubricating coating.

Figure 4-61: Wear scar repair progression; reciprocating wear scar (A), as sprayed repair (B), ground of repaired surface (C)
Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The current study demonstrated that wear performance can be significantly improved by embedding hexagonal boron nitride particles in a nickel matrix to form a coating using cold spray. Based on the experimental results the following can be concluded:

- Hexagonal boron nitride particles, between the sizes of 0.1 and 3 microns, can be encapsulated with nickel and nickel-phosphorous using the electroless nickel deposition process after activation with tin chloride and palladium chloride ions.
- Thick nickel and nickel-phosphorous alloy encapsulations of hBN can be obtained by using a two solution electroless nickel deposition procedure. The slow addition of the second solution is essential to avoid rapid reaction of the entire solution.
- During the encapsulation process, hBN lubricant particles are first coated in a layer of nickel and nickel-phosphorous alloys, then agglomerate to form larger particles.
- The hBN content in the cold spray feedstock powder can be controlled by adding more or less hBN to the electroless nickel deposition bath. This addition of hBN will consequently affect the thickness of the encapsulation.
- Hexagonal boron nitride encapsulated powder of varying content, between 1 and 10 vol.%, can be deposited on aluminum 6061 substrates using cold spray with nitrogen as the main process gas.
• Feedstock powders with a higher boron nitride content may fracture instead of plastic deformation upon impact due to the lower nickel encapsulation thickness; this ultimately reduces adhesion and the quality of the coating with a hBN particle of bi-modal particle size (0.17 and 6.72 microns).

• There exists a critical nickel thickness for optimal bonding of the particles and the substrate during cold spray. A nickel encapsulation thickness between 2-5 microns gave the best bond strength of the coatings studied.

• Embedded hBN particles in a nickel and nickel-phosphorous coating reduce the coefficient of friction and wear scar volume observed during a reciprocating wear test compared with pure nickel cold sprayed coatings. There exists a critical hBN content, between 1 and 5 vol.%, for optimal friction reduction.

• Hexagonal boron nitride-nickel coatings of 1 vol.% hBN exhibited the strongest bonding, highest Vickers hardness, lowest coefficient of friction, and the most wear resistance compared to coatings with higher hBN content and pure nickel cold sprayed coatings.

• Coatings with between 1 and 5 vol% hBN content exhibited improved pin-on-disk sliding wear resistance compared to coatings with 10 vol.% hBN and pure nickel cold sprayed coatings.

• Coatings exhibiting wear can be repaired by depositing cold spray powder and machining the surface.
5.2 Future Recommendations

Nickel and nickel-phosphorous coatings with 1 vol.% hBN content demonstrated the best wear resistance and bonding properties of all coatings studied. The limited hBN content allows for an increase in the nickel and nickel-phosphorous content within the coating. Based on the knowledge gained from this study the following recommendations are presented for consideration:

- The phosphorous content in the encapsulated hBN powder is a bi-product of the electroless nickel bath and be controlled by adjusting a combination of electroless bath parameters including the temperature, pH, and reacting chemicals. Experimental results have shown that with an increased phosphorous content, there is an improvement in the wear resistance. However, it has not been shown whether this is a direct or indirect correlation. To study the effect of the phosphorous in the feedstock powder, these parameters should be adjusted to create a higher phosphorous content in the feedstock powder. If the phosphorous content shows a strong correlation with wear resistance, further research should be directed towards optimization.

- The encapsulation of hBN is necessary due to the ductility needed for the cold spray process. It was found that the electroless nickel deposition process also gives favorable wear resistant properties, perhaps due to the phosphorous content. To provide a more direct comparison to the encapsulated hBN powder, the pure nickel powder should be encapsulated by the electroless nickel deposition process
to give it comparable properties to the Series A, Series B, and Series A+B feedstock powder.

- Post process heat treatments have been found to convert the atomic structure of amorphous nickel and nickel-phosphorous into their crystalline state. This process has been shown to increase the hardness, which could improve the wear resistance. Post process heat treatments should be studied to further increase the wear resistance of hBN embedded self-lubricating coatings.

- Fretting result for this study showed minimal damage for the current test parameters. Due to the likelihood concern of fretting in many potential applications for self-lubricating coatings, fretting tests should be conducted using more aggressive parameters.

- There have been many studies on the wear resistant and structural integrity of carbon nanotubes; carbon nanotubes have been successfully co-deposited with nickel on substrates via the electroless nickel deposition process. The beneficial properties of carbon nanotubes may make it useful as a lubricant. Carbon nanotubes should be encapsulated in nickel by the electroless process then deposited via cold spray and evaluated for friction and wear performance.
References


APPENDIX A: Additional Tables

Table A-1: Polishing Procedure for Mounted Samples

<table>
<thead>
<tr>
<th>Polishing Material</th>
<th>Polishing Cloth</th>
<th>Lubricant</th>
<th>Duration</th>
<th>Force</th>
<th>Polishing Direction</th>
</tr>
</thead>
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<tr>
<td>9 micron diamond suspension</td>
<td>MD-DAC</td>
<td>Alcohol Based-Blue Lubricant</td>
<td>2.5 minutes</td>
<td>30N</td>
<td>&gt;&gt;</td>
</tr>
<tr>
<td>6 micron diamond suspension</td>
<td>MD-DAC</td>
<td>Alcohol Based-Blue Lubricant</td>
<td>2.5 minutes</td>
<td>30N</td>
<td>&gt;&gt;</td>
</tr>
<tr>
<td>3 micron diamond suspension</td>
<td>MD-DAC</td>
<td>Alcohol Based-Blue Lubricant</td>
<td>2.5 minutes</td>
<td>30N</td>
<td>&gt;&gt;</td>
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<tr>
<td>1 micron alumina in dH₂O</td>
<td>MD-CHEM</td>
<td>None</td>
<td>5.5 minutes</td>
<td>30N</td>
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<td>0.04 micron alumina in dH₂O</td>
<td>MD-CHEM</td>
<td>None</td>
<td>3 minutes</td>
<td>30N</td>
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Table A-2: Summary of Pre-treatments and Electroless Nickel Baths

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<th>Process</th>
<th>Composition</th>
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<tr>
<td><strong>Tin Sensitization</strong></td>
<td>0.044 M Tin (II) Chloride&lt;br&gt;0.12 M Hydrochloric Acid&lt;br&gt;Distilled Water</td>
</tr>
<tr>
<td><strong>Palladium Activation</strong></td>
<td>5.6x10^-4 M Palladium Chloride&lt;br&gt;0.12 M Hydrochloric Acid&lt;br&gt;Distilled Water</td>
</tr>
<tr>
<td><strong>One-Solution Method</strong></td>
<td><strong>Nickel Solution 1</strong>&lt;br&gt;0.40 M Sodium Hypophosphate&lt;br&gt;0.16 M Nickel (II) Sulfate Hexahydrate&lt;br&gt;0.16 M Sodium Citrate Dehydrate&lt;br&gt;Ammonium Hydroxide to a pH of 10</td>
</tr>
<tr>
<td><strong>Two-Solution Method</strong></td>
<td><strong>Solution 1</strong>&lt;br&gt;0.48 M Sodium Hypophosphate&lt;br&gt;0.19 M Nickel (II) Sulfate Hexahydrate&lt;br&gt;0.19 M Sodium Citrate Dehydrate&lt;br&gt;Ammonium Hydroxide to a pH of 10</td>
</tr>
<tr>
<td></td>
<td><strong>Solution 2</strong>&lt;br&gt;2.00 M Sodium Hypophosphate&lt;br&gt;0.80 M Nickel (II) Sulfate Hexahydrate&lt;br&gt;Ammonium Hydroxide to a pH of 10</td>
</tr>
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</table>
Table A-3: Coating Bond Strength Data (1 of 2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating Thickness</th>
<th>Max Load (lbf)</th>
<th>Displacement Max (inches)</th>
<th>Max Stress (ksi)</th>
<th>Max Stress (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre-surface grinding</td>
<td>Post-surface grinding</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.063</td>
<td>0.016</td>
<td>2860</td>
<td>0.021</td>
<td>3.605</td>
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<tr>
<td>2</td>
<td>0.060</td>
<td>0.015</td>
<td>3058</td>
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<td>3</td>
<td>0.061</td>
<td>0.021</td>
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<td>4</td>
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<td>5</td>
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<td>0.018</td>
<td>3133</td>
<td>0.018</td>
<td>3.965</td>
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<tr>
<td>6</td>
<td>0.063</td>
<td>0.013</td>
<td>2861</td>
<td>0.018</td>
<td>3.614</td>
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Average = 3.738  25.771
Standard Deviation = 0.178  1.228

Test 2: Ni pre-coat (0.010") + Series A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating Thickness</th>
<th>Max Load (lbf)</th>
<th>Displacement Max (inches)</th>
<th>Max Stress (ksi)</th>
<th>Max Stress (Mpa)</th>
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<td>Post-surface grinding</td>
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<tr>
<td>1</td>
<td>0.036</td>
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<td>3103</td>
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<td>3.927</td>
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<tr>
<td>2</td>
<td>0.031</td>
<td>0.020</td>
<td>2670</td>
<td>0.018</td>
<td>3.380</td>
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<tr>
<td>3</td>
<td>0.030</td>
<td>0.017*</td>
<td>2568</td>
<td>0.016</td>
<td>3.263</td>
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<td>4</td>
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<td>0.020</td>
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<td>0.017</td>
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<td>5</td>
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<td>0.016</td>
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<td>6</td>
<td>0.031</td>
<td>0.020</td>
<td>2898</td>
<td>0.019</td>
<td>3.676</td>
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Average = 3.508  24.189
Standard Deviation = 0.266  1.831

Test 3: Series A (hBN-Ni)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating Thickness</th>
<th>Max Load (lbf)</th>
<th>Displacement Max (inches)</th>
<th>Max Stress (ksi)</th>
<th>Max Stress (Mpa)</th>
</tr>
</thead>
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<td>Post-surface grinding</td>
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<td>1</td>
<td>0.048</td>
<td>0.025</td>
<td>6211</td>
<td>0.036</td>
<td>7.924</td>
</tr>
<tr>
<td>2</td>
<td>0.056</td>
<td>0.019</td>
<td>9594</td>
<td>0.053</td>
<td>12.264</td>
</tr>
<tr>
<td>3</td>
<td>0.058</td>
<td>0.017</td>
<td>8858</td>
<td>0.049</td>
<td>11.324</td>
</tr>
<tr>
<td>4</td>
<td>0.056</td>
<td>0.018</td>
<td>5058</td>
<td>0.031</td>
<td>6.452</td>
</tr>
<tr>
<td>5</td>
<td>0.049</td>
<td>0.018</td>
<td>9595</td>
<td>0.056</td>
<td>12.242</td>
</tr>
<tr>
<td>6</td>
<td>0.053</td>
<td>0.018</td>
<td>9534</td>
<td>0.052</td>
<td>12.164</td>
</tr>
</tbody>
</table>

Average = 10.395  71.671
Standard Deviation = 2.551  17.592

Test 4: Series B (hBN-Ni)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating Thickness</th>
<th>Max Load (lbf)</th>
<th>Displacement Max (inches)</th>
<th>Max Stress (ksi)</th>
<th>Max Stress (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre-surface grinding</td>
<td>Post-surface grinding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.047</td>
<td>0.015</td>
<td>3586</td>
<td>0.025</td>
<td>4.640</td>
</tr>
<tr>
<td>2</td>
<td>0.050</td>
<td>0.014</td>
<td>4620</td>
<td>0.028</td>
<td>5.966</td>
</tr>
<tr>
<td>3</td>
<td>0.048</td>
<td>0.014</td>
<td>3555</td>
<td>0.024</td>
<td>4.618</td>
</tr>
<tr>
<td>4</td>
<td>0.045</td>
<td>0.013</td>
<td>2285</td>
<td>0.017</td>
<td>2.956</td>
</tr>
<tr>
<td>5</td>
<td>0.043</td>
<td>0.016</td>
<td>2691</td>
<td>0.019</td>
<td>3.496</td>
</tr>
<tr>
<td>6</td>
<td>0.055</td>
<td>0.017</td>
<td>2589</td>
<td>0.018</td>
<td>3.377</td>
</tr>
</tbody>
</table>

Average = 4.175  28.798
Standard Deviation = 1.114  7.680

*Grinding Defect
Table A-4: Coating Bond Strength Data (2 of 2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating Thickness</th>
<th>Max Load (lbf)</th>
<th>Displacement Max (inches)</th>
<th>Max Stress (ksi Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre-</td>
<td>Post-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>surface</td>
<td>grinding</td>
<td>grinding</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.034</td>
<td>0.014</td>
<td>5580</td>
<td>0.034</td>
</tr>
<tr>
<td>2</td>
<td>0.039</td>
<td>0.021</td>
<td>6307</td>
<td>0.036</td>
</tr>
<tr>
<td>3</td>
<td>0.040</td>
<td>0.014</td>
<td>5618</td>
<td>0.035</td>
</tr>
<tr>
<td>4</td>
<td>0.037</td>
<td>0.016</td>
<td>3373</td>
<td>0.023</td>
</tr>
<tr>
<td>5</td>
<td>0.040</td>
<td>0.015</td>
<td>3864</td>
<td>0.025</td>
</tr>
<tr>
<td>6</td>
<td>0.035</td>
<td>0.015</td>
<td>4180</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>Average =</td>
<td>6.244</td>
<td>43.054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Standard Deviation =</td>
<td>1.529</td>
<td>10.541</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test 5: Series A + B (hBN-Ni)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy - No Coating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>NA</td>
<td>NA</td>
<td>8871 0.047</td>
<td>11.455 78.979</td>
</tr>
<tr>
<td>2</td>
<td>NA</td>
<td>NA</td>
<td>6896 0.041</td>
<td>8.797 60.655</td>
</tr>
<tr>
<td></td>
<td>Average =</td>
<td>10.126</td>
<td>69.817</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Standard Deviation =</td>
<td>1.879</td>
<td>12.957</td>
<td></td>
</tr>
</tbody>
</table>

Table A-5: Summary of feedstock powder and cold spray coatings

<table>
<thead>
<tr>
<th>Cold Spray Feedstock Powderer</th>
<th>Series A</th>
<th>Series B</th>
<th>Series A+B (55% A, 45% B)</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>hBN content (by volume)</td>
<td>1%</td>
<td>10%</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>Phosphorous content (by weight)</td>
<td>13.35%</td>
<td>5.27%</td>
<td>unknown</td>
<td>0%</td>
</tr>
<tr>
<td>Nickel content (by weight)</td>
<td>91.31%</td>
<td>94.44%</td>
<td>unknown</td>
<td>99.35%</td>
</tr>
<tr>
<td>Average particle powder (microns)</td>
<td>24.6</td>
<td>21.2</td>
<td>unknown</td>
<td>19.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cold Spray Coatings</th>
<th>Series A</th>
<th>Series B</th>
<th>Series A+B (55% A, 45% B)</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (HV)</td>
<td>337</td>
<td>302</td>
<td>317</td>
<td>219</td>
</tr>
<tr>
<td>Bond strength (Mpa)</td>
<td>71.67</td>
<td>28.79</td>
<td>43.05</td>
<td>21.19</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td>0.34</td>
<td>0.50</td>
<td>0.42</td>
<td>0.59</td>
</tr>
<tr>
<td>Sliding wear rate (x10-5 cc/m)</td>
<td>0.03</td>
<td>16.33</td>
<td>0.11</td>
<td>6.43</td>
</tr>
<tr>
<td>Reciprocating wear scar volume (mm³)</td>
<td>442</td>
<td>550</td>
<td>448</td>
<td>587</td>
</tr>
</tbody>
</table>
Table A-6: Electroless nickel reaction equations for hypophosphate baths

Electroless Nickel partial reaction model for hypophosphate baths [66], [67], [68]

<table>
<thead>
<tr>
<th>Equation</th>
<th>Reaction</th>
<th>Adsorption</th>
<th>Energy</th>
<th>Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2PO_2^- + H_2O \xrightarrow{\text{catalytic}} H^+ + HPO_3^- + 2H_{ads}$</td>
<td>Nickel - phosphorous adsorption phenomena model for hypophosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Ni^{++} + 2H_{ads} \rightarrow Ni^{o} + 2H^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2H_{ads} \rightarrow H_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2PO_2^- + H_2O \xrightarrow{\text{catalytic}} H_2PO_3^- + H_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2PO_2^- + H_{ads} \rightarrow H_2O + OH^- + P$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3H_2PO_2^- \xrightarrow{\text{catalytic}} H_2PO_3^- + H_2O + 2OH^- + 2P$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nickel-phosphorous adsorption phenomena model for hypophosphate [69] [70]

<table>
<thead>
<tr>
<th>Equation</th>
<th>Reaction</th>
<th>Adsorption</th>
<th>Energy</th>
<th>Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2PO_2^- + OH_{ads}^- \rightarrow H_2PO_3^-<em>{ads} + H</em>{ads} + e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H^+ + e \approx H$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H + H \approx H_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Ni^{++} + H_2O \approx NiOH_{ads}^{+} + H^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$NiOH_{ads}^{+} + 2e \rightarrow Ni^{o} + OH^{-}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2PO_2^-_{ads} + e \rightarrow P + 2OH^-$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H2PO_2^- + 2H^+ + e \rightarrow P + 2H_2O$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX B: Non-Technical Abstract

Wear is defined as the removal of material from solid surfaces as a result of one contacting surface moving over another. This movement can be a surface sliding over a significant distance or as small as vibrations that cause fretting. It is beneficial to add hard and/or lubricous coatings to mechanical surfaces to improve the materials’ wear resistance. Hexagonal boron nitride (hBN) is a common compound that exhibits exceptional solid lubrication properties; as its loosely held stacks of atomic planes allow the shearing that is necessary for lubrication. A self-lubricating coating will incorporate hBN particles in a metallic matrix, allowing the release of the lubricant particles during intimate contact with mating surfaces. By creating a self-lubricating coating, the coefficient of friction can be decreased to create a more wear resistant surface.

These self-lubricating coatings were fabricated by high velocity particle consolidation (Cold Spray), a process in which particles are accelerated in a super-sonic stream of gas toward a substrate. Upon impact with the substrate, the particles plastically deform and create bonds with the substrate; this plastic deformation is essential for the success of the cold sprayed coatings.

Before cold spray is feasible, hexagonal boron nitride must be encapsulated by nickel due to its brittle nature. The nickel encapsulation was performed with the electroless nickel plating process. This encapsulation protects the brittle boron nitride and allows particle deformation, which is critical for the success of cold spray deposition.
Boron nitride has been successful encapsulated by nickel resulting in a powder which was used to cold spray coatings on aluminum substrates. The wear properties of the coatings were tested and compared to a pure nickel cold sprayed coating. The results showed that incorporating an appropriate amount of hexagonal boron nitride in the nickel coating will reduce the coefficient of friction and the wear rate. Coatings were tested via reciprocating ball-on-flat wear, sliding pin-on-disk wear, and fretting. Feedstock powder and coatings were characterized through optical microscopy, scanning electron microscopy, energy dispersive x-ray spectroscopy, focused ion beam, micro hardness, and density.