WEAR AND EROSION-CORROSION BEHAVIOUR OF ELECTROLESS NI-P COMPOSITE COATINGS WITH NITI NANOPARTICLE ADDITIONS

by

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Abstract

Petroleum pipelines are susceptible to degradation from corrosion and erosion due to their service conditions. Surface enhancements are developed to prolong their lifespan, including protective coatings. Electroless Ni-P coatings are a promising candidate due to their high hardness and corrosion resistance but have low toughness. The addition of superelastic NiTi nanoparticles have been previously developed and shown to improve the coating's ductility. However, the performance of a coating is greatly influenced by its internal stress. The internal stresses in Ni-P coatings depend on both the addition of nanoparticles and its thickness. Different thicknesses of Ni-P and Ni-P-NiTi coatings were developed on API X100 and AISI 1018 substrates and characterized using SEM, EDS, XRD, and micro-hardness. Their sliding wear resistance was tested by multiple-pass scratch tests with a sharp indenter and a spherical indenter. Slurry pot erosion-corrosion was conducted to assess their performance to potentially protect a pipeline under similar conditions. Using both the material loss rates and observable wear behaviour, the effect of coating thickness and the presence of particles was evaluated. It was found that the thickness of the coating greatly influences its durability and its effectiveness differs depending on the wear process. Under sliding wear conditions, the thicker coatings are preferable. However, in erosion-corrosion conditions, the thinner coatings provided better protection. The addition of NiTi nanoparticles demonstrated toughening mechanisms that resulted in less cracking.

List of Abbreviations Used

AE	Acoustic Emission
AISI	American Iron and Steel Institute
API	American Petroleum Institute
CoF	Coefficient of Friction
Е	Elastic Modulus
EDS	Energy Dispersive Spectrometry
EN	Electroless Nickel
HV	Vickers Hardness
PDF	Powder Diffraction File
SE	Super-Elastic Effect
SEM	Scanning Electron Microscope
SME	Shape Memory Effect
SPEC	Slurry Pot Erosion-Corrosion
WR	Wear Rate
XRD	X-Ray Diffractometry

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Chapter 1 Introduction

Large volumes of oil and gas are transported at efficient rates over long distances to meet the high demand of petroleum products. One of the safest and most cost-effective transportation methods are through steel pipelines. [1, 2] They are typically made using low carbon steel due to its strength, durability, and wide availability. [3] However, often there is Cl⁻, O₂, H₂S or CO₂ present in petroleum, which are corrosive species. There could also be particulates such as sand or other solid particles. Those service conditions in the pipeline can significantly degrade the steel through corrosion and erosion. [2, 4, 5] When the mechanical abrasion and electrochemical corrosion are coupled, a material loss mechanism known as erosion-corrosion occurs. [2, 6] This results in a synergistic effect, where there is a higher mass loss than the summation of the mass loss from pure erosion and pure corrosion. [1, 6, 7] Therefore, the material degrades at a faster rate which reduces the steel pipeline's lifespan. [8] Frequent replacement of damaged pipeline steel is not efficient, and wear prevention through high durability material alternatives is costly. [2, 8] A promising method for slowing the rate of metal loss is with the use of surface enhancement to protect the base material from the environment. [5, 9, 10]

A potential method for reducing metal loss is by applying a protective coating on the inner pipeline. This would only be efficient if the coating does not require frequent reapplication. [9] Epoxy and polymer have been shown to improve steel's wear resistance but have limitations on their usage. [2] Epoxy coatings are susceptible to corrosion from certain chemicals in crude oil. [11, 12] Fortunately, there are other coatings that could be satisfactory candidates. [10, 13] A seemingly suitable option is electroless nickelphosphorus (Ni-P) coating due to its exceptional adhesion and high corrosion resistance from the lack of grain boundaries. [2, 5, 10, 14] Additionally, the coating is hard but brittle, conductive, and lubricous. It has been thoroughly researched and is already widely used as protective coating in many industries. More recently, Ni-P based composite coatings have been developed to improve the properties for specific applications. However, the composites developed mostly have used ceramic particles such as SiO₂, ZnO, and Al₂O₃. The ceramic particle additions in Ni-P improved its hardness and corrosion resistance but had minimal effect on toughness. [15, 16, 17, 18] This is inadequate for pipeline protection since Ni-P has considerably low toughness, which makes it particularly susceptible to erosion. Instead of hard particles, the addition of ductile particles into the coating could increase its toughness while maintaining Ni-P's high adhesion and corrosion resistance. [2, 14, 19]

The nickel-titanium (NiTi) alloy has uniquely high toughness and ductility, allowing it to be a potential candidate for an addition to Ni-P coating. In fact, electroless Ni-P composite coating with NiTi nanoparticles have been developed, and its characterization has shown promise for protecting oil and gas pipelines. [20, 21] The concentration of nanoparticles in the deposit was shown to have correlations with the mechanical properties. With increasing numbers, the wear resistance improved. However, its resistance decreases when the particles surpass a concentration threshold. At excessively high concentrations, the coating could not have proper adherence to the substrate. [22] This indicates that although the nanoparticles could improve wear resistance, there are limitations to the amount that should be included.

The reasoning for this could be partly attributed to the stress concentrations in the matrix surrounding the particle. It has already been shown that in composites, the number of particles present in the matrix has a relationship to the internal stress present in the material. [23, 24] Furthermore, R. Taheri [25] extensively evaluated electroless nickel-phosphorus coatings and found that its mechanical and corrosion properties are directly related to the state of internal stress. Therefore, excessive particles present in the matrix could cause a state of high residual stresses and its detrimental effects on wear resistance begin to outweigh the benefits of NiTi's ductility.

The state of internal stress is highly influential on the composite coating's reliability and performance. [26] However, the effects that the factors related to internal stresses in Ni-P-NiTi coating have on its durability has not been thoroughly explored. There are other variables that effect the degree of internal stress in addition to the concentration of the nanoparticles. Studies have found that the state of internal stress in many kinds of coatings are correlated with its thickness. [27, 28] This infers the possibility that the thickness of a Ni-P coating influences its internal stresses, and consequently its tribological behaviour. Furthermore, it can be expected that a Ni-P coatings' performance can be further influenced when the effect of thickness is coupled with the addition of particles' consequential stress concentrations. There has been no work in investigating how thickness effects electroless Ni-P nanocomposite coatings.

To further assess the capabilities of Ni-P-NiTi coatings, there needs to be an understanding on how the factors that cause internal stresses could affect its mechanical properties and tribological behaviour. This would include comparing the performances of monolithic Ni-P coating to Ni-P-NiTi composite coating, as well as the effect of varying the thicknesses of each type. This should include hardness measurements to understand its mechanical properties, and degenerative conditions such as sliding wear to evaluate its wear resistance. Furthermore, data on the synergistic conditions from corrosion and erosion are needed to understand their capability to protecting a pipeline from harsh conditions. To the authors knowledge, the erosion-corrosion behaviour of Ni-P-NiTi composite coating has not been studied in the open literature. With previous findings considered, the objectives are as follows:

- 1. Successfully prepare electroless Ni-P coatings and composite coatings that include NiTi nanoparticle additions on low carbon steel substrates.
- 2. Further characterize Ni-P-NiTi composite coating by controlling procedures to obtain a variety of thicknesses.
- 3. Study the tribological behaviour and wear mechanisms of Ni-P-NiTi composite with varied thicknesses and compare to Ni-P coating.
- 4. Inspect performance and degradation mechanisms of the coatings during erosion-corrosion as a function of coating thickness.

The second chapter contains a literature review on electroless Ni-P coating, electroless nickel (EN) composite coatings, NiTi alloy, toughening mechanisms, fracture mechanics, and residual stresses in coatings. Chapter 3 outlines the experimental methodology, and the results are discussed in Chapter 4. Chapter 5 is on the work's conclusions and future recommendations.

Chapter 2 Literature Review

2.1 NiTi Alloy

NiTi is a unique alloy that has super-elastic and shape memory effects, and their addition as a nanocomposite has been proven to toughen Ni-P coating. [21, 22]

2.1.1 NiTi Binary System and Phase Transformations

Figure 2-1 shows the Ni-Ti binary phase diagram. [29] There are three equilibrium intermetallic phases, NiTi, NiTi₂, and Ni₃Ti. NiTi is the phase that is associated with the alloy's martensitic transformation mechanism, which allows for its super-elasticity and shape memory effects. NiTi phase transformation includes three different possible crystal structures. Those being austenite, martensite, and R phase. [29, 30]



Figure 2-1 Ni-Ti Phase Diagram [29]

The austenite parent NiTi phase has a B2 (CsCl) type structure, which is highly ordered body centered cubic. This is shown in Figure 2-2, where the blue spheres on the boarder are Ti atoms and the inner red spheres are Ni atoms. [30]



Figure 2-2 Ni-Ti B2 Austenite Phase [30]

When the high temperature B2 parent phase is cooled below its transformation temperature, it's structure changes to the martensite phase. There is an intermediate martensite phase B19, which has an orthorhombic crystal structure shown in Figure 2-3. However, the B19 phase is not stable. Therefore, the transformation results in B19' martensite phase shown in Figure 2-4. B19' has a monoclinic crystal structure. [30]



Figure 2-3 Ni-Ti B19 Martensite Phase [30]



Figure 2-4 Ni-Ti B19' Martensite Phase [30]

When B2 phase directly transforms into B19', it is known as a one-step martensitic transformation. However, under certain conditions this transformation can be two steps and would include a distinct martensitic transformation phase known as R-phase. R-phase has a trigonal crystal structure and competes with the formation of B19' phase. If R-phase begins to form before B19', the transformation is two step and occurs as B2 to R to B19'. However, if B19' formation occurs first, the formation of R-phase, is suppressed and the transformation is only two steps.

R-phase formation is dependent on the presence of precipitates, alloy additions, heat treatment processes, and internal stresses. [30, 31]

Figure 2-5 is a schematic that shows the paths of phase transformation from B2 austenite to B19' martensite. It includes crystal structures and possible transformations. [31]



Figure 2-5 Ni-Ti Phase Transformation Paths [31]

2.1.2 Shape Memory Effect

Shape memory alloys have the unique ability to endure large recoverable strains and return to their original shape. In very simplified terms, NiTi has phase transformations that allow recovery to its original shape when heated. At lower temperatures and no deformation, NiTi is in a twinned-martensite phase that is extremely ductile. At high temperatures, it undergoes diffusion-less shear phase transformation into austenite phase. With a sufficient load applied at lower temperatures, the twinned martensite undergoes detwinning and changes into deformed martensite. Heating the deformed martensite initiates a reorientation process, and the crystal structure transforms back into the austenite phase as if the material remembers the original shape-hence the term "shape memory". After cooling out of the austenite phase, twinned martensite phase is the result. [32, 33, 34, 35] Figure 2-6 is a schematic of the shape memory effect in relation to temperature and load. [33]



Figure 2-6 Shape Memory Effect [33]

2.1.3 Super-Elastic Effect

Elasticity simply refers to the level of strain a material can undergo without plastic deformation. NiTi being referred to as "super-elastic" means the amount of strain it can undergo is factors more significant than most common metal alloys. Similarly to the shape memory effect, the reasoning for NiTi's super-elasticity is also its phase transformation mechanisms. When in austenite, the martensitic transformation can be induced by stress and strain. The phase change occurs when an applied load stress exceeds the stress needed for martensite transformation. This transformation is reversible upon unloading that allows for a recoverable elastic strain up to 10-12%. When compared to the typical alloy \that only has elastic strain of around 2-3%, the significance and reasoning is clear for NiTi's recoverable strain to have the special distinction of super-elastic. [32, 35, 36, 37]

2.2 Electroless Ni-P Coatings

Ni-P plating is deposited by the reduction of nickel and phosphorous cations using either an electrolytic cell or electroless bath. Electrolytic deposition uses an external electrode to drive a non-spontaneous redox reaction, while electroless deposition relies on an autocatalytic reaction mechanism. The spontaneous reactions use a chemical reducing agent in the solution to reduce the ions. Electroless nickel plating is more efficient and produces a more uniform and less porous deposit than electrolytic deposition. The first successful electroless nickel plating method was first introduced by Brenner and Riddell in 1946. [38] Since, the process had been refined and improved to optimize the coating's effectiveness. For proper coating adhesion, efficient deposition, and uniformity the plating bath conditions must be optimized and stable. This requires an understanding of the factors for a stable bath that include its temperature, pH, concentration of ions, and bath load. [39, 40]

2.2.1 Synthesis Mechanisms

Typically, either a nickel sulfate or nickel chloride is used as a source of nickel. Sodium hypophosphite serves as a reducing agent for the nickel ions and the supply of phosphorous. Once the nickel ions are reduced into a thin layer of nickel on the substrate surface, the deposit then serves as a catalyst for the co-deposition of phosphorous to form Ni-P coating. [25, 40] The phosphorous deposit is supplied by H₂PO₂⁻ reduction and shown below in equations 1 and 2. [22, 25]

$$H_2PO_2^- + 12H_2 \to H_2O + OH^- + P$$
 (Equation 1)

$$3H_2PO_2^- \rightarrow H_2PO_3^- + H_2O + 2OH^- + 2P$$
 (Equation 2)

Equations 3, 4, and 5 show the reduction of nickel using $NaH_2PO_2 \cdot H_2O$ as the reducing agent and NiSO₄ for supplying the nickel ions. Once the NaH_2PO_2 is oxidized, the Ni²⁺ ions from the NiSO₄ are then reduced and bond with the substrate surface. [22, 25]

$$3NaH_2PO_2 + 3H_2O + NiSO_4 \rightarrow 3NaH_2PO_3 + H_2SO_4 + 2H_2 + Ni$$
 (Equation 3)

$$2H_2PO_2^- + Ni^{2+} + 2H_2O \rightarrow 2H_2PO_3^- + H_2 + 2H^+ + Ni$$
 (Equation 4)

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni^0 + H_2PO_3^- + 2H^+$$
 (Equation 5)

Following the formation of the first layer of deposited nickel, it is available to act as a catalyst and co-deposition can occur with the phosphorous produced from equations 1 and 2. The reaction mechanisms of Ni-P deposition are not fully verified, however a widely accepted hypothesis uses atomic hydrogen theory. This means that while hydrogen absorbed, it is subsequently consumed which drives the coating deposition reactions. Equation 6 shows water and hypophosphite producing the hydrogen, and equations 7 and 8 show the reactions for Ni-P deposition. [22, 25]

$$H_2PO_2^- + H_2O \to H^+ + H_2PO_3^{2-} + 2H$$
 (Equation 6)

$$Ni^{2+} + 2H \rightarrow Ni + 2H^{+}$$
 (Equation 7)

$$H_2PO_2^- + H \rightarrow P + OH^- + H_2O$$
 (Equation 8)

2.2.2 Preparation Requirements

2.

Ni-P coating requires a strong adhesion bond to the substrate for effective protection. This requires proper substrate preparation and optimized bath conditions. The substrate needs to have a smooth clean surface and pre-treatment. Metal substrates such as steel and aluminum should be first grinded using abrasive grit paper, next polished with diamond suspensions, and then degreased. The subsequent surface pre-treatment typically involves using an alkaline cleaning solution and acid etchant. A heated solution composed of sodium hydroxide or sodium carbonate is commonly used for alkaline cleaning, whereas a diluted H₂SO₄ or HCl solution is used for the acid etch. However, this pre-treatment process varies based on the substrate material. [21, 40]

As previously mentioned, the properties of the coating also are directly dependent on the conditions of the bath. Key parameters include temperature and pH, which control the deposition rate. If they are out of optimal range, the deposition rate slows and the bath becomes unstable. [21, 22, 25] Molla et al. [41] studied how Ni-P deposition on carbon steel was affected by the parameters. The findings included the effect of temperature and pH on deposition rate, shown below. Figure 2-7 shows the effect of temperature and Figure 2-8 shows the effect of pH. [41]



Figure 2-7 Effect of Bath Temperature on Ni-P Deposition Rate [41]



Figure 2-8 Effect of pH on Ni-P Deposition Rate [41]

High temperature is the supplied energy that drives the autocatalytic reactions. This means that the temperature determines the rate of reactions and therefore the deposition

rate. When the temperature decreases, the reactions lose energy and causes a decrease in deposition rate. For the autocatalytic reactions to take place the bath needs to remain above 70°C. Below that 70°C threshold, the solution is steady and does not form a deposit. Through the same reasoning, increasing the temperature increases the deposition rate. However, there are limits on the effectiveness of elevated temperature has on increased deposition. When the temperature exceeds 95°C, the bath becomes excessively active. This makes the plating solution susceptible to decomposition which decreases the deposition rate. On the other hand, pH level is correlated specifically to Ni and P reduction reactions. With increasing pH, Ni reduction increases and P reduction decreases. This means if the pH either too high or too low, the Ni and P are deposited at different rates and the deposit composition is affected. In general, higher pH baths have an increased deposition rate and produce a lower phosphorous deposit. Conversely, lower pH baths produce a higher phosphorous deposit and a decreased deposition rate. There is also better coating adhesion associated with lower pH, but when it is lower than 4.0 the deposition rate is too low. [41, 42] Optimal bath conditions vary slightly depending on the solution used for plating. In this work, the solution used had optimal conditions of a temperature of $88 \pm 2^{\circ}$ C and a pH of 4.7 ± 0.2 [21, 22, 25]

2.2.3 Coating Microstructure and Properties

Phosphorous content drastically changes the coating's microstructure and properties. There are three categories of Ni-P coatings: low phosphorous, medium phosphorous, and high phosphorous. Between 1-5wt%P is considered low phosphorous, medium phosphorous has a range of 6-9wt%P, while high phosphorous has 9-11wt%P. Lower phosphorous content is associated with crystallinity and becomes more amorphous as phosphorous content increases. [22, 39, 40] Figure 2-9 shows the amorphous formation region in the Ni-P phase diagram in relation to the category phosphorous content in a coating. [43]



Figure 2-9 Phosphorous Content in Ni-P [43]

Depending on the phosphorus content and subsequent heat treatments, ductility and hardness properties vary. Lower phosphorous content is associated with low ductility, but high hardness and wear resistance. On the other hand, the amorphous structures present with higher phosphorous content coatings allow for higher ductility and corrosion resistance. Typically, where $HV_{0,1}$ is the Vickers Hardness at 100g load, the as-deposited coatings' hardness ranges from 500-700 $HV_{0,1}$, and with subsequent heat treatment can be up to 1100 $HV_{0,1}$. [44] The ductility starts at 0.7% elongation for crystalline Ni-P but increases to 1.5% elongation with a purely amorphous microstructure. Furthermore, the modulus of elasticity is around 130GPa in purely crystalline Ni-P and approximately 170GPa in purely amorphous Ni-P. However, when the Ni-P is a mixture of crystalline and amorphous, the modulus of elasticity ranges from 100 to 120GPa. The internal stress also changes with the phosphorous concentrations and the level of crystallinity in the coating. [45]

2.3 Ni-P Composite Coating

Composite electroless Ni-P coatings are classified by the incorporation of particles into the Ni-P matrix to enhance a property. This is to maximize the coating's performance to suit the needs for a specific application. By maintaining a powder suspension in the bath, the particles are enveloped by the coating matrix as they settle on the substrate surface. This allows for co-deposition, and the powder is incorporated into the deposit. In theory, virtually any material could be added if the particles are of appropriate size could withstand the electroless bath conditions. [22, 39] Commonly studied nanoparticle incorporations for Ni-P include diamond, ceramics, and metal alloys. [39, 46, 47, 48]

2.3.1 Incorporation of Second Phase Particles

Powder properties and plating bath parameters influence the effectiveness of particle incorporation into the coating matrix.

Firstly, particle size needs to be considered. There needs to be a balance where the particles are large and heavy enough to settle onto the substrate surface, but not large to the degree that they cannot maintain suspension. Furthermore, if the particles are too large relative to the coating thickness the deposit surface becomes excessively rough. Balaraju et al. [39] has suggested the optimal particle size to be 4-7µm for electroless Ni-P composites. However, this is not consistently recommended as some studies have found that the optimal particle size to be even smaller. For instance, Reddy et al. [49] found that smaller particles can be firmly held by the matrix leading to better integrity and improved wear resistance. Similarly, particle shape also influences deposition of the composite. With proper particle integration, a common belief is that angular shaped particles have a higher tendency to hold onto the matrix than rounder shapes. However, findings by Apachitei et al. [50] found that with alumina the spherical shaped particles had an improved matrix incorporation as opposed to their irregular shaped equivalent. [50] Generally, rough deposit surfaces have been associated with the addition of large, angular particles while smooth deposit surfaces correlates to the use of small, rounded particles. [39]

Plating conditions that need to be considered for proper particle incorporation can include agitation, sample orientation, and particle concentration. Agitation allows for the

prevention of particle agglomeration with a uniform particle distribution in the bath. Stir speed is correlated with fluid flow, and therefore the particle dispersion. Laminar flow is associated with lower stirring speeds and prevents a uniform distribution of particles. A composite prepared by a bath that had excessive laminar flow will exhibit poor particle distribution. On the other hand, higher stirring speeds are associated with turbulent flow. In this scenario, the particles do not have the sufficient time on the substrate surface needed to adhere since they are removed at such a rapid rate. A composite prepared by a bath that had excessive turbulent flow results in poor particle incorporation. An optimized stir speed should create a flow that lies within the transition between laminar and turbulent flow. [39]

Another important consideration for composites is sample orientation. The substrate needs to be placed in accordance with gravity which allows the particles to settle on the surface. The number of particles on the surface of a sample doubles when the substrate placement is changed from a vertical placement to horizontal. However, the high particle amount would only be on the upwards facing horizontal surface and there will be little to no particles present on the downward facing surface. [21, 22, 39]

However, the most important factor for particle incorporation is irrefutably the concentration of the particles in the bath. There is a very strong correlation between particle concentration in the bath and particle content in the deposit. As particle concentration in the solution increases, the particle content in the deposit also increases. However, this relationship is only maintained up to the saturation point. When the saturation limit is exceeded, the particle concentration becomes too high to maintain adequate space between the particles. This causes agglomeration and particle settling, which hinders particle incorporation therefore decreasing the number of particles in the deposit. [21, 22, 39]

2.3.2 Properties of Various Composites

The motivation behind most studies on Ni-P composites have been to improve the coating's hardness, wear resistance, or corrosion resistance. Promisingly, many varieties of nanoparticle additions have been shown to improve properties of Ni-P coatings.

Coating hardness and wear resistance can be improved using ceramic nanoparticles. This effect was replicable on different substrate materials. F. El-Taib Heakal et al. [18] used a magnesium substrate to test NiP/Al₂O₃ wear and corrosion resistance. Z. Abdel Hamid et al. [48] used an aluminum substate and tested multiple ceramic nanoparticles. ZrO₂, TiO₂, and Al₂O₃ all had their effect of concentrations in the bath on the amount deposited, and it was found the nanoparticles provided satisfactory improvement in hardness and wear resistance of the deposits.

Different types of titanium-based ceramics including TiO₂ and TiN have been studied as nanocomposites for the Ni-P coating. I. Saravanan et al. [51] studied the wear behaviour of electroless Ni-P and Ni-P-TiO₂ composite coatings on a EN8 steel substrate, and it was found that the composite coating had better wear properties comparatively to the Ni-P coating. [51] Recently, B. Chen et al. [52] studied the effects of Re on electroless Ni-P-TiN nanocomposite coating and had promising results for further improving the nanocomposite. This was done by comparing the microstructures and properties of three coatings Ni-P, Ni-P-TiN and Ni-P-TiN-Re. It was found that the Re addition significantly increased the deposition rate and had better hardness and wear resistance than the Ni-P-TiN coating. [52]

Overall, electroless Ni-P coating has excellent corrosion resistance due to the absence of grain boundaries. [53] However, many studies have found that the incorporation of certain kinds of nanoparticles can increase corrosion resistance for Ni-P coating. For example, recently A. R. Shashikala et al. [16] compared the corrosion resistance of Ni-P and Ni-P/ZnO nano composite coatings. The nanoparticle addition was found to enhance both its corrosion resistance and microhardness. [16]

Several types of nanoparticle additions have even been shown to reduce the synergistic effect of erosion-corrosion. J. A. Calderón et al. [19] also found a nanoparticle addition to dramatically improved the Ni-P coatings' corrosion resistance. Ni-P/Ni(OH)₂-ceramic nanoparticle composite coatings were used on a magnesium substrate to improve its resistance to erosion-corrosion damage. The corrosion rate was four times lower with the nanoparticle composite addition comparative to the Ni-P without particles. [19] Another erosion-corrosion behaviour study was done by T. R. Tamilarasan et al. [10] using Ni-P-rGO coatings. It was found that the incorporation of reduced graphene oxide (rGO) particles greatly improved the erosion-corrosion resistance of Ni-P coating. [10] In a similar study, A. Rana et al. [5] studied how Ni-P coating's erosion-corrosion behaviour was affected by the addition of graphene nanoplates (GNPs). It was found that the GNPs

improved pure erosion and erosion-corrosion resistance. [5] Z. Li et al. [54] studied the erosion-corrosion resistance of electroless Ni-P-Ti coating, and the ductile titanium particle addition significantly improved pure corrosion, pure erosion, and erosion-corrosion resistance. [54]

2.4 Residual Stresses

Overall, most coatings will have high internal tensile stress near the substrate. As the thickness increases, the tensile stress decreases rapidly and at higher thicknesses compressive stress is present. For instance, A. Vereschaka et al. [27] studied the effect that varying the thickness of the composite coating Zr-ZrN-(Zr,Al,Si)N had on its residual stresses and wear properties. Thicknesses of about 2.0, 4.3, 5.9, and 8.5µm were studied. It was found that from 2.0-5.9µm exhibited a decrease in tensile stress as the thickness increased, and when the coating thickness reached 8.5µm compressive internal stress was present. This effect has been found in composite coatings as well, and that particle additions could also decrease internal tensile stress. For instance, E. Saraloğlu Güler et al. [28] studied how residual stress was affected by the electrodeposition parameters of electrodeposited Ni and Ni-MoS₂ composite coatings. The findings included that increasing the thickness and MoS₂ addition both resulted in the decrease in the internal tensile stress values. The particle additions also contributed to a change of the nature of the internal stresses, from tensile to compressive. [28] Relatedly, another study of electroless nickel nano-composite coating by Z. Zhang [55], which used ZrC as a nanoparticle addition, found that with an increased thickness and an increased particle amount resulted in decreased tensile internal stresses. [55]

There have been studies on the residual stresses in electroless nickel coatings, including the influence that coating thickness has. K. Parker [56] measured the internal stress of electroless Ni-P coating using what is known as the Rigid Strip Method. Thin metal strips have coating on one side, and they bend to accommodate the residual stresses in the coating. If the strips were bent convex to the coating side, the coating has compressive residual stress. However, if the strip bends concave, the coating has tensile residual stress. Figure 2-10 shows how the stress of the plate is calculated. [56]

STRESS OF PLATE



From there, the stress of the entire body can be converted to stress in the coating exclusively. This experiment used thin, straight strips of aluminum, beryllium, and mild steel. It was found that the residual stress in the coating varied mostly from substrate material, phosphorous content in the coating, and plating bath conditions. Notably, compressive stress increases with increasing phosphorus content of the Ni-P deposit. [56] A study by J. Y. Song et al. [57] had also found a decrease in tensile stress when phosphorous content increased in the electroless Ni-P coating deposit. However, in this study there were no coatings that had compressive residual stress. Regardless of phosphorous content, the internal stress remained tensile but did decrease in magnitude as the phosphorous increased. [57]

The level of residual stress has shown to correlate with a coating's corrosion resistance. H. Liu et al. [58] compared electroless Single Ni–P, single Ni–Mo–P, and duplex Ni–P/Ni–Mo–P coatings' residual stresses and corrosion behaviours. The single Ni-Mo-P coating had high residual tensile stress, while the duplex Ni–P/Ni–Mo–P coating

exhibited high compressive stress. It was found that the duplex Ni-P/Ni-Mo-P had the best corrosion resistance. The higher residual compressive stress in the duplex Ni-P/Ni-Mo-P impeded the growth of porosity during corrosion, therefore improving corrosion resistance. [58]

2.5 Cracking and Toughening Mechanisms

Assessing the effectiveness of a coating greatly relies on understanding its wear behaviour. This is because observable cracking and deformation that occurs gives context to the mechanical properties. To do so, it is important to understand contact modelling and the mechanisms involved in improving wear resistance.

2.5.1 Hertzian Contact Model

When load is applied to two surfaces in contact, consequential localized deformation and stress distribution can be modeled. A variety of analysis assumptions and techniques exist to define parameters of different contact models. This includes Hertzian contact, which is a common simple model that assumes a linearly elastic sphere indenting an elastic sphere when the contact radius is significantly smaller than the bodies. Hertzian stress distribution can be used to define the internal stresses and strains in the elastic bodies using a set of elastic body equilibrium equations. The boundary conditions include that there is zero pressure force on the surfaces not in contact with each other and that the contact area has equal and opposite pressure forces. The contact is also frictionless with no adhesion. [59]

Although the Hertzian contact model is defined by elastic contact, it is useful for approximating elastic-plastic contact behaviour. Hertzian indentation analysis is utilized to assess the contact of brittle materials and their failure modes. [60] Indentation from a rigid sphere on the contact body induces a region of compressive stress, with generated tensile stresses on the edges of the region. The maximum tensile stress occurs at the surface along the contact circle. If the applied load exceeds the critical load, hertzian cracks form from the opposing compressive and tensile stresses. Hertzian cracks are also known as cone cracks, which propagate from the region of maximum tensile stress. They appear as rings on the surface that extend downwards into a cone shape. There could also be a network of microcracks in the quasi-plastic zone under the indenter. The hertzian cracks and quasiplastic zone relative to the intender are shown in Figure 2-11. 'P' represents the applied load, 'a' is contact radius, and ' ρ ' is the indenter radius. [60]



Figure 2-11 Hertzian Cracks [60]

Through this model, the mathematical relationship between indenter load (P), indenter radius (ρ), contact radius (a), and maximum tensile stress, (σ_{max}) can be defined. [59] To be able to find the contact radius, the elastic modulus of both the contact body and indenter (E*) needs to be calculated. 'E*' is defined using equation 9, where v and E are the Poisson's ratio and elastic modulus. The variables 'v_i' and 'E_i' are properties of the indenter, while 'v_b' and 'E_b' are properties of the contact body's surface.

$$\frac{1}{E^*} = \frac{1 - v_i^2}{E_i} + \frac{1 - v_b^2}{E_b}$$
(Equation 9)

When ' E^* ' is defined, the contact radius is calculated using equation 10.

$$a^3 = \frac{3P\rho}{4E^*}$$
(Equation 10)

The maximum tensile stress can be calculated using equation 11.

$$\sigma_{\max} = (1 - 2\nu) \frac{P}{2\pi a^2}$$
(Equation 11)

2.5.2 Crack Types

Cracking in the coating mean that it has failed, therefore the substrate is no longer properly protected and is susceptible to wear and corrosion. [61] There are several types of applicable crack types that have different origins and consequences which can be applied to the hertzian contact model. Types include cone, radial, median, half-penny, and lateral shown in Figure 2-12. [62] Cone cracks were previously defined as Hertzian cracks, that form from hertzian indentation. Radial cracks extend outward from the edge of plastic contact and are parallel to the load axis. Median cracks propagate parallel to the loading axis and are formed beneath the plastic deformation zone. Half-penny cracks are formed from median cracks extending to the surface. Lastly, lateral cracks are parallel to the surface and formed beneath the deformation zone. [59, 62]



Figure 2-12 Types of Cracks [62]

2.5.3 Toughening Mechanisms

When ductile particles are added into the matrix of a brittle material such as Ni-P coating, the increase in toughness can be explained through the crack's interaction with the particles. [25] There are different toughening mechanisms involved that include crack bridging, crack deflection, micro-cracking, and transformation toughening.

When a crack propagates and interacts with the secondary ductile phase, the high forces in the crack could plasticly deform the particles. However, plastic deformation uses the energy behind the driving force of the crack wake. This means that with every particle that is plastically deformed, there is less energy available for the crack to continue to propagate. Therefore, the amount of plastic deformation that the particle endures lessons as the crack loses its driving energy until it eventually stops expanding. This is known as crack bridging and occurs when the ductile particles have high adhesion to the brittle coating matrix. [63, 64] Figure 2-13 is a schematic of the crack bridging mechanism with the relationship between the crack's force with the amount of particle deformation. [63]



Figure 2-13 Crack Bridging Mechanism [63]

Similarly, crack deflection is when the crack loses driving force when the direction of propagation is changed by interacting with the secondary phase without plastic deformation. This path change uses energy, therefore lessening the stress available for the crack wake. [65] This can occur with or without direct contact with the particle. Figure 2-14 shows both cases of interaction with the particles during crack deflection. In the case of Figure 2-14 (a), the stress field around the crack tip causes elastic deformation of a nearby particle. The elastic deformation absorbs the crack's driving energy, and the tip deflects. For Figure 2-14 (b), the crack's driving force is not high for either for plastic deformation or for the particles to de-bond from the matrix. However, the interaction from the crack and the particle changes the propagation's path, which still absorbs the driving energy. [65]



Figure 2-14 Crack Deflection [65]

Microcracking is when the secondary ductile phase induces a large crack to branch into many microcracks. This consumes crack energy, and therefore increases the toughness of the material. [64]

Transformation toughening uses the NiTi's stress-induced phase transformation mechanism. [21] This phase transformation toughens the material in two ways. First, similarly to previously discussed fracture toughness mechanisms, the transformation absorbs the energy that would be needed for the driving force behind crack propagation. Secondly, the phase transformation increases the volume of the particle which creates a surrounding stress field in the matrix. This stress field is compressive, which reduces the tensile stresses involved in crack opening. [66]

2.6 Sliding Wear

With contact models and cracks defined, these concepts can be applied to understand the mechanisms of sliding wear. Sliding wear involves a combination of complex wear mechanisms which all simultaneously affect the contact surface. The wear behaviour that a material exhibits is greatly dependent on it's mechanical properties and the sliding parameters. The basic wear mechanisms that are applicable to sliding wear of coating include delamination, abrasion, and adhesion.

2.6.1 Delamination

Delamination is of great concern for coatings. In short, coating delamination is when it peels off from undergoing sliding wear. This occurs when the material cracks at the interface between material layers, which causes coating to de-bond from the subsurface and therefore the layers separate. Figure 2-15 shows delamination occurring from sliding wear. [67]



Figure 2-15 Delamination [67]

2.6.2 Abrasion

The most universally common type of wear damage across most materials is abrasion. Abrasive wear is classified as the plastic deformation of a softer material that occurs from contact with hard asperities. The type of material and dynamics of the sliding contact greatly affect the characteristics of the plastic deformation. There are damage modes caused by abrasion that differ depending on the surface material and asperity. [68, 69] These include cutting, fracture, fatigue from ploughing, and grain pull-out, which are depicted in Figure 2-16. [68] Cutting is when a sharp and hard asperity cuts the surface of the softer material. The cut material is removed from further sliding which forms wear debris. Fractures occur when the material surface is brittle. Cracks form from the sliding force, and wear debris is generated when the cracks converge. Fatigue happens when the material surface is ductile, and the abrasion particle has a blunt shape. The repeated ploughing causes the worn surface to be repeatedly deformed, and eventually forms wear
debris. Grain pull-out occurs in materials with grain boundaries, which allows for entire grains to be removed from the material body to generate wear debris. [68]



Figure 2-16 Abrasion Damage Modes (a) Cutting (b) Fracture (c) Fatigue by Repeated Ploughing (d) Grain Pull Out [68]

There are two classifications of abrasion: two body wear and three body wear. Two body abrasion occurs when two bodies are in contact, and one material is substantially harder than the other. In this case, the damage exclusively occurs on the softer surface and does not occur on the harder material body. This type of wear is often seen in mechanical industrial processes such as machining, grinding, and cutting. On the other hand, threebody abrasion's wear is from a hard abrasive particle that has different properties than either of the moving bulk surfaces. The particle acts as an interfacial third body and is responsible wear on either or both surfaces. This type of wear is seen during material polishing. [68, 69]

Figure 2-17 [69] shows a schematic of the differences between two body abrasion, three body abrasion, and erosion. Both erosion and abrasion involve surface wear from particles, but they have different forces that drive the particle contact on a surface. Erosion damage happens when particles impact the material due to outside forces, but during abrasion the particles are from the sliding force of opposing surfaces. [69]



Figure 2-17 Abrasion Comparisons [69]

2.6.3 Adhesive Wear

Adhesive wear occurs when two surfaces are sliding against each other and asperities on the surface are the contact points. Therefore, the contact load is concentrated to the asperity's small area. This means there is very high pressure on the contact point, which leads to adhesion between the asperities that are known as adhesive junctions. As continued sliding occurs, the junctions sheer and break away. This fracture at asperity contact causes the most substantial adhesive wear damage. However, prior to fracture the adhesion junctions could cause other damage to the sliding surfaces including plastic deformation and crack formation. The adhesive wear mechanism is shown in Figure 2-18. [70]



Figure 2-18 Adhesive Wear [70]

Chapter 3 Experimental Details

3.1 Fabrication and Microstructural Characterization of Coating

3.1.1 Substrate Characterization

Two types of low carbon steels substrates were used as coating substrates. These included rectangular AISI 1018 steel coupons and cylindrical API X100 steel. The rectangular substrates had the dimensions of 18mm × 10mm × 6mm, and were used in the erosion-corrosion tests and Vickers microhardness tests. The API X100 cylinders had a diameter of 1cm with a thickness of 1cm and were used for scratch tests. The standard elemental compositions of AISI 1018 and API X100 are shown below in Table 3-1. [71] Their properties are listed in Table 3-2. [2]

Weight %	AISI 1018	API X100
С	0.182	0.103
Mn	0.754	1.221
Cu	0.186	0.009
Cr	0.181	0.070
Ti	0.008	0.018
Si	0.095	0.121
V	0.001	0.36
Р	0.040	0.010
S	0.021	0.001
Fe	Balance	Balance

 Table 3-1 Composition of AISI 1018 and API X100 Steel Substrates [71]

Properties	AISI 1018	API X100
Density (g/cm3)	7.87	7.87
Young's Modulus (GPa)	205	210
Vickers hardness (GPa)	1.70	2.50
Yield strength (MPa)	370	690
Tensile strength (MPa)	440	820

Table 3-2 Properties of AISI 1018 and API X100 Steel Substrates [2]

3.1.2 Particle Characterization

US Research Nanomaterials Inc. supplied the NiTi alloy nanopowder that used as the secondary addition in the composite coatings. It was advertised to be 99.9% 60nm and a Ni:Ti ratio of 1=1.

Previous work had conducted analysis on the same powder and used inductively coupled plasma optical emission spectrometry (ICP-OES) to find the chemical composition. The results were that approximately 53wt.%Ni, and 40.25wt.%Ti are in the powder as received. There were minor amounts of In, Sn, S and Cu included in the composition. The characterization also included analyzing the powder morphology with images taken by a Hitachi S-4700 Scanning Electron Microscope (SEM), and it was found that the particles were spherical with a broad size distribution. The D10, D50 and D90 values were found to be 0.0218µm, 1.06µm, and 9.51µm respectively. [22]

3.1.3 Coating Preparation

The substrate surface pre-treatment steps are listed below in Figure 3-1. The steps were grinding, polishing, alkali cleaning, and lastly acid cleaning.



Figure 3-1 Substrate Pre-Treatment Steps

After pre-treatment, the substrates were rinsed with distilled water and then immersed into the industrial grade Ni-P plating solutions. Each bath consisted of 1L of solution that would be used to coat two or three substrates. The solution comprised of deionized water, NiSO4 as a source of nickel, and NaPO₂H₂ as a reducing agent. For the monolithic coatings, the substrates were left in the same bath for the full duration of their deposition. For composite coatings, two baths were used. One that was pure Ni-P monolithic solution, which was used as a pre-coating to increase the composite's adhesion. Depending on the substrate and desired thickness, the pre-coat deposition ranged from 5 to 30 minutes. Immediately after, the substrates were put into the composite solution had 1g of NiTi nanopowder added per 1L of solution. Figure 3-2 shows the set-up for depositing composite coatings, which includes the Ni-P pre-coat on the hot plate and two composite coating cells. In both monolithic and composite baths, the samples were hung horizontally.



Figure 3-2 Composite Coating Deposition Set-Up

For each type of coating, there needs to be a thin and thick variety. The thicknesses were controlled through the plating deposition time and bath composition. The deposition times were chosen by deposition rates that were reported in previous work with monolithic Ni-P, and nanoparticle composites of Ni-P-NiTi and Ni-P-Ti. However, deposition rates can vary based on pH, stirring variations, and sample load. Therefore, experiments could produce different results. This served as a starting place and adjusted as needed. Figure 3-3 shows monolithic Ni-P deposition rates that were found experimentally. From that data, the monolithic Ni-P would require 1 hour of plating time for a 10µm thickness and 3 hours of plating time for 30µm. [72]



Figure 3-3 Electroless Ni-P Plating Time vs Thickness [72]

Figure 3-4 shows Ni-P-NiTi coating thicknesses produced after a 6-hour plating time from various particle concentrations in the plating bath that was found in previous work. [22] Deposition rate is not constant over the entire deposition time, so it is very likely that a short and long deposition would produce different deposition rates. For 1g of NiTi, the deposition rate was found to be approximately 5µm per hour. [22]



Figure 3-4 NiTi Particle Concentration in Plating Bath vs Coating Thickness [22]

After plating, to ensure a smooth and even surface for testing the samples were carefully polished. Some of the composite samples had a particularly rough surface after coatings and required a very brief with light pressure grind on 600 grit paper. Coatings were polished using the 1µm diamond suspension to minimize material removal.

3.1.4 Coating Characterization

X-Ray Diffractometry (XRD) analysis was done on API X100 steel, NiTi nanopowder, Ni-P coating surface, and Ni-P-NiTi composite coating surface to identify the phases present. A Bruker D8 Advanced X-Ray Diffraction System was used with Cu K α radiation. The scan went from 20° to 120° a with a fast scan speed, and the generated peaks were identified using Powder Diffraction Files (PDF) to evaluate their crystal structure.

To confirm that the coatings have varied thickness with proper deposition, the first batch of samples had a side of each coating type on a rectangular substrate were polished so that the substrate and coating cross section could be examined. The cross sections were examined using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) mapping. After the procedure is proven to be effective using EDS, the samples made later simply had micrographs of the cross section taken to find their thickness. Those images were taken on a Keyence confocal laser microscope.

3.2 Mechanical Properties of Coatings

Micro-hardness tests were done on the monolithic Ni-P and nanocomposite Ni-P-NiTi coatings. A Vickers indenter was used with an applied load of 6N. The tests were repeated multiple times over the surfaces to ensure replicable results.

The Young's modulus was calculated from the load-depth curve by using the Oliver and Parr method. Figure 3-5 shows a schematic of a typical load versus displacement curve. The curve features elastic–plastic loading followed by elastic unloading. [73]



Figure 3-5 Load-Depth Curve [73]

' P_{max} ' is the maximum load and 'dP/dh' is the slope of the unloading curve. The variable ' h_{max} ' is the total depth relative to the surface at maximum load, which includes both the depth of the indenter contact and the additional indentation depth. The contact depth is ' h_a ', while the indenter's depth is ' h_c '. The indenter depth ' h_c ' calculation is shown in equation 12. [59, 73]

$$h_{c} = h_{max} - \left(\frac{2(\pi - 2)}{\pi}\right) \left(\frac{P_{t}}{dP_{dh}}\right)$$
(Equation 12)

The hardness 'H' is then calculated using equations 13 and 14 where 'A_c' is the contact area. The variable 'k' is a constant and is assumed to be 24.5 when a Vickers indenter is used. [59, 73]

$$A_{c} = kh_{c}^{2}$$
(Equation 13)
$$H = \frac{P_{max}}{A_{c}}$$
(Equation 14)

For Young's Modulus of the tested material to be found, the combined elastic modulus of the system 'E*' needs to be calculated. This is shown in equation 15. [59, 73]

$$E^* = \left(\frac{dP}{dh}\right)\frac{\sqrt{\pi}}{2\sqrt{A}}$$
(Equation 15)

Equation 16 can then be used to find the young's modulus of the tested material, 'E_s'. 'E_i' is the known young's modulus of the indenter, ' v_s ' and ' v_i ' are the Poisson's ratio of the tested material and indenter. [59][73]

$$\frac{1}{E^*} = \frac{(1 - v_s^2)}{E_s} + \frac{(1 - v_i^2)}{E_i}$$
(Equation 16)

Indentations on both a monolithic and composite coating samples were using a Rockwell hardness tester with a 60kg load was done to observe the coatings' indentation behaviour. Images and 3D profiles of the indents made from both the Rockwell tester and the Vickers micro-hardness tester were taken using a Keyence confocal laser microscope.

3.3 Tribological Behaviour

3.3.1 Scratch

Scratch resistance of Ni-P and Ni-P-NiTi coatings with varied thicknesses were evaluated using a Universal Micro-Tribometer (UMT). Multiple pass scratch tests were used to evaluate how the coefficient of friction (CoF), acoustic emission (AE), and wear volume loss progressed with scratch distance. The testing set-up is shown in Figure 3-6. The number of passes tested were 1, 25, 50, 75, and 100 which all had a constant load with a pass length of 5mm. One pass was made in 30 seconds, making the indenter speed to be 0.17mm/second. An acoustic emission sensor was used during the tests to monitor crack development during the passes. This test was repeated with two different styles of indenters. A sharp diamond indenter with a diameter of 0.4mm and a spherical WC-6Co indenter with a diameter of 1.59mm. The diamond indenter used a load of 1kg and the spherical WC-6Co

indenter used a load of 4kg. Images of the sharp indenter are shown in Figure 3-7 and the spherical indenter is shown in Figure 3-8.



Figure 3-6 Scratch Tester



Figure 3-7 Sharp Diamond Indenter (a) Top View (b) Side View



Figure 3-8 Spherical WC-6Co Indenter (a) Top View (b) Side View

After the tests were completed, a Keyence confocal laser microscope was used to measure the scratch scar width and depth.

Volume loss was calculated based on indenter radius and scar width, shown in equation 17. 'D' is the diameter of the scratch indenter tip, 't' is the scratch length, and 'b' is the width of the scratch scar. [74] The number of passes was multiplied by the scratch length to determine sliding distance. The volume loss per sliding distance is then graphed to observe how wear progresses. The wear rate of the coating was then able to be calculated using the slope of the curve of volume loss at steady state divided by the scratch distance.

Volume Loss =
$$\frac{D^2 t}{8} \left[2\sin^{-1} \frac{b}{D} - \sin\left(2\sin^{-1} \frac{b}{D}\right) \right]$$
 (Equation 17)

After scratch testing and imaging was completed, the samples were sectioned using a Buehler IsoMet 1000 Precision Saw. Low loads and speed were used with a IsoMet Diamond Wafering Blade to minimize damage on the coating. Figure 3-9 shows the saw and Figure 3-10 shows a sample positioned to be cut. Images of the cross-sections were taken on the same Keyence laser confocal microscope.



Figure 3-9 Buelher IsoMet 1000 Precision Saw



Figure 3-10 Sample in Cutting Position

3.3.2 Erosion-Corrosion

Pure corrosion, pure erosion, erosion-enhanced corrosion, and erosion-corrosion tests were conducted on Ni-P and Ni-P-NiTi of various thicknesses in a slurry pot erosion-corrosion (SPEC) tester. The coatings' results were compared to those of AISI 1018 steel substrate. Figure 3-11 shows a schematic of a SPEC unit. A 4L glass vessel held the samples and the slurry that was impelled by a motor driven impeller. The impeller speed was 900rpm and the slurry temperature was approximately 45°C for all tests. The slurry had a mixture of 3.5wt%NaCl solution as a corrosive medium and 35wt% AFS 50-70 silica sand for erosion. The samples were mounted in epoxy so that only the test surface was exposed. Each coating type had three samples used for this experiment. One sample for pure erosion, one for erosion-corrosion, and one was used for pure corrosion and erosion-enhanced corrosion.

The corrosion rates of pure corrosion and erosion-enhanced corrosion were found using the polarization resistance technique. The corrosion rates from both these tests allowed for the synergistic effects on corrosion to be evaluated, and then to find the synergistic effects of erosion. Pure corrosion had only the 3.5wt%NaCl solution with no silica sand, while erosion enhanced corrosion had the complete slurry.

Both the erosion-corrosion tests and pure erosion tests ran for a duration of six hours each. The material loss rate was calculated from the test duration and the change of sample weight before and after the test. A high precision micro-balance scale with a reading accuracy of 0.01mg to measure material losses of the samples before and after testing. Pure erosion used the same slurry mixture as erosion-corrosion, but the samples were catholically protected during the test. This allowed for the material loss to be from exclusively erosion.



Figure 3-11 Slurry Pot Erosion-Corrosion Tester

The material loss rate was calculated in cm³/h/cm². According to ASTM G119-09, the erosion-corrosion synergy is expressed through equation 18. ' K_{ec} ' is material loss under erosion-corrosion conditions, ' K_{eo} ' is material loss due to pure erosion, ' K_{co} ' is material loss due to pure corrosion, and ' K_s ' is material loss due to synergy. [75]

$$K_{ec} = K_{eo} + K_{co} + K_{S}$$
 (Equation 18)

Similarly, the total material loss rate can be expressed through equation 19, where 'K_e' is total erosion rate, 'K_c' is total corrosion rate, ' Δ K_e' is the corrosion enhanced erosion rate, and ' Δ K_c' is the erosion-enhanced corrosion rate. [75]

$$K_{ec} = K_e + K_c = K_{eo} + K_{co} + \Delta K_e + \Delta K_c$$
 (Equation 19)

By combining equations 18 and 19, the synergy material loss rate and its components can be expressed as shown below to create equations 20, 21, and 22. [75]

$$K_{s} = \Delta K_{e} + \Delta K_{c} = K_{ec} - (K_{eo} + K_{co})$$
(Equation 20)
$$\Delta K_{c} = K_{c} - K_{co}$$
(Equation 21)
$$\Delta K_{e} = K_{s} - \Delta K_{c}$$
(Equation 22)

Images of the coating surfaces after being subjected to rather pure erosion or erosion-enhanced corrosion were taken using a Keyence laser confocal microscope. A Ni-P coating and Ni-P-NiTi coating after erosion-corrosion were selected to have their surfaces inspected using SEM imaging and EDS mapping analysis.

Chapter 4 Results and Discussion

4.1 Coating Characterization

X-ray diffraction patterns of the API X100 substrate, NiTi nano-particle powder, monolithic Ni-P coating, and Ni-P-NiTi composite coating are shown below in Figure 4-1.



Figure 4-1 XRD Patterns

The Ni-P was mostly amorphous, but the pattern had a broad peak that covered the 52° to 56° 20, which was a close match to a Nickel Phosphide PDF (PDF 04-003-6331). Similar patterns have been reported in other studies. [21, 22] Both Fe and NiTi are cubic structures that would diffract at the 110 plane, which happens around 45-55°. This very clearly is present in the API X100 pattern, which has a high intensity peak at 52°. The NiTi powder matches a Nickel Titanium PDF (PDF 04-020-1330) that has a peak at 49.8° from the 110 plane. This crystal structure is documented to have a weight percent ratio of 54.08Ni:45.92Ti. The Ni-P-NiTi coating resembles the Ni-P broad peak that extended from 52° to 55°, and includes a visible smaller 49.8° peak which reflects what was seen in the powder's pattern.

SEM micrographs of the cross sections confirmed the coating had adherence to the substrate, shown in Figures 4-2 and 4-3 at 1000x magnification. In each sample, the coating adhesion is visible by a distinct change in colouring between the substrate and the coating. Figure 4-2 is the thin Ni-P coating and Figure 4-3 is the thick Ni-P coating.



Figure 4-2 Cross Section SEM Image of Thin Ni-P Coating at 1000x Magnification

Figure 4-3 Cross Section SEM Image of Thick Ni-P Coating at 1000x Magnification

The lighter colouring at the top shows the uneven surface that later would need to be polished off to create a smooth surface for testing.

Figures 4-4 and 4-5 show 1000x magnification SEM images of thick and thin Ni-P-NiTi composite coatings, respectively. Each coating shows relatively uniformly distributed dark circles having a well-defined interface. Those dark circles are the NiTi nanoparticles in the Ni-P matrix. Both thick and thin coatings also show uniform adherence to the steel substrate.



Figure 4-4 Cross Section SEM Image of Thin Ni-P-NiTi Composite Coating at 1000x Magnification

Figure 4-5 Cross Section SEM Image of Thick Ni-P-NiTi Composite Coating at 1000x Magnification

A SEM image of the composite coating in Figure 4-6 shows a rough surface. It appeared to be due to the particles settling in different areas. This would later need to be lightly polished down to have an even surface for testing.



Figure 4-6 Side View of the Rough Surface SEM Image of Thin Ni-P-NiTi Composite Coating at 2000x Magnification

The remaining SEM images of the coating cross sections, which include different magnification levels, can be found in Appendix A.

The chemical compositions were confirmed using EDS mapping. Figure 4-7 is the EDS cross section of the thinner Ni-P. The coatings consisted of an even mix of nickel and phosphorous with a distinct difference between the coating and the substrate, which proves adherence. Figure 4-8 is the EDS cross section of thinner Ni-P-NiTi. The particles are highlighted with the titanium element and are distinct from the matrix. The remaining EDS maps of the cross sections of the thicker Ni-P and thicker Ni-P-NiTi coatings can be found in Appendix A. Table 4-1 shows the averaged chemical compositions in each type of coating found from the EDS Analysis.



Figure 4-7 EDS Map of Thin Ni-P Coating Cross Section



Figure 4-8 EDS Map of Thin Ni-P-NiTi Coating Cross Section

Table 4-1 Coating Compositions from EDS Analysis

	Thin Ni-P	Thick Ni-P	Thin Ni-P- NiTi	Thick Ni-P- NiTi
Nickel	95.49%	94.31%	92.51%	92.365%
Phosphorous	4.595%	5.69%	6.125%	6.015%
Titanium	0%	0%	1.365%	1.62%

The weight percent of NiTi present in the composite coatings were calculated using equation 23. The weight percent ratio of nickel to titanium was from the XRD PDF match, 54.08Ni:45.92Ti.

wt%NiTi = %Ti +
$$(54.08/_{45.92})$$
%Ti (Equation 23)

The thinner composite was found to be Ni-P-2.97wt%NiTi while the thicker composite was Ni-P-3.53wt%NiTi. Therefore, the average composite composition would be Ni-P-3.25wt%Ti.

4.2 Hardness

Monolithic Ni-P coating had seven load-depth measurement points shown in Table 4-2 and Ni-P-NiTi composite coating had six shown in Table 4-3. Ni-P had an average hardness of 5.75GPa and an average elastic modulus of 142.68GPa. These were higher values than the composite Ni-P-NiTi, which had an average hardness of 3.55GPa and an average elastic modulus of 99.80GPa. The indenter penetrated deeper into the composite coating than the monolithic, which is expected given the difference in hardness.

Measurement Point ID	Hardness (GPa)	Elastic Modulus (GPa)	Maximum Indenter Depth
1	2.61	100.7	10µm
2	3.63	122.4	9µm
3	6.67	165.7	7µm
4	7.15	160.1	7µm
5	6.64	151.0	7µm
6	5.89	125.2	7µm
7	7.66	173.71	6.5µm
AVERAGE	5.75	142.68	7.64µm

Table 4-2 Monolithic Ni-P Coating Vickers Hardness Measurements

Table 4-3 Ni-P-NiTi Composite Coating Vickers Hardness Measurements

Measurement Point ID	Hardness (GPa)	Elastic Modulus (GPa)	Maximum Indenter Depth
1	3.44	108.22	9µm
2	2.53	88.14	11µm
3	2.60	70.96	11µm
4	3.67	102.48	9µm
5	4.12	111.36	9µm
6	4.97	117.64	8µm
AVERAGE	3.55	99.80	9.5µm

Figure 4-9 shows representative examples of the load-depth curves using Point 5 on the Ni-P coating and Point 4 on the Ni-P-NiTi coating. The load-depth curves of all the measurement points can be found in Appendix B.



Figure 4-9 Micro-Indentation Load-Depth Curve Examples

Table 4-4 compares the hardness and elastic modulus values of the Ni-P and Ni-P-NiTi coatings found experimentally to the typical values of Ni-P coating, the NiTi alloy, and the AISI 1018 substrate. Both coatings had considerably higher values than the typical range of AISI 1018. The monolithic coating experimental values were within the range of the typical values. The experimental values of Ni-P-NiTi composite coating were lower than the typical ranges of Ni-P but higher than the NiTi alloy. This indicates that the coating did lose some hardness by the NiTi addition, however the lower elastic modulus shows that in return it gained some elasticity.

	Hardness (GPa)	Elastic Modulus (GPa)
Experimental Ni-P	5.75±1.90	142.68±26.89
Typical Ni-P	5-6.5	140-160
Experimental Ni-P-NiTi	3.55±0.93	99.80±17.31
Typical NiTi	2.8-3.2	70-100
AISI 1018	1.7-2	200

Table 4-4 Experimental Data Compared to Typical Values

Figures 4-10 and 4-11 show a Vickers measurement points on the monolithic coating compared to the composite. Figure 4-10 is a point on the monolithic Ni-P coating and shows how the indent has a smaller width than the indent in the Ni-P-NiTi composite coating shown in Figure 4-11. This is what was implied with the difference in hardness, elastic modulus, and indentation depth between the two coating types.



Figure 4-10 Vickers Indent on Ni-P Coating

Figure 4-11 Vickers Indent on Ni-P-NiTi Coating

Images and 3D profiles of the rockwell hardness tester indentations are shown below in Figures 4-12 and 4-13. Figure 4-12 shows two examples of indents with large Hertzian indentation cracks on the monolithic Ni-P coating. Additionally, there is significant radail cracks. This cracking is visual confirmation of its low toughness and ductility. The cracks and brittleness of Ni-P are even more jarring when compared to the indentation on Ni-P-NiTi coating shown in Figure 4-13. Due to the composite's high toughness, it had minimal cracking and plastic material pile-up due to its higher ductility.



Figure 4-12 Rockwell Indentations on Ni-P Coating (a) Radial and Hertzian Cracks (b) Hertzian Cracks



Figure 4-13 Rockwell Indentation on Ni-P-NiTi Coating

4.3 Sliding Wear Behaviour

4.3.1 Wear Tracks

Micrographs of the sectioned samples that were used in scratch testing are shown below in Figures 4-14, 4-15, 4-16, and 4-17. From these images, it was determined that the coatings used in scratch testing were a 45µm thick Ni-P, 9µm thick Ni-P, 9µm thick Ni-P. NiTi, and 4µm thick Ni-P-NiTi.



Figure 4-14 45µm Thick Ni-P Coating

Figure 4-15 9µm Thick Ni-P Coating



Figure 4-16 9µm Thick Ni-P-NiTi Coating Figure 4-17 4µm Thick Ni-P-NiTi Coating

Wear tracks are categorized by coating type, indenter shape, and number of passes. Micrographs were taken at five evenly spaced intervals along the wear track to allow the full scratch to be examined for its wear mechanisms. When the micrographs were taken, a laser scanned the surface to take the 3D profile for analysis. Most of the wear tracks had relatively consistent widths, apart from either end. Examples of the micrographs of wear tracks are shown in Figures 4-18 and 4-19. Both scratches are 50 pass wear tracks on 9μ m thick Ni-P, but the wear track in Figure 4-18 had used the sharp indenter and Figure 4-19 had used the spherical indenter.



Figure 4-18 Wear Track from 50 Passes of the Sharp Indenter on 9µm Thick Ni-P Coating

Figure 4-19 Wear Track from 50 Passes of the Spherical Indenter on 9µm Thick Ni-P Coating

Increased number of scratch passes equates to the surface undergoing a greater degree of wear. Consistently, when comparing the scratches made with the same indenter shape on the same coating, increasing the number of passes correlates to a larger wear track.

Furthermore, with increased volume loss in the wear track there is more material pile up on the edges. Figures 4-20 and 4-21 are examples of how the wear track changed with sliding distance using the middle of 9µm thick Ni-P's wear tracks. Figure 4-20 is the scratches from the sharp indenter and Figure 4-21 is from the spherical indenter. Across all coating samples, the spherical tracks were wider than the sharp tracks of equivalent number of passes and coating.



Figure 4-20 Wear Profiles from the Sharp Indenter on 9µm Thick Ni-P Coating (a) 1 Pass (b) 25 Passes (c) 50 Passes (d) 75 Passes (e) 100 Passes



Figure 4-21 Wear Profiles from the Spherical Indenter on 9µm Thick Ni-P Coating (a) 1 Pass (b) 25 Passes (c) 50 Passes (d) 75 Passes (e) 100 Passes

The wear tracks from the same number of passes and indenter shape are unique to the type of coating. Figures 4-22 to 4-29 compare the 3D profiles of the 100-pass wear tracks for each coating. Figures 4-22 to 4-25 are from the sharp indenter and Figures 4-26 to 4-29 are from the spherical indenter. In the case of both indenters, the 45µm thick

monolithic coating had the shallowest scratch profile. The spherical scratch profiles mostly had rough wear tracks with uneven depth throughout, but the 9µm thick Ni-P-NiTi had a rather smooth curve that was evenly deformed throughout the scratch profile. These differences in profile shapes correlate with the differences in properties between monolithic Ni-P and Ni-P-NiTi nanocomposite. Namely, the higher hardness in monolithic Ni-P and the higher toughness in the composite. Ni-P-NiTi is more prone to localized plastic deformation due to its lower hardness, and the higher toughness would allow for the deformation to be uniform with minimal cracking. By the same reasoning, monolithic Ni-P is susceptible for concentrated failures such as large cracks as opposed to plastic deformation due to its brittleness.



Figure 4-22 45µm Thick Ni-P Coating 100 Passes of the Sharp Indenter



Figure 4-23 9µm Thick Ni-P Coating 100 Passes of the Sharp Indenter



Figure 4-24 9µm Thick Ni-P-NiTi Coating 100 Passes of the Sharp Indenter



Figure 4-25 4µm Thick Ni-P-NiTi Coating 100 Passes of the Sharp Indenter



Figure 4-26 45µm Thick Ni-P Coating 100 Passes of the Sphere Indenter



Figure 4-27 9µm Thick Ni-P Coating 100 Passes of the Sphere Indenter



Figure 4-28 9µm Thick Ni-P-NiTi Coating 100 Passes of the Sphere Indenter



Figure 4-29 4µm Thick Ni-P-NiTi Coating 100 Passes of the Sphere Indenter

The remaining 3D profiles and laser images of the scratch profiles can be found in Appendix C.

4.3.2 Volume Loss and Wear Rates

Figures 4-30 and 4-31 show how volume loss changes with the scratch sliding distance for each coating, where Figure 4-30 compares the sharp indenter scratches and Figure 4-31 compares the spherical indenter scratches. The pileup at the scratch edges was excluded in the calculations of volume loss, and further confirms the scratch depth profile observations. The standard deviations were found using the five intervals of scratch depth measurements taken on the scratch scar. In both indenters, the 4µm thick Ni-P-NiTi coating experienced the greatest degree of volume loss while 45µm thick Ni-P coating experienced the least.



Figure 4-30 Volume Loss from the Sharp Indenter



Figure 4-31 Volume Loss from the Spherical Indenter

The wear rate was calculated from the slope of the volume loss curve at steady state. Figure 4-32 compares the wear rates of each coating and indenter. The wear rates reflect what was shown on the volume loss graphs, where the highest wear rate was 4μ m thick Ni-P-NiTi coating and the lowest wear rate was 45μ m thick Ni-P coating. Consistently, the spherical indenter produced a higher wear rate than the sharp indenter. This was due to both the difference in geometries between the indenter styles and the higher load on the spherical indenter. Thinner coatings have higher amounts volume loss and a lower wear rate than their thicker counterpart. Comparing the 9μ m thick Ni-P-NiTi to the 9μ m thick Ni-P, the composite had lower wear rates. This was particularly drastic in the spherical indenter scratches.



Figure 4-32 Wear Rates from Scratch Tests

The percent difference in wear rate of the same coating type of different thickness was calculated to quantify the effect coating thickness has on wear rate. The formula is shown in equation 24, where 'WR_{Thick}' represents the wear rate of the thicker coating, and 'WR_{thin}' is the wear rate of its thinner counterpart. The resultant values are all relatively close and shown Table 4-5.

$$\% \text{Difference} = \frac{|WR_{\text{Thick}} - WR_{\text{Thin}}|}{(WR_{\text{Thick}} + WR_{\text{Thin}})/2} * 100$$
(Equation 24)

	Sharp Indenter	Spherical Indenter
Monolithic Ni-P	129.2%	105.5%
Nanocomposite Ni-P-NiTi	155.4%	137.0%

Table 4-5 Percent Difference in Wear Rate for Coating Thicknesses

Regardless of indenter shape, there is an over 100% difference of wear rate between an equivalent thick and thin coating. The scratch profiles, volume loss, and wear rate all confirm that there is an apparent relationship between coating thickness and susceptibility to wear that is seen in both indenter styles. For the scratches from the sharp indenter, both the thicker monolithic and composite coatings had scratch profiles that were narrower and less deep than their thin counterparts. This is also observable on the scratches made from the spherical indenter, where the thinner monolithic and composite coatings had more damage than the thicker counterpart. The thicker monolithic coating's wear profile is considerably shallower than its thinner version. Furthermore, although the composite scratch depth does not have the same visible depth in the thin coating, it is apparent in Figures 4-28 and 4-29 that there was catastrophic failure that the thicker version did not have. The wear track goes as deep as the approximate coating thickness, and therefore the substrate was not fully protected. The 4µm thick Ni-P-NiTi coating has delaminated at the substrate-coating interface, shown in Figure 4-31 in the optical image and 3D profile. The thinner coating's higher wear rate compared to the thick coating can be explained through the relationship between internal stresses present in the coating, and their expected effects on tribological behaviour. Work by A. M. Laera et al. assessed the relationship between the residual stress in ZrO coating with its tribological behaviour and had found that compressive internal stresses correlate with higher wear resistance. [80] It can be assumed that the residual stresses in Ni-P coating thicknesses are as described in Section 4.6, where prior literature has found that thicker coatings have compressive residual stress while thinner coatings are in tensile. [56] Therefore, the thicker coatings' lower wear rates are because of their compressive stresses induced in plating. Thus the thicker coatings are preferable over their thinner counterparts for sliding wear resistance.

Comparing all four coating types, the best resistance to sliding wear is the 9μ m thick Ni-P-NiTi. Although it is much thinner than the 45μ m Ni-P, it has a comparable wear rate and has less cracking due to the presence of the super-elastic NiTi particles. The thick composite therefore is the superior choice for protecting against sliding wear. Furthermore, choosing a 9μ m thick Ni-P-NiTi over the 45μ m Ni-P would also have the benefit the lower cost that is associated with a lower coating thickness.

4.3.3 Wear Mechanisms

In brittle materials like monolithic Ni-P, their yielding would more likely appear as severe cracking. Volume loss does not account for fractures, so it likely is not a fully equivalent assessment of wear resistance when comparing a brittle material to a material that is more ductile. Examining the scratch tracks for the dominant wear mechanisms can give a deeper understanding on the materials compared. Figures 4-33 to 4-36 shows the 100 pass wear tracks from the sharp indenter and Figures 4-37 to 4-40 shows the 100 pass wear tracks from the spherical indenter.

In both indenters, the 9µm thick Ni-P-NiTi coating had the least amount of cracking. In the sharp indenter scratch, the monolithic 9µm thick Ni-P coating had long cracks on the surface parallel to the scratch track. The wear track itself has both parallel and perpendicular to the scratch direction. Contrastingly, the 9µm thick Ni-P-NiTi coating wear track has uniform deformation and very little cracking. Similarly under the spherical indenter, the 9µm Ni-P coating had long large cracks and areas of delamination but the 9µm thick Ni-P-NiTi coating has small cracks and less delamination. This suggests that the NiTi nanoparticles are toughening the coating and improving wear properties, despite the higher measurable wear rate in the 9µm composite coating compared to the monolithic 9µm thick Ni-P.



Figure 4-33 45µm Thick Ni-P 100 Passes of Sharp Indenter

Figure 4-34 9µm Thick Ni-P 100 Passes of Sharp Indenter

Figure 4-35 9µm Thick Ni-P-NiTi 100 Passes of Sharp Indenter

Figure 4-36 4µm Thick Ni-P-NiTi 100 Passes of Sharp Indenter








Figure 4-37 45µm Thick Ni-P 100 Passes of Sphere Indenter

Figure 4-38 9µm Thick Ni-P 100 Passes of Sphere Indenter

Figure 4-39 9µm Thick Ni-P-NiTi 100 Passes of Sphere Indenter

Figure 4-40 4µm Thick Ni-P-NiTi 100 Passes of Sphere Indenter

To understand the composite's wear mechanisms, it needs to be confirmed if transformation toughening of the NiTi nanoparticles occurred. If so, the contact stress during testing would have exceeded the stress required for martensitic phase transition. The transition stress has been approximated to be around 410MPa at room temperature. [76] Using equations 9 and 10 that were presented in Chapter 2, the mean contact pressure 'pm' can be calculated using equation 25. The coating is assumed to have v_i=0.29 and E_i=198 GPa. [77] The sharp diamond indenter properties are assumed to be v_i=0.20 and E_i=1050GPa [78] while the spherical tungsten carbide indenter properties are assumed to be v_i=0.26 and E_i=600GPa. [22][37]

$$p_{\rm m} = \frac{P}{\pi A_{\rm c}^{3}}$$
(Equation 25)

The mean contact pressures of both indenters were found to exceed the 410MPa transformation stress, with the diamond indenter having a mean contact pressure of

7.71GPa and the tungsten carbide spherical indenter was 4.53GPa. Therefore, the scratch testing experiments would have induced transformation toughening of the NiTi nanoparticles. This is further confirmed by the evidence of the toughening mechanisms provided by the nanoparticles that are visible in images of the wear tracks.

The heavy degree of plastic deformation that is visible on 4µm thick Ni-P-NiTi coating's 100 pass wear track from the sharp indenter allows for insight on the wear mechanisms from the particles. SEM images were taken to examine the particle interaction with cracks. As explained in Chapter 2, as an applied load causes hertzian cracks on the surface, they intersect with subsurface cracks which creates plate-like wear debris. Figure 4-41 shows a region on the wear track where a hertzian crack had propagated causing delamination. The hertzian crack was perpendicular to the surface, and the crack parallel to the wear track is due to the subsurface lateral cracks crossing the surface. There were also particles removed from the coating, also shown in Figure 4-41. The high degree of stress in the material led to the particles to be de-bonded from the coating. A removed particle and a particle that had begun to be displaced are pointed out in the image.



Figure 4-41 SEM Image of Hertzian Crack, Delamination, and Particle Removal on the 100 Pass Wear Track on the $4\mu m$ Thick Ni-P-NiTi Coating

As the scratch progressed, material was displaced to accommodate the wear. With every scratch pass, more material would be pushed outward. This is visible in Figure 4-42 by the layers of material that were squeezed out of the wear track. Material deformation is indicative of ductility, as opposed to brittle fracture such as the wear track that was seen in the monolithic Ni-P coatings in the confocal images of Figures 4-33, 4-34, 4-37, and 4-38.

Those tracks had long cracks that were parallel to wear track and did not show evidence of material pile up.



Figure 4-42 SEM Image of Material Layers on the 100 Pass Wear Track on the $4\mu m$ Thick Ni-P-NiTi Coating

Further delamination and particle removal are visible in Figure 4-43. Additionally, Figure 4-43 and Figure 4-44 show indications of toughening mechanisms from particlecrack interaction. The images have both forms of crack deflection, one with particle-crack interaction and one without. The spots labelled as crack deflection are where the crack contacted the particle which caused it to change paths and lose its fracture energy in the process. The cracks around a particle that are pointed out are a form of crack deflection, but the stress field around the particle is what changed the propagation's path instead of a crack contacting the particle directly. The deflection of cracks when they come close to a NiTi particle is due to transformation toughening. The transformation occurs because as the crack approaches a NiTi particle, it produces a high stress field. The stress induces the super-elastic NiTi to transform into martensite and expands which surrounds the particle with compression. This leads to crack deflection and loss of crack energy. Furthermore, the transformation also absorbs the crack energy leading to crack arrest. This mechanism is what causes toughening of the coating.



Wear Track
Unack deflection
Crack deflection
Crack around
particle
Coating Surface
7.04/12.2mm v600 SE(1)
50.0um

Figure 4-43 SEM Image of Delamination, Particle Removal, and Particle-Crack Interaction on the 100 Pass Wear Track on the 4µm Thick Ni-P-NiTi Coating

Figure 4-44 SEM Image of Particle-Crack Interaction on the 100 Pass Wear Track on the 4µm Thick Ni-P-NiTi Coating

4.4 Erosion-Corrosion

Figure 4-45 show the material loss rates for the AISI 1018 steel substrate, the monolithic Ni-P coatings, and the composite Ni-P-NiTi coatings. The material loss rates are for erosion-corrosion (K_{ec}), erosion only (K_{eo}), corrosion only (K_{co}), and total synergy (K_s). As hypothesized, AISI 1018 had the highest material loss rates during erosion-corrosion, pure erosion, and pure corrosion. The 12µm thick Ni-P coating had the highest erosion-corrosion and pure erosion resistance, however the 60µm thick Ni-P coating had the highest corrosion resistance.

The total synergistic effect was found by simply subtracting the pure erosion and pure corrosion rates from the erosion-corrosion rate, as described in equation 20 in Chapter 2. Both erosion-corrosion and pure erosion had their material loss rate calculated from the measured sample's mass loss and test duration. However, to be able to study the effects of corrosion, material loss rates were extrapolated from potentiodynamic curves on both pure corrosion and erosion-enhanced corrosion.



Figure 4-45 Material Loss Rates in Erosion-Corrosion Experiments

Tafel extrapolation found the corrosion current density (i_{corr}) and corrosion potential (E_{corr}), which were then used to find the corrosion rate using equation 25. This equation is shown below, where 'EW' is the sample's equivalent weight and 'D' is the density of the sample. Figures 4-46 and 4-47 show each sample's first out of the two potentiodynamic curves made for pure corrosion and erosion-enhanced corrosion. Figure 4-46 is for the pure corrosion and Figure 4-47 is for erosion-enhanced corrosion. The potentiodynamic Tafel curves for the repeated pure corrosion and erosion-enhanced corrosion tests are in Appendix D. Tables 4-6 and 4-7 summarizes the corrosion variables that were found. Table 4-6 is for pure corrosion and Table 4-7 is for erosion-enhanced corrosion.



Current Density (A/cm²)

Figure 4-46 Representation of Pure Corrosion Potentiodynamic Polarization Curves



Figure 4-47 Representation of Erosion-Enhanced Corrosion Potentiodynamic Polarization Curves

(Equation 25)

$$CR = \frac{i_{corr} * EW}{D} * 3270$$

Table 4-6 Pure Corrosion Results

Pure Corrosion	Icorr (amp/cm ²)	Ecorr (volts)	Corrosion Rate (cm ³ /(cm ² *hr))
AISI 1018	9.61±0.07 * 10 ⁻⁵	-	1.24±0.009 * 10 ⁻⁵
70µm Thick Ni-P- NiTi	6.73±0.59 * 10 ⁻⁶	-1.66±0.0009 * 10 ⁻¹	7.87±0.69 * 10 ⁻⁷
60µm Thick Ni-P	4.37±1.46 * 10 ⁻⁶	-9.63±1.08 * 10 ⁻²	4.50±0.85 * 10 ⁻⁷
12µm Thick Ni-P	$3.78\pm0.55*10^{-6}$	-1.14±0.35 * 10 ⁻¹	4.45±0.65 * 10 ⁻⁶
25μm Thick Ni-P- NiTi	7.18±2.45 * 10 ⁻⁶	$-1.44\pm0.003 * 10^{-1}$	8.37±2.86 * 10 ⁻⁷

Table 4-7 Erosion-Enhanced Corrosion Results

Erosion-Enhanced Corrosion	Icorr (amp/cm ²)	Ecorr (volts)	Corrosion Rate (cm ³ /(cm ² *hr))
AISI 1018	7.88±0.26 * 10 ⁻⁴	-	$1.02\pm0.03 * 10^{-4}$
70µm Thick Ni-P- NiTi	1.00±0.12 * 10 ⁻⁴	-1.76±0.004 * 10 ⁻¹	1.17±0.14 * 10 ⁻⁵
60µm Thick Ni-P	6.27±1.99 * 10 ⁻⁵	-1.47 ± 0.10 * 10 ⁻¹	7.31±2.32 * 10 ⁻⁶
12µm Thick Ni-P	3.95±2.82 * 10 ⁻⁴	-1.96±0.03 * 10 ⁻¹	4.64±3.31 * 10 ⁻⁵
25µm Thick Ni-P- NiTi	2.17±0.52 * 10 ⁻⁴	-1.85±0.05 * 10 ⁻¹	2.54±0.61 * 10 ⁻⁵

The 60µm thick Ni-P coating's corrosion rate was almost 100% lower than the AISI 1018 substate. The significant corrosion resistance of the monolithic coating is explainable by its microstructure and chemical composition. Generally, amorphous structures have high corrosion resistance due to their lack of grains. This is because grain boundaries that are in most crystal structures are high energy sites which are susceptible to corrode. Furthermore, nickel and phosphorus reaction mechanisms both contribute to preventing rapid corrosion.

Initially, the phosphorus can react with water to form hypophosphite anions. It has been theorized that a layer of these anions acts as a barrier on the surface that shields the material from the environment. This inhibits the nickel's hydration reaction that is needed for the active dissolution of nickel. When nickel does react, it forms a passive layer of NiO on the surface which protects the material below from further corrosion. [79]

During erosion-corrosion, the formation of the passive layer is greatly affected by the surface roughness introduced by erosion. The impact energy of the particles is absorbed, and the surface is plastically deformed. Plastic deformation from erosion is evident on the coating's surface. Figures 4-48 and 4-49 show micrographs and 3D imaging of the 70 μ m thick Ni-P-NiTi surface after pure erosion. The micrographs show the uneven surface, and the material displacement is quantified by the 3D images. Figure 4-48 shows the formation of a crater, where the particle impact presses the coating material outward to create a cavity and displaces to form a hill. The rough edges of the crater are noteworthy, as it shows how the material was deformed. Figure 4-49 shows a similar crater. However, the hill has been broken off due to repeated particle impact.



Figure 4-48 Crater Formation on a Pure Erosion Surface of 70µm Thick Ni-P-NiTi



Figure 4-49 Pure Crater with Edges on a Pure Erosion Surface of 70µm Thick Ni-P-NiTi

The plastically deformed crater sites are visible on the erosion-corrosion surface and the effects of corrosion are observable. The plastically deformed hill is dissolved as a result of corrosion, along with the rough edges on crater sites. This appears as a much smoother indent site than seen in pure erosion. Figure 4-50 shows an example on the surface the 70µm thick Ni-P-NiTi coating.



Figure 4-50 Crater from Erosion influenced by Corrosion on the surface of $70\mu m$ Thick Ni-P-NiTi after Erosion-Corrosion

The erosion rates are highlighted in Figure 4-51, shown below. The highest erosion rate was the thickest coating at 70 μ m thick Ni-P-NiTi, while the thinnest coating at 12 μ m thick Ni-P had the lowest rate. When comparing all four coatings regardless of the differences in compositions, the erosion rate increases with increased thickness.



Figure 4-51 Pure Erosion Rates

The erosion rate and coating thickness correlation can be explained by the residual stresses. The deformation produces compressive residual stresses and consequently tensile stresses at the subsurface. This cold working process modifies the mechanical properties of the material. The principle is applied in industry as a mechanical treatment method to improve wear resistance, which is known as shot peening. [81]

As previously discussed, the residual stress induced during plating in the coating is tensile near the substrate and transitions into compressive stress as the thickness increases. During erosion, which is effectively equivalent to shot peening, this thick coating surface undergoes further compression. However, in shot peening the tensile stresses develop at the subsurface to accommodate the additional surface compressive stresses and is depicted graphically in Figure 4-52. [82] This figure shows the residual stress distribution that is induced due to shot peening, which is equivalent to the present case of erosion. Conversely, thin coatings are subjected to surface compressive stresses during erosion, which cancels

some or all tensile stress developed during plating. Therefore, the thin coating has less tensile residual stress than it had as plated but the thick coatings have higher near surface tensile residual stress. This effect is evident by the lower erosion resistance and observable wear mechanisms for thick coatings.



Figure 4-52 Residual Stress Distribution Induced by Shot Peening [82]

The coatings with higher tensile residual stress are more susceptible to delamination wear. Figures 4-53 and 4-54 show SEM images of the 60µm thick Ni-P and 70µm thick Ni-P-NiTi coatings after erosion-corrosion. Figure 4-53 is 60µm thick Ni-P coating that shows the initiation of delamination. The coating is lifted from the substrate, but not fully peeled off yet. Figure 4-54 shows the completion of delamination on the 70µm thick Ni-P-NiTi coating.



Figure 4-53 SEM Image of Initial Stages of Delamination on the $60\mu m$ Thick Ni-P Surface After Erosion-Corrosion



Figure 4-54 SEM Image of Delamination on the $70\mu m$ Thick Ni-P-NiTi Surface After Erosion-Corrosion

Without the shot-peening effect from erosion, the pure corrosion has a different correlation between the coating thickness and the material loss rate. Figure 4-55 shows the corrosion only material loss rates. The thinnest coating tested, 12µm thick Ni-P, had the highest rate comparative to the other thicknesses.



Figure 4-55 Pure Corrosion Rates

Since the thinner Ni-P coating is only 12µm thick, it is likely that the coating fractured and exposed the steel substrate to the corrosive environment for part of the test duration. The corrosion of the steel substrate accounts for the spike in material loss compared to the other coatings. The 60µm thick Ni-P coating had the lowest material loss rate due to the NiO passive layer formation, its mostly amorphous microstructure, and the high thickness that prevents fractures from reaching the steel substrate. However, despite the 70µm thick Ni-P-NiTi composite coating being slightly thicker than 60µm thick Ni-P monolithic coating, it was not as effective due to presence of the NiTi nanoparticles. Titanium has a higher reactivity to form oxide than nickel does, and therefore a higher tendency for the formation of a TiO₂ passive layer. However, since the NiTi content is limited and dispersed throughout the matrix, the TiO₂ layer is thin and sporadically

distributed. This means that the TiO_2 is not as effective at protecting the surface. The nickel is susceptible to react with the environment, but the amount of NiO formation is limited due to the tendency for the oxygen to combine with the titanium. Consequently, the dissolution of nickel increases and allows for the 70µm thick Ni-P-NiTi coating to have a slightly higher corrosion rate compared to the 60µm thick Ni-P. Evidence of the sporadically distributed oxide is seen in localized corrosion sites, known as corrosion pitting. This can be seen in Figure 4-56, an SEM image of the 70µm thick Ni-P-NiTi coating surface after erosion-corrosion. Notably, plastic deformation and delamination from erosion is also present.



Figure 4-56 SEM Image of Localized Corrosion on the $70\mu m$ Thick Ni-P-NiTi Surface After Erosion-Corrosion

EDS mapping was done after erosion-corrosion testing to confirm the presence of oxygen. Figure 4-57 is the EDS map of the 70µm thick Ni-P-NiTi coating and Figure 4-58 is the EDS map the 60µm thick Ni-P coating.



Figure 4-57 EDS Mapping of 60µm Thick Ni-P Surface After Erosion-Corrosion





Figure 4-58 EDS Mapping of 70µm Thick Ni-P-NiTi Surface After Erosion-Corrosion

Figure 4-59 is to characterize the total synergy effect on material loss rate by its synergistic components: increase in corrosion due to erosion (ΔK_e) and increase in erosion due to corrosion (ΔK_c). The 70µm thick Ni-P-NiTi coating had the highest synergistic effect, mostly from its significantly higher ΔK_e compared to the other coatings.



Figure 4-59 Synergistic Material Loss Rates

The 70µm thick Ni-P-NiTi coating had almost 148% times the ΔK_e than the 60µm thick Ni-P coating. Since they have close thicknesses, this infers that there is a significant effect of the presence of NiTi particles within the Ni-P matrix. As the corrosion dissolves the cold worked surface formed from erosion, the softer coating sublayer is exposed. This softer surface would be more susceptible to erosion damage, giving rise to the high erosion rate. As the surface erodes, the NiTi particles protrude from the surface. The presence of these particles resulted in higher surface roughness, while the Ni-P coatings would remain smoother. Increased surface roughness is a known effect from increased erosion, which would explain why the smoother 60µm thick Ni-P coating would not experience as drastic of an increase of ΔK_e as the 70µm thick Ni-P-NiTi coating.

The 12 μ m thick Ni-P coating had the highest ΔK_c out of all the coatings. The impacted surface from erosion particles had high stress and strain, which are known to be more anodic and therefore more susceptible to corrosion. The thin coating likely fractured

and exposed the steel to the environment. The steel and remaining coating would continue to be impacted by erosion, therefore continuously exhibiting anodic behaviour after material loss and accelerates corrosion. Surface damage and deep pits on the surface of 12µm thick Ni-P coating after erosion-corrosion are shown in Figures 4-60 and 4-61.



Figure 4-60 Deep Pit from Erosion-Corrosion on the 12µm Thick Ni-P Surface



Figure 4-61 Deep Pits and Surface Roughness from Erosion-Corrosion on the $12\mu m$ Thick Ni-P Surface

As shown previously in Figures 4-62 and 4-63, the 12µm thick Ni-P coating had deep pits throughout the surface after erosion-corrosion. This was also seen on the 60µm thick Ni-P coating surface after erosion corrosion. Figure 4-62 shows several deep pits, of

which are not found to the same degree on the composite coatings. Figure 4-63 shows a deep crack, which was an exclusive feature unique to the Ni-P monolithic coatings.



Figure 4-62 Cluster of Deep Pits from Erosion-Corrosion on the $60 \mu m$ Thick Ni-P Surface



Figure 4-63 Crack from Erosion-Corrosion on the 60µm Thick Ni-P Surface

When comparing the Ni-P monolithic coatings to the Ni-P-NiTi composite coatings, the monolithic had lower material loss rates from erosion-corrosion. However, this does not necessarily reflect on if they provide better protection to the substrate. Deep narrow pits could show to have minimal material loss, but are more detrimental than the equivalent of evenly distributed loss. Furthermore, deep cracks would not be accounted for but would also expose the steel substrate to the environment.

Figure 4-64 is a representation of the overall damage that was seen in the 70µm thick Ni-P-NiTi coating. There was no evidence of pitting corrosion and no cracks. The absence of cracking can be explained by the NiTi toughening mechanisms. This coating had the mildest damage defects from erosion-corrosion.



Figure 4-64 Surface of the 70µm Thick Ni-P-NiTi After Erosion-Corrosion

Given the observable damage mechanisms, the Ni-P-NiTi coatings would provide better protection for the steel substrate from erosion-corrosion. However, the 70µm thick Ni-P-NiTi coating did have the highest material loss rates which should not be disregarded. Therefore, when accounting both the visible damage and material loss rate, the 25µm thick Ni-P-NiTi coating seems to have the highest erosion-corrosion resistance. Furthermore, thinner coatings can have significant cost savings in terms of time and materials. This strengthens the appeal of using the thinner Ni-P-NiTi composite coating for protecting steel pipelines from erosion-corrosion.

Chapter 5 Conclusions and Recommendations

In summary, monolithic Ni-P coatings and Ni-P-NiTi coatings were prepared on API X100 and AISI 1018 steel substrates. Different thicknesses of the coatings were able to be made by changing the deposition time. As the coating thickness changes, so does its internal residual stress. Furthermore, the NiTi powder addition to produce a composite Ni-P would also cause a variation of residual stress when compared to the monolithic Ni-P. Residual stresses greatly influences a coating's performance, which was found in literature. Therefore, by changing the thicknesses and the powder addition, the effect of residual stress has on properties and wear behaviour of Ni-P and Ni-P-NiTi coatings were able to be studied. The results were examined using the well-documented principle that thinner coatings have high tensile residual stresses on their surface, which decreases with increased thickness and eventually becomes compressive. The thickness and presence of nanoparticles proved to be significant factors in the coating's performance, which is suggestive on the substantial role that the degree of residual stress has on the coating. The following conclusions can be made:

- 1. Presence of super-elastic NiTi in Ni-P coating improves its toughness by transformation toughening.
- 2. In sliding wear, monolithic Ni-P coating showed cracking, ridged surfaces, and material removal that was concentrated in certain areas. These features expose a steel substrate to the environment rapidly, despite the measured lower material loss. The composite had evenly distributed material loss, toughness, and minimal cracking which is more effective at protecting a steel substrate.
- 3. During erosion-corrosion, monolithic Ni-P coatings had low weight loss but had pitting corrosion and cracking. These degradation features are more detrimental to than the higher amount of evenly distributed material loss that the Ni-P-NiTi coatings had. When the thicknesses of the coatings were compared, it showed that

the thicker coatings had more degradation from particle impact than the thinner coatings.

4. Ni-P-NiTi having a thickness in the range of 10μm to 25μm exhibit superior wear and erosion-corrosion protection over all other coatings tested.

The following work is recommended to further understand erosion-corrosion and wear behaviour of Ni-P-NiTi composite coatings:

- 1. Assess how the annealing of the composite coatings effects its erosion-corrosion behaviour.
- 2. Study the effect that the NiTi particle size has on the coating's tribological properties.
- 3. Use XRD to quantify the residual stresses in Ni-P and Ni-P-NiTi coatings.

Publications generated from this work include:

- Z. Li, R. Jensen, Z. Farhat, G. Jarjoura, and M.A. Islam, "Improved Erosion-Corrosion Resistance of Electroless Ni-P Coating by the Formation of Super-Elastic NiTi Nanoparticles," Conference of Metallurgists 2021, Canada.
- R. Jensen, Z. Farhat, G. Jarjoura, and M.A. Islam "Erosion-Corrosion of Novel Ni-P-NiTi Coating," -Undergoing editing process
- 3. R. Jensen, Z. Farhat, and G. Jarjoura "Effect of Coating Thickness on Wear Behaviour of Ni-P-NiTi Coatings," -Undergoing editing process

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Appendix A Characterization



Figure A-1 Cross Section SEM Images of Thin Ni-P Coating (a) 3000x Magnification (b) 5000x Magnification



Figure A-2 Cross Section SEM Images of Thick Ni-P Coating (a) 3000x Magnification (b) 5000x Magnification



Figure A-3 Cross Section SEM Images of Thin Ni-P-NiTi Coating (a)1000x Magnification (b) 3000x Magnification (c) 5000x Magnification



Figure A-4 Cross Section SEM Images of Thick Ni-P-NiTi Coating (a) 3000x Magnification (b) 5000x Magnification

10.0um

15.0kV 12.5mm x5.01k SE(L)





Ni Ka1

P Ka1

Figure A-5 EDS Map of Thick Ni-P Coating Cross Section



Figure A-6 EDS Map of Thick Ni-P-NiTi Coating Cross Section

Appendix B Hardness



Figure B-1 Combined Load-Depth Curves of all Points on the Ni-P Coating



Figure B-2 Combined Load-Depth Curves of all Points on the Ni-P-NiTi Coating



Figure B-3 Load-Depth Curves of Ni-P Coatings from Hardness Software



Figure B-4 Load-Depth Curves of Ni-P-NiTi Coating from Hardness Software
Appendix C Scratch Profiles



Figure C-1 Laser Confocal Images of 45µm Thick Ni-P Coating Scratch Profiles



Figure C-2 Laser Confocal Images of 9µm Thick Ni-P Coating Scratch Profiles



Figure C-3 Laser Confocal Images of 9µm Thick Ni-P-NiTi Coating Scratch Profiles



Figure C-4 Laser Confocal Images of 4µm Thick Ni-P-NiTi Coating Scratch Profiles

Appendix D Erosion-Corrosion



Figure D-1 70µm Thick Ni-P-NiTi Coating Tafel Curves (a) Pure Corrosion (b) Erosion-Corrosion



Figure D-2 60µm Thick Ni-P Coating Tafel Curves (a) Pure Corrosion (b) Erosion-Corrosion



Figure D-3 12 μ m Thick Ni-P Coating Tafel Curves (a) Pure Corrosion (b) Erosion-Corrosion



Figure D-4 25µm Thick Ni-P-NiTi Coating Tafel Curves (a) Pure Corrosion (b) Erosion-Corrosion