FINAL REPORT

Directed Vapor Deposition of a Cadmium Replacement Coating for High Strength Fasteners

SERDP Project WP-1615

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Strategic Environmental Research and Development Program

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1.0 List of Acronyms

AMS ..... Aerospace Materials Society
ASTM ..... American Society for Testing and Materials
CTE ..... Coefficient of Thermal Expansion
CVD ..... Chemical Vapor Deposition
DVD ..... Directed Vapor Deposition
EB-PVD ..... Electron Beam Physical Vapor Deposition
EDS ..... Energy Dispersive Spectroscopy
EPA ..... Environmental Protection Agencey
IVD ..... Ion Vapor Deposition
NLOS ..... Non Line of Sight
OSHA ..... Occupational Safety and Health Administration
PVD ..... Physical Vapor Deposition
RMS ..... Root Mean Square
SEM ..... Scanning Electron Microscopy
XRD ..... X-Ray Diffraction

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4.0 Acknowledgments

Luna would like to thank Mr. Derek Hass and Directed Vapor Technologies International (DVTI) for all of their generous help in coating substrates and providing vapor deposition expertise. Luna would also like to thank Mr. Joe Osborne of Boeing for his support on the program. Luna would like to acknowledge the financial support of the U.S. Department of Defense Strategic Environmental Research and Development Program (SERDP) for this project.

5.0 Executive Summary

Corrosion protection of high strength fasteners is of utmost importance due to the critical nature of structural loads transferred through them and their potential for galvanic corrosion. Therefore, adequate corrosion protection is a necessity to sustain both the structural integrity of fastener connections and to prevent preferential corrosion of connected members at the expense of galvanically-coupled fasteners. Traditionally, electroplated cadmium layers and hexavalent chromium rinses have been employed for these applications due to their excellent corrosion performance and lubricity for threaded applications; however, cadmium and chromate are hazardous substances, known human carcinogens and subsequently have high handling and disposal costs. These environmental, health and safety issues have resulted in more stringent OSHA and EPA regulations. These factors have increased the need to develop new coating technologies and corrosion protection systems for cadmium plating and chromate conversion coating replacement. As a result, several alternative deposition options for protective coatings have been considered; however, the desired combination of corrosion protection, tribological properties, and production rates has been difficult to achieve with an environmentally benign system.

Luna Innovations Incorporated, in partnership with Directed Vapor Technologies International, Inc. (DVTI, Inc.), performed work on a reduced-scope solution to SERDP WPSON-08-01 by using a directed vapor deposition (DVD) process to deposit Zn-Ni-Co ternary alloy coatings onto high strength steel substrates as a cadmium plating replacement option. The main objective of the program was to demonstrate the feasibility of producing a vapor deposited Zn-Ni-Co ternary alloy that exhibits improved corrosion resistance over that of typical cadmium coating processes while at the same time reducing the propensity for hydrogen embrittlement on coated fasteners in service. The reduced-scope research program consisted of a year of funding to demonstrate coating feasibility and culminated in corrosion performance characterization of several coated high strength steel substrates.

Directed vapor deposition, is an advanced approach for depositing high quality coatings from vapor. It provides the technical basis for a flexible, high quality coating process capable of atomistically depositing dense, compositionally controlled coatings onto line-of-sight and non line-of-sight (NLOS) regions of high strength fastener components. Unlike other PVD approaches, DVD is specifically designed to enable the transport of vapor atoms from a source to a substrate to be highly controlled. Additionally, this novel vapor deposition solution serves to eliminate hazardous cadmium waste streams while improving fastener corrosion performance and should offer a competitive production throughput as compared to traditional fastener cadmium plating production lines.

For this program, directed vapor deposition technology has been used to produce several alloy coatings with good corrosion properties. Specifically, coatings were deposited onto 4340 steel substrates and evaluated using SEM, EDS, and XRD techniques. Analyses revealed that both Zn-Ni and Zn-Ni-Co alloys can be deposited onto substrates with microstructural and compositional consistencies that exhibit corrosion resistant structures. By controlling the substrate temperature during the deposition process and other parameters including electron beam current, scanning frequency, source material feed rate, and carrier gas flow behavior, Luna

and DVTI have shown the ability to deposit a unique set of Zn-Ni and Zn-Ni-Co alloys that appear to have good density coupled with good adhesion.

Electrochemical tests revealed that several coatings exhibit galvanic corrosion potentials and currents that are comparable to an AMS-QQ-P-416 Class 2 Type I electroplated cadmium coating and supersede the performance of a traditional AMS-2417 Type I electroplated Zn-Ni coating. Salt fog testing conducted in accordance with ASTM B117 has revealed that several of the coatings are outperforming the AMS-2417 Type I electroplated Zn-Ni sample, as indicated by the time to red rust in sample scribes.

While cadmium has demonstrated excellent sacrificial coating properties during this work, it is important to note that the DVD process has demonstrated the feasibility of depositing Zn-Ni and Zn-Ni-Co coatings that outperform traditional electroplated Zn-Ni coatings. Due to this demonstrated success, the overall program objectives have been met within this work. More significant work will be needed to optimize coatings for additional performance including hydrogen embrittlment resistance, excellent adhesion to a variety of substrates and geometries, mechanical durability, and lubricity. Future funding will allow Luna and DVTI to explore this interesting technology concept to move it from a demonstration phase to a realized process that can be applied to numerous coating situations, not limited only to high strength steel fastener applications.

6.0 Objective

The main objective of the program is to demonstrate the feasibility of producing a vapor deposited Zn-Ni-Co ternary alloy that exhibits improved corrosion resistance over that of typical cadmium coating processes while at the same time reducing the propensity for hydrogen embrittlement on coated fasteners in service. Once this objective was achieved, follow on funding will allow Luna and DVTI to fully explore the proposed technology and carry out the necessary testing and scale-up activities to implement the DVD process for high strength steel fastener application. The directed vapor deposition technology employed in this work is an environmentally benign process that eliminates hazardous cadmium waste streams and in-process hydrogen embrittlement concerns associated with traditional electroplating processes. The program consists of two main technical objectives that, when combined, demonstrate the potential of the DVD approach as a viable alternative deposition strategy. The specific technical objectives were:

- **Technical Objective 1 – Identify the most applicable alloying constituents and optimal deposition parameters** to achieve the desired highly-refined coating microstructure necessary to improve corrosion performance. This was accomplished through careful selection of elemental vapor deposition source chemistries (i.e. source rod purity) and deposition characteristics including appropriate electron beam current settings, scanning rates, and applied substrate temperatures. The time to accomplish this objective was minimized through careful consideration of deposition parameters and by carrying out initial deposition rate determinations for each elemental constituent of interest.
- **Technical Objective 2 – Fabricate and characterize coated high strength steel coupons** to determine the best combination of alloy stoichiometry, deposition parameters, and overall

approach to minimizing corrosion and enhancing mechanical properties. Numerous coated high strength steel coupons were prepared and characterized via chemical, physical (i.e. XRD, SEM, EDS), and electrochemical (e.g. corrosion potential, galvanic current) means.

7.0 Background

Corrosion protection of high strength steel fasteners is of utmost importance due to the critical structural functions they serve. Corrosion maintenance, including detection and treatment, costs the Air Force in excess of $800 million per year.[1] It is therefore extremely important that adequate corrosion protection is employed to sustain both in-service fastener life and reduce the need for costly maintenance. Traditionally, electroplated cadmium coatings have been employed on high strength steel components due to their excellent corrosion performance and tribological properties; however, cadmium is a hazardous substance, known human carcinogen, and consequently has high handling and disposal costs. These environmental, health, and safety issues have resulted in more stringent OSHA and EPA regulations in recent years with cadmium being placed on the Toxic 17 EPA list. These factors have increased the need to develop new coating technologies and corrosion protection systems for cadmium plating replacement. As a result, several alternative deposition options for protective coatings have been considered; however, the desired combination of corrosion protection, tribological properties, and production rates has been difficult to achieve with an environmentally benign system.

The benefits of the DVD process employed during this program are numerous. The process serves to eliminate hazardous cadmium waste streams while improving fastener corrosion performance, reducing risk of in-service component hydrogen embrittlement, extending the service life of protected components, and may offer, through further development, a competitive production throughput rate as compared to traditional fastener cadmium plating production lines. In addition the DVD process allows for fine compositional and microstructural control of uniform, well adhered, fully-dense, metallic coatings on irregular surfaces.[2] Lastly, the DVD process is environmentally benign and produces no liquid, solid, or airborne waste streams.

7.1 Cadmium Plating Replacement Overview

Several Cadmium replacement technologies have gained interest and use in recent years. Perhaps the most widely used replacement technology is ion vapor deposition (IVD) of aluminum.[3] IVD is an environmentally clean, commercially available processing approach, but is limited by poor coating density, its inability to deposit materials other than aluminum, long chamber pumpdown times and an inability to coat regions not in the line-of-sight of the vapor source. Aluminum coatings deposited using this technique are used in stringent corrosive environments only after additional treatments and the application of easily damageable sacrificial topcoats. IVD aluminum components are also subject to hydrogen re-embrittlement in service.

Other approaches under consideration also have limitations. For example, electroplating of Zn-Ni and Zn-Sn alloys have exhibited good corrosion protection and electroplating has good throwing power, however, the electroplating of alloys is difficult since the chemistry is dependent on the continuously changing solution chemistry and the current density.[4] The incorporation of hydrogen into the coating during the electroplating process can also lead to

hydrogen embrittlment of the substrate unless post deposition heat treatments are applied.[5] Hazardous waste is still an issue in electroplating processes even with non-Cadmium chemistries due to the large volumes of plating bath solutions that require handling and post-use processing.[4]

Chemical vapor deposition (CVD) and thermal spray are also under consideration for niche applications, but these also have many issues. In CVD, coatings can be deposited onto surfaces because the flux is distributed over the part surface using a gas flow. However, the deposition process requires the use of toxic and frequently expensive precursor materials. In addition, the deposition of the multi-component metallic alloys is difficult, deposition rates are low and high substrate temperatures are often required.[6] Thermal spray coatings of Al and Al-Zn are used in some applications as these approaches are commercially available and can coat large areas economically. However, the coatings are thick, rough and often porous limiting their effectiveness for fasteners.

Physical vapor deposition processes such as sputtering and electron beam-physical vapor deposition (EB-PVD) typically deposit the highest quality coatings enabling thin, dense layers (under some conditions) of a wide range of coating materials. For these cases, dense layers are only obtained if depositing atoms have sufficient surface mobility to diffuse to low energy sites on the deposition surface. This can occur via thermal energy (i.e. from the heat of adsorption or from heating the substrate) or via kinetic energy (i.e. high velocity atomic impacts resulting from plasma activated processes).[6] These processes also often operate under stringent vacuum conditions that increase their ultimate cost, primarily due to difficulties in achieving and maintaining ultra high vacuum.

Based on these outlined alternative coating shortcomings, there exists a need for an advanced environmentally-benign vapor deposition approach that allows flexible control of coating composition and microstructure while being economically advantageous over traditional corrosion protective coating technologies.

7.2 Directed Vapor Deposition

Directed vapor deposition, is an advanced approach for depositing high quality coatings from vapor (Figure 1). It was initially developed at the University of Virginia and is licensed to DVTI, Inc.[7]. It provides the technical basis for a flexible, high quality coating process capable of atomistically depositing dense, compositionally controlled coatings onto line-of-sight *and* non line-of-sight (NLOS) regions of high strength fastener components. Unlike other PVD approaches, DVD is specifically designed to enable the transport of vapor atoms from a source to a substrate to be highly controlled. To achieve this, DVD technology utilizes a trans-sonic gas jet to direct and transport a thermally evaporated vapor cloud onto a component. Typical operating pressures are in the 1 to 50 Pa range requiring that only fast and inexpensive mechanical pumping need be used resulting in short (several minutes) chamber pumpdown times. In this processing regime, collisions between the vapor atoms and the gas jet create a mechanism for controlling vapor transport. This enables several unique capabilities including:

1) High rate deposition: Vapor phase collisions between the gas jet and vapor atoms allow the flux to be "directed" onto a substrate. Since a high fraction of the evaporated flux impacts the

substrate (i.e. the materials utilization efficiency is increased) instead of undesired locations (such as the walls of the vacuum chamber) a very high deposition rate (> 10 μm min^{-1}) can be obtained.

2) Non Line-of-Sight Deposition: The gas jet can be used to carry vapor atoms into internal regions of components and then scatter them onto internal surfaces to result in significant NLOS deposition. This allows for complex fastener coating geometries with reliable deposition quality.

3) Controlled intermixing during multiple source evaporation: The use of high frequency e-beam scanning (100 kHz) allows multiple source rods to be simultaneously evaporated. By using binary collisions with the gas jet atoms, the vapor fluxes are intermixed allowing the composition of the vapor flux (and thus, the coating) to be uniquely controlled. This allows alloys with precise compositional control to be created even when large vapor pressure differences exist between the alloy components.

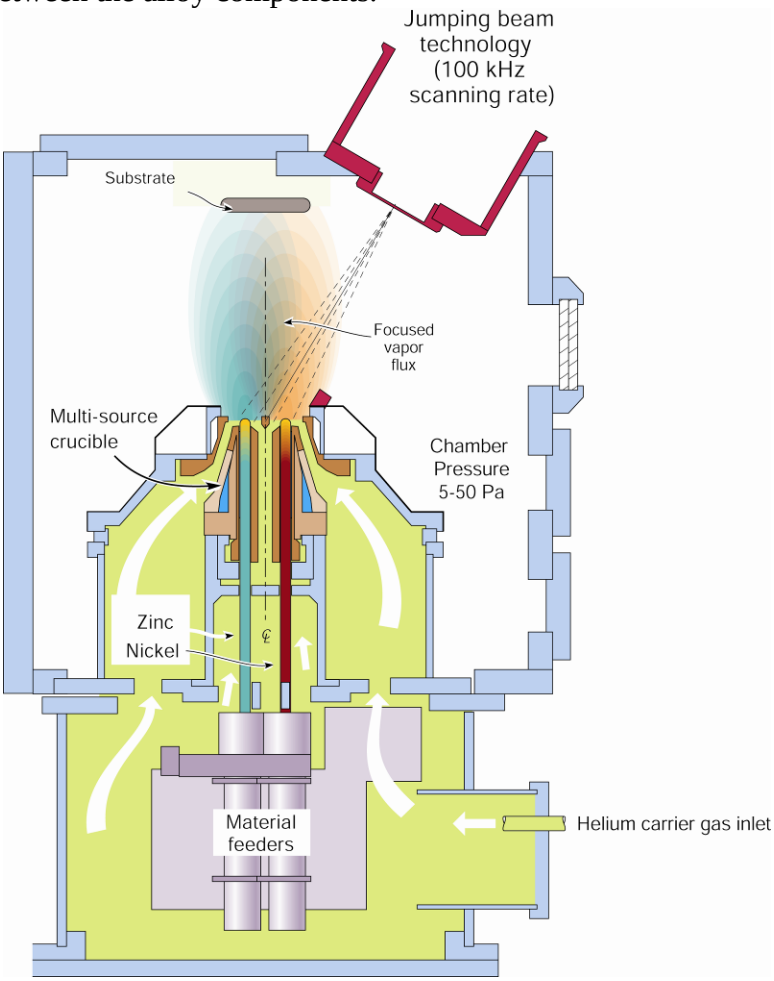


Figure 1: Schematic of the DVD process.

8.0 Materials and Methods

8.1 Combinatorial DVD Approach

Materials used for corrosion protection coatings for steel components have historically been either pure elements or binary alloys. This is due to the excellent success with Cadmium coatings limiting the need to explore advanced systems and the fact that increasingly complex (three or more elements) systems are difficult to investigate. This is due to a general lack in understanding of the composition / property relationships and the large number of potential combinations that exist. Serial experimental approaches for alloy development often miss compositional "sweet spots" due to the time and cost involved in evaluation. A combinatorial synthesis approach which allows high throughput screening of many compositions in a given materials system vastly accelerates the discovery of novel compositions especially when alloy properties are sought that are difficult to predict from theory.

In this work, a DVD combinatorial method was employed for the deposition of lateral compositional gradients on steel substrates. The process conditions for making coatings of this type are well established resulting in the ability to process small samples that contain a wide range of compositions. This technique has allowed Luna and DVTI to evaluate numerous coating chemistries that might not otherwise be possible using other approaches.

8.2 Zn-Ni-Co Ternary Alloy

Highly anodic sacrificial coatings will serve to corrode more readily/actively when a scratched or otherwise damaged coated substrate area becomes exposed to the in-use environment. This results in an increased hydrogen evolution driving force regardless of whether the component service environment is acidic or alkaline and can lead to component embrittlement.[8] Unlike electrodeposition processes, an important advantage of the DVD process is that no hydrogen embrittlement can occur during deposition; therefore, no post coating heat treatment is required. Further, the addition of the cobalt constituent combined with nickel can result in a less anodic overall zinc protective coating, thus serving to reduce the driving force for hydrogen generation during sacrificial corrosion reactions and possible in-service component hydrogen embrittlement.

8.3 Test Methods and Equipment

Several different test methods were utilized in this work. The overarching approach was to evaluate a wide range of coating chemistries via scanning electron microscopy and energy dispersive spectroscopy to develop an understanding into the microstructure – coating chemistry relationship. Specifically, the SEM used in this work was a LEO 1430VP with Oxford EDS. Coatings identified for further analysis were evaluated electrochemically using a standard three electrode technique. Furthermore, down selected coatings were also evaluated using x-ray diffraction. The XRD used in this work was a Panalytical XpertPro MPD. Lastly, the best performing coatings were selected for modified salt fog testing in a Singleton cyclic salt spray chamber in accordance with ASTM B117 using acceptance criteria guidelines outlined in *JG-PP*

Joint Test Protocol BD-P-1-1 for Validation of Alternatives for Electrodeposited Cadmium for Corrosion Protection and Threaded Part Lubricity Applications.

9.0 Results and Accomplishments

9.1 Substrate Materials

As the overall goal of the program is to develop an environmentally benign cadmium replacement coating for use on high strength steel fasteners, the first decision on the program was to determine which steel material to use as a substrate. For this, Luna discussed which substrate materials would best be suited for initial directed vapor deposition trials with Mr. Bruce Sartwell. It was determined that fully hardened 4340 steel would be the best choice for this work. Therefore, three inch and one inch diameter 4340 steel round stock was procured for use in combinatorial directed vapor deposition trials. The material was sectioned into 1/8"thk pieces and ground to achieve a 64-32 RMS finish. This finish was chosen to correspond to the typical surface finish exhibited by high strength steel fastener components per the *High Strength Steel Fastener Joint Test Protocol for Validation of Alternatives to Electrodeposited Cadmium For High Strength Steel Fastener Applications*. Luna decided to perform deposition trials on annealed 4340 steel stock due to the cost associated with hardening deposition substrates and the fact that it is believed that a hardened versus annealed surface shouldn't be chemically different, and therefore would not result in different deposition parameters.

9.2 Selection of DVD Elemental Sources

After a thorough evaluation of Zn-Ni-based ternary alloy systems for improved performance including Co, Al, Cu, and Fe, Luna selected Co and Cu as the most promising ternary constituents to be alloyed with Zn-Ni for combinatorial directed vapor deposition trials. DVTI acquired vapor deposition source materials in a variety of different purities for the work. The reason the original research focus was opened up from looking exclusively at the Zn-Ni-Co system to include the Zn-Ni-Cu system was based on the fact that the Cu system was believed to potentially offer similar performance benefits without the added perceived hazards associated with processing Co. Additionally, it was felt that the Zn-Ni-Cu system could be used for practice deposition runs in order to minimize the number of early runs that required Co.

9.3 Acquisition of Baseline Coated Samples

As a means to compare Luna's coatings to field-approved sacrificial coatings, Luna acquired both Cadmium and Zn-Ni coated 4340 steel substrates for comparison testing. Specifically, five 1" diameter x 1/8" thick annealed 4340 steel coupons were cadmium plated in accordance with AMS-QQ-P-416 Class 2 Type I specification at Central Metal Finishing. Additionally, five 1" diameter x 1/8" thick annealed 4340 steel coupons were coated with Zn-Ni in accordance with AMS-2417 Type I except that no chromate conversion coating was applied. The conversion coating was left off of the Zn-Ni control samples such that Luna could compare the DVD-deposited Zn-Ni-ternary systems similarly without conversion coating. The average thicknesses were measured to be 0.00035" (~9µm) for both coatings. Figure 2 shows both the Cd and Zn-Ni control coupons used during this evaluation.

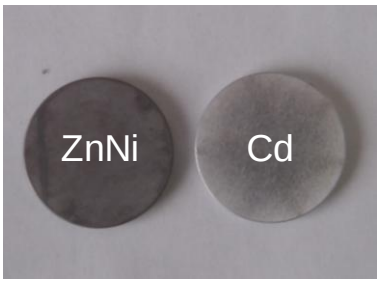


Figure 2: Control samples obtained for comparison.

9.4 Selection of Initial Deposition Parameters

It was determined early on that each elemental constituent to be vapor deposited should be baselined in order to develop the relationship between deposition parameters and evaporation rate. Therefore, evaluations were conducted for Zn, Ni, Cu, and Co to determine vapor deposition rates as a function of electron beam current, time, and source material feed rate. This data enabled us to predict the application parameters needed to achieve the desired alloy compositions on the 4340 steel samples. For each element, three different beam currents were selected and the mass loss of the source rods measured. This method was used to accurately determine the deposition rates for each material. The acquired data was later used to selectively apply constituent chemistries to the desired substrates.

9.5 Coating Application and Evaluation

9.5.1 Initial Deposition Results

It was decided to employ a combinatorial evaluation strategy to the program early on so that a wide range of alloy chemistries could be evaluated quickly in order to down select to the most-promising systems. For this, several Zn-Ni-Cu and Zn-Ni-Co coatings were deposited on 3" diameter 4340 steel substrates throughout the course of the program. Initial coating evaluations were focused on depositing the Zn-Ni-Cu ternary alloy system in order to optimize coating parameters before switching over to the Zn-Ni-Co ternary system. In early deposition trials, deposition parameters were used to attain coating compositions within the desired Ni-Cu-Zn range. In addition, previous vapor deposition work has demonstrated the fact that optimum coating densification occurs when the ratio of the substrate temperature to the coating melting temperature is greater than about 0.5. Therefore substrates were heated appropriately during deposition to achieve increased densification. Figure 3 and Figure 4 show the deposition setup and operation.

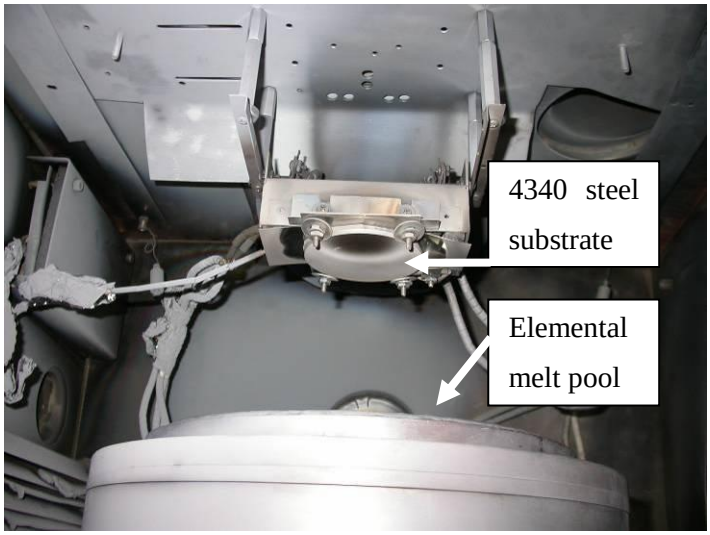


Figure 3: Orientation of the 3" combinatorial samples in the DVD chamber. The deposition profile can be seen on the sample as indicated by discoloration across the substrate surface.

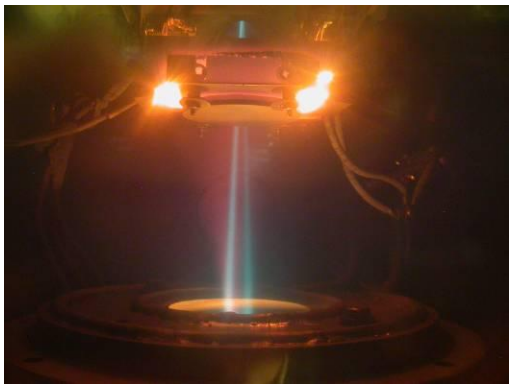


Figure 4: The split e-beam can be seen as well as part of the heating element used to heat the 4340 steel substrates.

Scanning electron microscopy (SEM) of two Zn-Ni-Cu coated combinatorial substrates revealed the absence of Zn. It was theorized that the substrate temperature was too hot to allow the Zn to condense due to the fact that it was above the melting point of pure Zn. Additional deposition runs were performed at lower temperatures to determine whether this was indeed the cause. It was determined that a moderate substrate temperature gave the best combination of compositional control while allowing the Zn to deposit on the substrate.

Once optimum deposition parameters were found for the Zn-Ni-Cu system, several substrates were coated with the Zn-Ni-Co system. SEM and EDS analysis revealed one substrate with an area that contained a composition close to the desired stoichiometry. The sample was designated as SER 26 and an example picture of the coated substrate is shown in Figure 5.

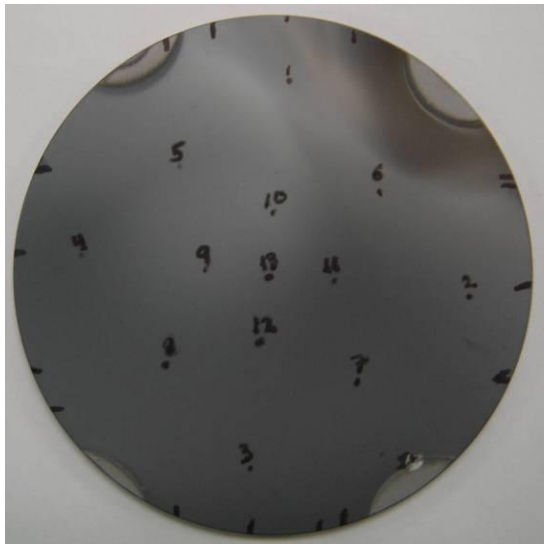
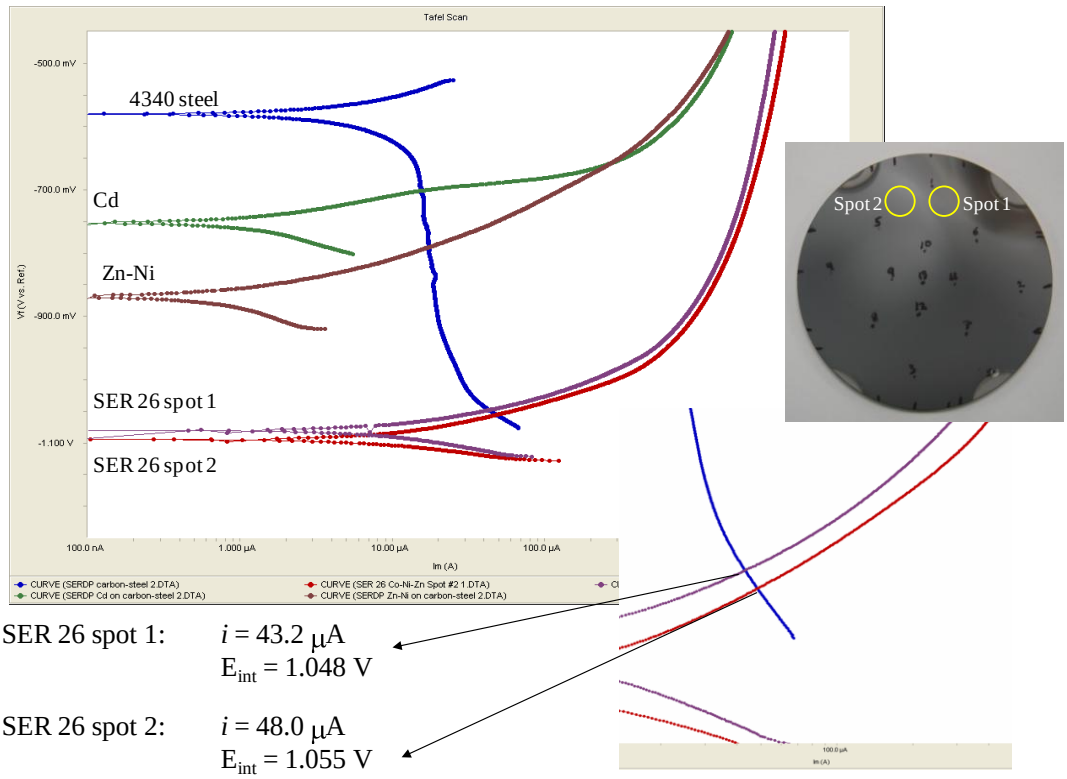


Figure 5: A Zn-Ni-Co coated 3" diameter 4340 steel substrate exhibiting a shading gradient across the surface corresponding to compositional variation.

Based on SEM and EDS analysis, it was decided that electrochemical testing should be performed at specific locations. Although SEM imaging revealed a slightly porous coating structure, it was decided that the best path forward would be to check the electrochemical potential of these areas in comparison to the base 4340 steel and the Cd and Zn-Ni coated control samples.

Using a conventional three electrode technique, the galvanic corrosion potential and galvanic current density of locations marked as spot #1 and #2 on the SER 26 sample (see Figure 6) were measured against a saturated Calomel electrode in 3.5% sodium chloride solution. The galvanic corrosion potential and current were compared to the base 4340 steel, an electroplated Cd sample, and an electroplated Zn-Ni coated sample as controls. Results of these tests are shown in Figure 6. It can be inferred that the particular SER 26 sample locations exhibited a higher galvanic current density and a greater corrosion potential, as taken from the intersection of the cathodic portion of the coating locations with the anodic portion of the 4340 steel scan. This indicates a faster coating galvanic corrosion rate as compared to the Cd and Zn-Ni coatings.



SER 26 spot 1: $i = 43.2\ \mu A$, $E_{int} = 1.048$ V

SER 26 spot 2: $i = 48.0\ \mu A$, $E_{int} = 1.055$ V

Figure 6: Measured corrosion potential and current density of spot #1 and #2 on the SER 26 sample (see inset) as compared to the base 4340 steel, a traditional electroplated Cd sample, and an electroplated Zn-Ni coated sample. The Zn-Ni-Co coating exhibits a higher galvanic current density indicating a faster corrosion rate as compared to the Cd and Zn-Ni coatings.

Post-test inspection of the SER 26 corrosion sites revealed that the coating was brittle and exhibited flaking. This led to the conclusion that either the deposited coating exhibited poor barrier properties due to excessive porosity and low density, or the coating consisted of individual elemental constituents as opposed to a true ternary Zn-Ni-Co alloy. Because of this, it was decided that metallographic analysis should be performed on the coating cross-section to determine the relative coating morphology and structure.

Several attempts at using standard metallographic preparation techniques were not successful. This was because the polishing and grinding steps caused the coating to flake off and be removed from the substrates, demonstrating the theory that perhaps the coatings were indeed fairly porous and poorly adhered to the 4340 steel substrate. A freeze-fracture method was then employed that solved this problem. Specifically, the SER 26 sample was partially sectioned, equilibrated in liquid nitrogen, and impact fractured to reveal a pristine coating cross-section. Fractured samples were then evaluated using SEM in order to quantify coating structure and specific location-to-location chemistry. SEM results indicated that the coating structure around the compositions of interest primarily consisted of a Zn-rich grain structure accompanied by a thin Ni-Co-rich top layer.

SEM analysis therefore confirmed the presence of distinct elemental compositions as opposed to a true ternary alloy system. In addition, while the bottom structure appeared relatively dense, the

top structure appeared quite porous. Lastly, several gaps were witnessed along the interface between the base 4340 steel substrate and the Zn-rich structure. It's unclear as to how much of this could be attributed to the sudden "freezing" of the coating during the fracturing process, which would tend to cause delamination associated with CTE mismatch.

Attempts were made to increase the density of the deposited coatings via shot peening and heat treatment processes. Shot peening resulted in minimal observed densification while heat treatment attempts appeared to help in some cases, but were ultimately abandoned in order to focus on achieving as-deposited fully-dense coating processes.

9.5.2 Coating Refinement and Evaluation

9.5.2.1 Zn-Ni Alloys

Based on the initial coating deposition results, it was decided that focus would be shifted from ternary Zn-Ni-Co alloys to achieve the correct deposition parameters needed to facilitate Zn-Ni binary compositions. Once control over the binary system had been established, the intent was to switch back to the ternary Zn-Ni-Co system in hopes of developing the necessary Co deposition parameters to apply in combination with the Zn-Ni parameters to achieve the desired final composition. In addition, smaller 1” diameter 4340 steel substrates were used for all subsequent evaluations and low carrier gas jet flow rates and DVD chamber pressures allowed for more homogeneous sample deposition. These conditions enabled denser coatings to be applied than the baseline DVD combinatorial conditions. The use of plasma assisted DVD was also considered as the process enables denser coatings at reduced substrate temperatures by ionizing the evaporated vapor atoms and, through the use of substrate biasing, increasing their kinetic energy during deposition. However, the low substrate temperatures required for Zn deposition were exceeded when using the current configuration of the plasma activation unit. As a result, this approach was not further employed during the program.

As mentioned previously in 9.5.1, initial coating trials at DVTI revealed that substrates received an inadvertent Zn-rich initial strike layer prior to the desired coating deposition. This occurred due to the fact that the Zn source material evaporated more quickly and readily (lower melt point) than the Ni (or Co) as the electron beam rastered across the sources, resulting in an initial Zn vapor that coated the substrates. While this may not be entirely undesirable, it was not ideal as part of our compositional evaluations. Therefore, all further coating runs were prepared utilizing a fixture such that control was maintained as to when the coupons were exposed to incident vapor. In addition, a sample mounting stage was built so that samples could be rotated during the deposition process in order to aid in compositional homogeneity.

The first results obtained for Zn-Ni coatings on 1” diameter substrates indicated that, while the Zn-rich strike layer was absent, the desired composition was still not being deposited on the substrates. Therefore, DVTI further refined their deposition parameters to achieve the desired Ni content. Specifically, four sets of 1” diameter 4340 steel coupons were prepared using improved deposition parameters to achieve the desired chemistries. The sample designations were labeled as SER 40, 41, 42, and 43. Three coupons were coated simultaneously for each SER sample set

and were identical in all respects. The freeze-fracture process detailed previously was used to acquire coating cross section samples for SEM/EDS analysis.

Based on these results it was determined that all of the samples exhibited coating compositions within the desired range, however coatings SER 40, 41, and 42 generally appeared slightly more porous than sample SER 43. Additionally, the open circuit potential was measured on one coupon from each set to rapidly determine which set(s) were worth more extensive evaluation. From these tests it was determined that SER 43 should be evaluated more thoroughly. Therefore, potentiodynamic scans were performed to measure the galvanic corrosion potential and current of one SER 43 coupon in the same manner as previously detailed in 9.5.1. The galvanic corrosion potential and current were compared to bare 4340 steel, one of the Cd control samples, and one of the Zn-Ni control coupons. Results of these tests are shown in Figure 7.

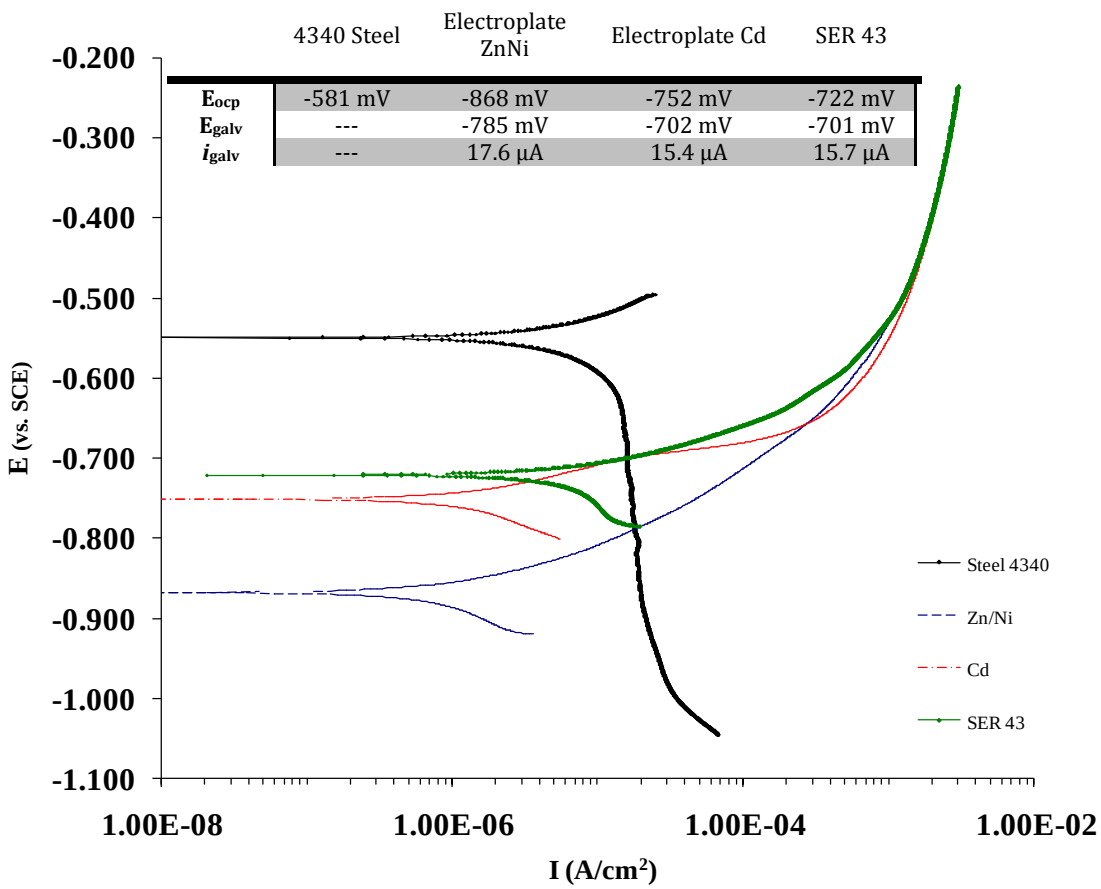


Figure 7: Potentiodynamic scans of a vapor deposited Zn-Ni coating (SER 43) as compared to the base 4340 steel substrate and traditional electroplated Cd and Zn-Ni coatings.

It can be inferred from Figure 7 that sample SER 43 exhibited a lower galvanic current density and a more positive galvanic corrosion potential as compared to the electroplated Zn-Ni control. Additionally, the galvanic performance was actually comparable to the Cd sample. This result means that the coating has the ability to sacrificially protect the steel; however it will corrode more slowly thereby decreasing the potential for hydrogen generation via oxidation-reduction reactions and subsequent steel embrittlement. This electrochemical behavior may be a result of

the specific Ni content present, a refinement in grain size, or a combination of both. This was a significant discovery for the program and further evaluation should be performed during future work. It should be mentioned that the coating thickness for SER 43 was measured to be ~ 14 µm.

9.5.2.2 Zn-Ni-Co Alloys

With the success of attaining excellent performing binary Zn-Ni coatings, DVTI scaled up to apply ternary Zn-Ni-Co coatings on several 1" x 1" 4340 steel substrates. Specifically, four sets of coupons were prepared that contained varying amounts of Zn, Ni, and Co. The sample designations were labeled as SER 48, 49, 50, and 51. Three to four identical coupons were coated simultaneously for each sample set. Figure 8 below shows typical coated coupons as prepared by DVTI during the refinement period.

Figure 8: Representative 1"x1" 4340 steel substrates coated with a Zn-Ni-Co alloy.

The open circuit potential (OCP) was measured on one coupon from each set to rapidly determine which ones were worth more extensive evaluation using SEM/EDS analysis and Luna's electrochemical three electrode setup. From these tests it was determined that SER 48 should be eliminated from the test plan due to it exhibiting an OCP value close to the base 4340 steel. This finding equates to the coating's inability to galvanically protect the steel and it is therefore not of beneficial interest to the program.

One sample each from SER sets 49, 50, and 51 was freeze-fractured and evaluated via SEM/EDS analysis. Based on these results it was determined that samples SER 49 and 50 exhibited coating compositions close to the desired composition, however sample SER 51 a thickness much too thin to be an effective corrosion protective coating. On the contrary, samples SER 49 and 50 exhibited average coating thicknesses of 13µm and 14µm, respectively. Additionally, sample set SER 50 was not further evaluated based on inferior OCP values as compared to SER 49.

The galvanic corrosion potential and current of one SER 49 coupon was measured using the same three electrode setup previously detailed and compared to the same bare 4340 steel, Cd, and Zn-Ni data mentioned previously. Results of these tests are shown in Figure 9.

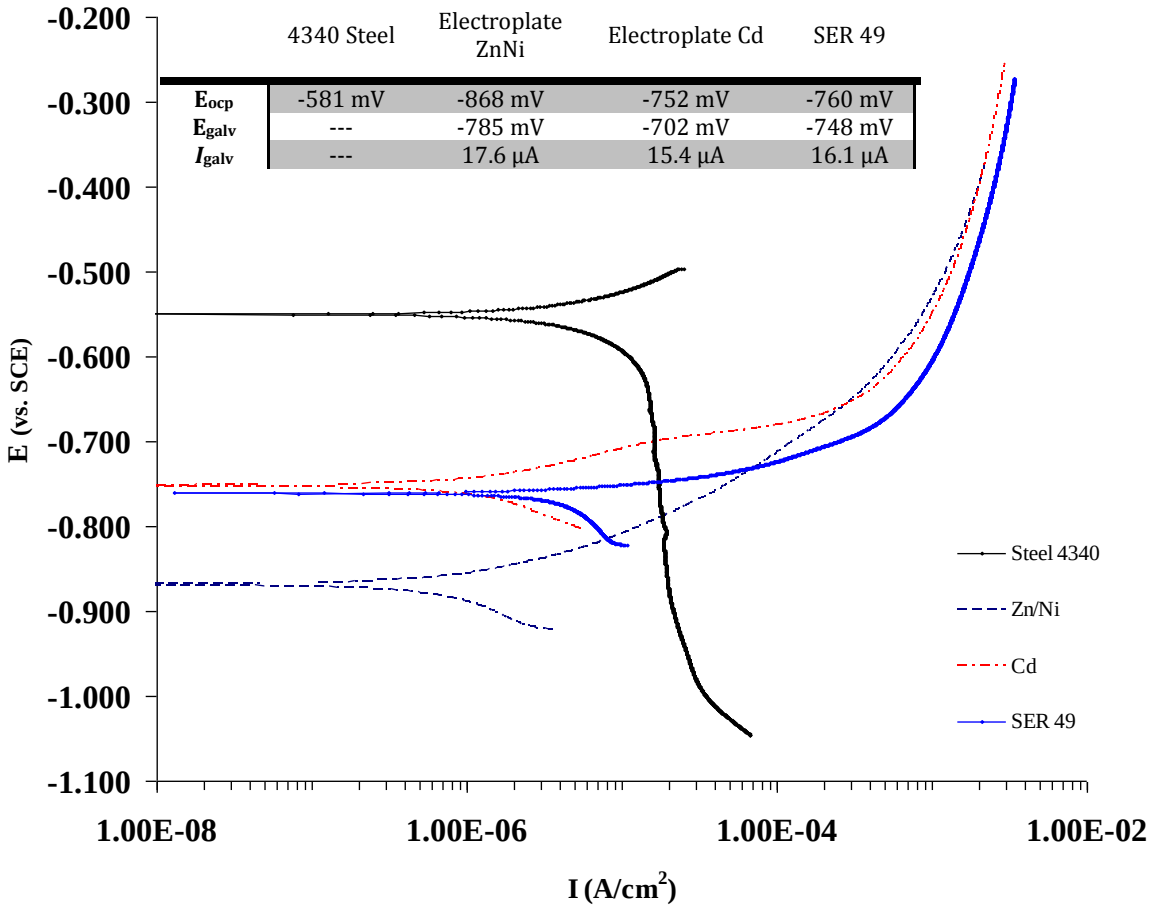


Figure 9: Potentiodynamic scans of a vapor deposited Zn-Ni-Co coating (SER 49) as compared to the base 4340 steel substrate and traditional electroplated Cd and Zn-Ni coatings.

It can be inferred from Figure 9 that sample SER 49 exhibited a lower galvanic current density and a more positive galvanic corrosion potential as compared to the base 4340 steel and electroplated Zn-Ni coating, and a slightly higher current density as compared to the Cd sample. This result is indicative of the coating's ability to potentially offer adequate galvanic protection to 4340 steel with a less-aggressive corrosion rate as compared to the traditional electroplated Zn-Ni coating and comparable corrosion rate with the Cd sample – similarly to the binary Zn-Ni SER 43 sample previously presented. The improved electrochemical properties may be due to grain refinement, crystallographic orientation, the specific phase compositions present in the deposited coating, or a combination of all.

9.5.2.3 X-Ray Diffraction

X-ray diffraction (XRD) was performed on samples SER 43 (binary Zn-Ni), SER 49/50 (ternary Zn-Ni-Co) and compared to the control electroplated Zn-Ni coating. XRD analysis was employed in an attempt to quantify the phase compositions present in the vapor deposited coatings. Based on the XRD results, it appears that both the best binary Zn-Ni coating (SER 43)

and ternary Zn-Ni-Co coatings (SER 49 and 50) are comprised almost entirely of the desired phase.

This is an excellent result in that it proves that, with the specific deposition conditions used for SER 43, 49, and 50, homogeneous coatings can be applied to 4340 high strength steel substrates without additional post-deposition heat treatments. This is important in that it shows the capability of utilizing vapor deposition to deposit both binary Zn-Ni and ternary Zn-Ni-Co coatings that contain the correct phase composition with a minimum number of processing steps.

9.5.2.4 Salt Fog Testing

Once improved electrochemical results were demonstrated, DVTI prepared additional coated coupons in an attempt to replicate the best performing coating chemistries for salt fog testing in accordance with ASTM B117. Specifically, DVTI prepared 12 additional coupon sets of varying coating composition. Based on SEM/EDS analysis, samples from sets SER 49, 52, 54, 55, 56, 57, 58, 59, 60, and 62 were chosen for salt fog testing.

Salt fog testing can be broken up into two groups. Test Set #1 consisted of samples from SER sets 49, 52, 54, 55, 56, and 57. At the time of this report, Set #1 has been in test for 900 hours. Test Set #2 consisted of samples from SER 58, 59, 60, and 62 and were not included in Set #1 due to time and salt fog chamber space limitations. The samples in each set were scribed using a carbide tipped tool to acquire an approximate 1/8” cross in the center of the sample. Additionally, one Cd and Zn-Ni control sample was prepared in the same manner for comparison purposes within each test set. The backs and edges of each coupon were masked with wax and the samples were fixed to a plastic sheet that was then placed appropriately in Luna’s B117 salt fog chamber. Samples were evaluated periodically for the presence of red rust both inside and outside of the scribe. Times were noted and representative pictures of the samples were acquired. We can only present data for test Set #1 as Set #2 has only been in test for ~100 hrs and there is no presence of red rust noted on any of the samples. Results for Set #1 are shown in Table 2 in the appendix.

It can be seen that the Cd control sample has yet to exhibited red rust in the scribe up to 900 hrs, whereas all of the other samples have. It should be noted though that the Zn-Ni control sample exhibited red rust in the scribe after only 450 hrs. In comparison, Luna samples 57A and 54A didn’t exhibit red rust in the scribe until 900 hrs into the test. It should be reminded that neither the control nor any of the Luna samples received a post-coating chromate treatment. Therefore, salt fog performance is expected to significantly increase after a conversion coat process.

The samples currently being evaluated in test Set #2 (58, 59, 60, and 62) were selected based on their galvanic corrosion performance. The galvanic corrosion potential and current of one coupon from each of the mentioned sets was measured using the same three electrode setup previously detailed and compared to the bare 4340 steel, Cd, and Zn-Ni data mentioned previously. Results of these tests are shown in Figure 10.

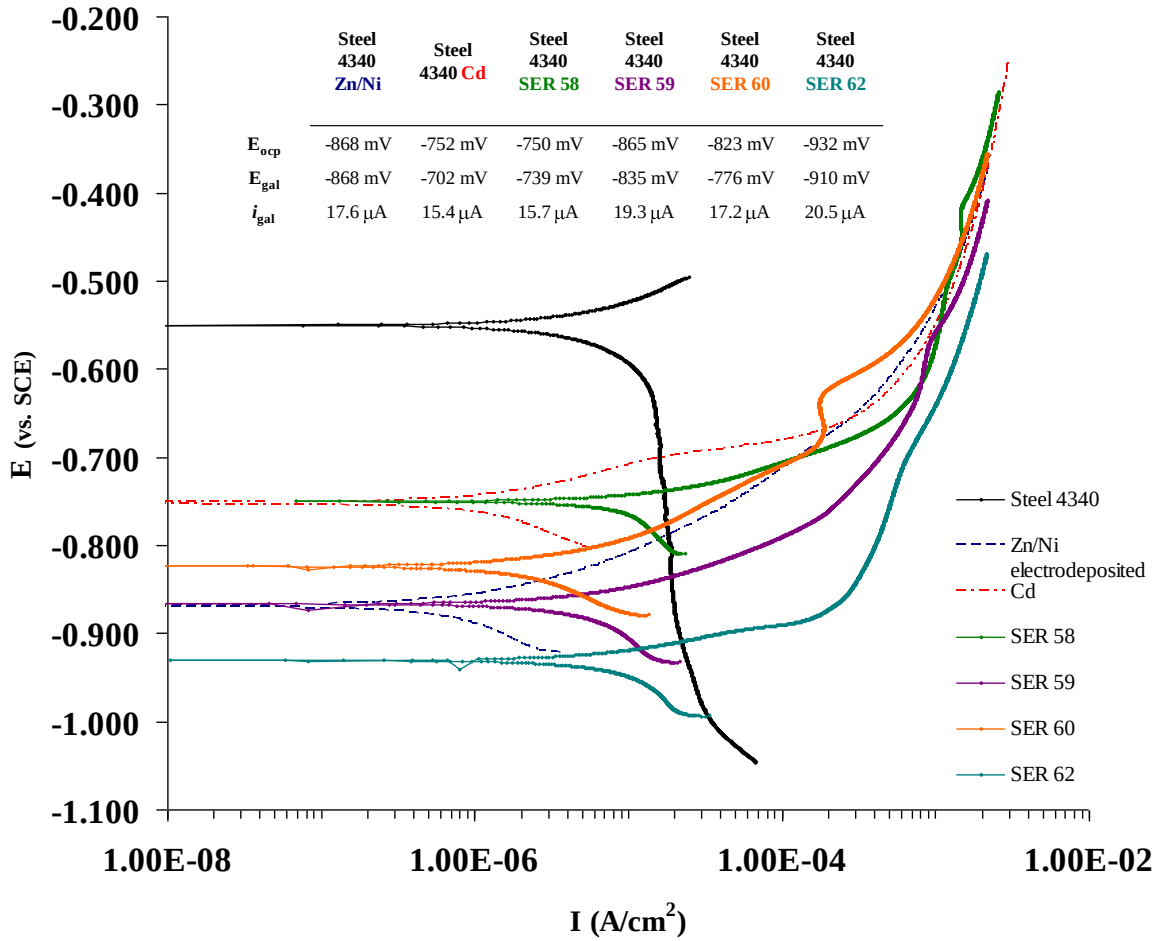


Figure 10: Potentiodynamic scans of vapor deposited Zn-Ni-Co coatings (SER 58, 59, 60, 62) as compared to the base 4340 steel substrate and traditional electroplated Cd and Zn-Ni coatings.

It can be seen in these results that SER 58 exhibited a comparable galvanic corrosion potential and current to the Cd control and a significant improvement over that of the Zn-Ni control. The order of best galvanic coating to worst galvanic coating based on this data follows as Cd, 58, 60, Zn-Ni control, 59, and 62. It's interesting to note that samples SER 58 and 62 in general contained more Co and Ni than samples SER 59 and 60 which one would expect should translate into less anodic behavior during electrochemical testing. This was not the case however in that the OCP values for SER 58 and 62 diverged in that SER 62 exhibited the most anodic OCP value at -932mV and SER 58 exhibited the least anodic OCP value at -750mV. SER 59 and 60 exhibited values within this bracketed range coming in at -865mV and -823mV, respectively. It's unclear as to why the increased addition of the more-noble Ni and Co constituents didn't result in less anodic OCP values. The result could be a function of the crystal structure and morphology of the deposited coatings, the specific grain size of each coating, and/or the overall coating density. Additional evaluation is necessary to determine the specific reasons for this behavior.

An attempt was made at estimating both the galvanic corrosion rate and the free corrosion rate of the Luna coatings as compared to the Cd and Zn-Ni control samples. This was accomplished by utilizing standard corrosion rate practices and estimating the Tafel slopes from the anodic portions of the polarization scans shown in Figure 7, Figure 9, and Figure 10. The intersection of the Tafel slope with the open circuit potential provides a rough estimate on the free corrosion rate. These estimates are summarized in Table 1 below.

Table 1: Estimate of the galvanic and free corrosion rates of several Luna alloys as compared to a Cd and Zn-Ni control coating.

Sample ID	I_{Corr} ($\mu A/cm^2$)	Free Corrosion Rate (mpy)	I_{Gal} ($\mu A/cm^2$)	Galvanic Corrosion Rate (mpy)
Cd	0.99	0.8	15.40	12.9
ZnNi	1.44	0.7	17.60	8.8
SER 43	4.19	2.1	15.70	7.9
SER 49	6.58	3.3	16.10	8.1
SER 58	8.90	4.4	15.72	7.9
SER 59	3.10	1.5	19.34	9.6
SER 60	1.40	0.7	17.20	8.5
SER 62	3.60	1.8	20.45	10.2

It can been in the corrosion rate data that the Cd, Zn-Ni, and SER 60 samples exhibit the slowest free corrosion rate, which is good from a longevity standpoint when a blemish-free coating is present. Once the coating is scratched or otherwise compromised, the SER 58, SER 43, and SER 49 samples exhibit the slowest galvanic corrosion rate. This is good from a sacrificial coating performance standpoint and also translates into a potential for less substrate in-service hydrogen embrittlement issues due to a slower corrosion driving force/rate.

While salt fog data is not available yet for samples SER 58, 59, 60, and 62, it is believed that samples 58 and 60 should perform quite well due to their low associated galvanic corrosion rates.

10.0 Conclusions

Luna and DVTI have explored several Zn-Ni based coatings for use as cadmium replacement options for high strength steel fasteners. Numerous coatings were deposited onto 4340 steel substrates using an environmentally benign directed vapor deposition approach. SEM, EDS, and XRD analyses have revealed that both Zn-Ni and Zn-Ni-Co alloys can be deposited onto substrates with microstructural and compositional consistency that exhibit good corrosion resistant structure. By controlling the substrate temperature during the deposition process and other parameters including electron beam current, scanning frequency, source material feed rate, and carrier gas flow behavior, Luna and DVTI have shown the ability to deposit a unique set of Zn-Ni and Zn-Ni-Co alloys that appear to have good density coupled with good adhesion.

Electrochemical tests revealed that several coatings, especially samples SER 43, 49, and 58, exhibit galvanic corrosion potentials and currents that are comparable to an electroplated cadmium coating and supersede the performance of a traditional electroplated Zn-Ni coating. Salt fog testing conducted in accordance with ASTM B117 has revealed that several of Luna's coatings are outperforming that of an electroplated Zn-Ni sample, as indicated by the time to red rust in the sample scribe.

While cadmium appears to be outperforming all of the coatings tested, it is important to note that the DVD process has demonstrated the feasibility of depositing Zn-Ni and Zn-Ni-Co coatings that outperform traditional electroplated Zn-Ni coatings. As this was the main objective of the reduced scope program, we feel success has been achieved in the phase of this work. Further work will be needed to optimize coatings for additional performance including hydrogen embrittlment resistance, adhesion to substrates, mechanical durability, and lubricity. Future funding will allow Luna and DVTI to explore this interesting new technology to take it from a demonstration phase to a realized process that can be applied to numerous coating situations, not solely limited to high strength steel fastener applications.

11.0 References

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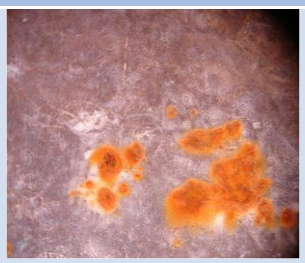
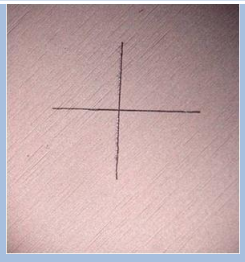
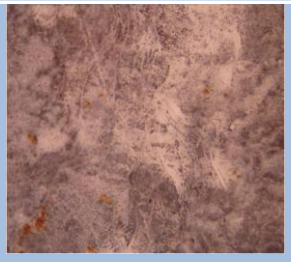
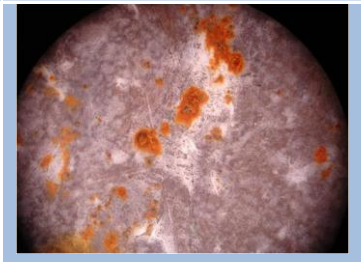
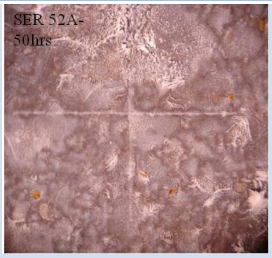
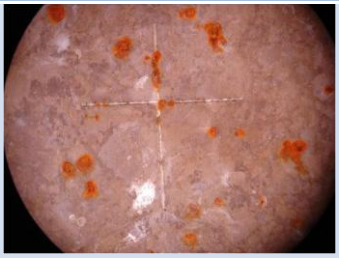
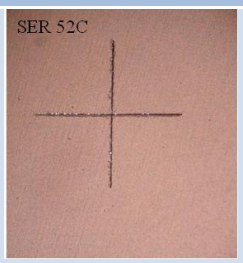
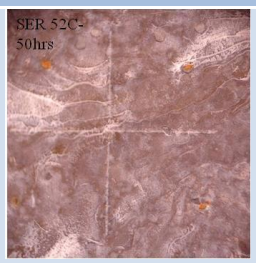
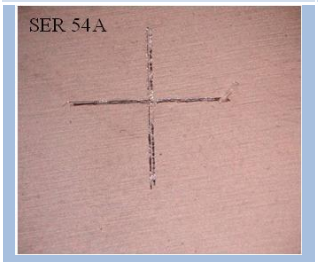
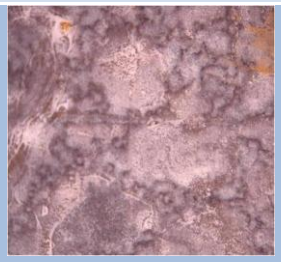
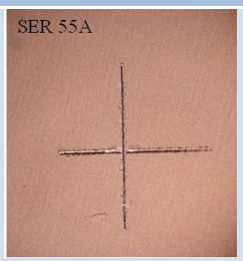
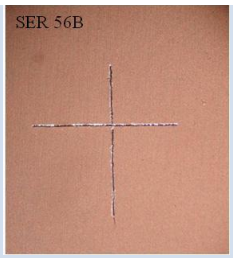
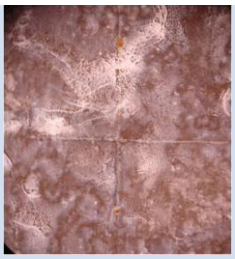
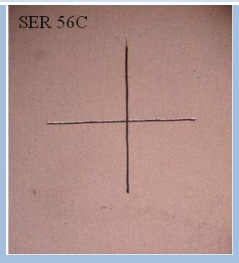
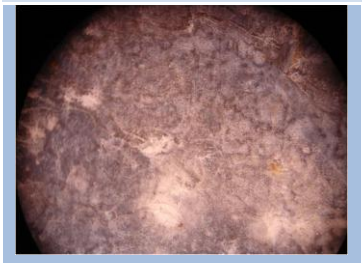
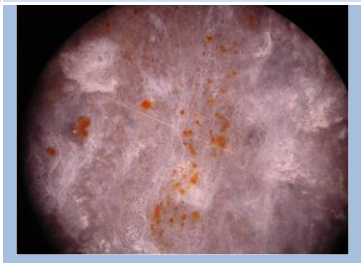
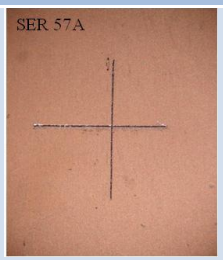
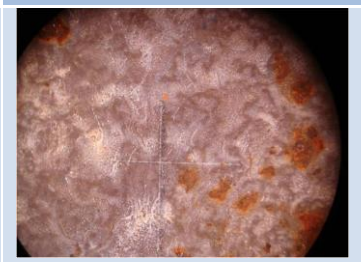
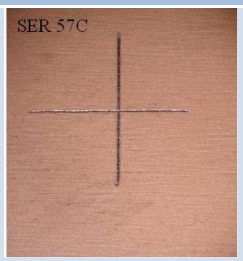
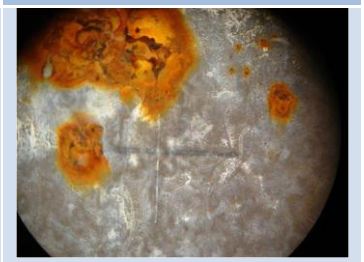
12.0 Appendices

Table 2: Salt fog test results for several different Zn-Ni and Zn-Ni-Co coatings evaluated during the program

Sample	Composition	Starting Appearance	Time to red rust/pic	Time to red rust in scribe/pic
Cd Control	AMS-QQ-P-416 Class 2 Type I		300 hrs	NA
Zn-Ni Control	AMS-2417 Type I (no chromate), ~ 16%Ni – 84%Zn (EDS)		300 hrs	 450 hrs
49C	Zn-Ni-Co		 300 hrs	 450 hrs
52A	Zn-Ni-Co		 50 hrs	 450 hrs

52B	**Zn-Ni-Co**		**50 hrs**	**450 hrs**
52C	**Zn-Ni-Co**		 **50 hrs**	**450 hrs**
54A	**Zn-Ni-Co**		 **200 hrs**	**900 hrs**
55A	**Zn-Ni-Co**		**450 hrs**	**450 hrs**
55D	**Zn-Ni-Co**		**300 hrs**	**450 hrs**

56A	**Zn-Ni-Co**		 **50 hrs**	**450 hrs**
56C	**Zn-Ni-Co**		 **300 hrs**	 **450 hrs**
57A	**Zn-Ni-Co**		**200 hrs**	 **900 hrs**
57B	**Zn-Ni-Co**		**300 hrs**	**450 hrs**
57C	**Zn-Ni-Co**		**300 hrs**	 **900 hrs**