

# NAVAL POSTGRADUATE SCHOOL

**MONTEREY, CALIFORNIA** 

# THESIS

# CORROSION BEHAVIOR OF COLD SPRAYED ALUMINUM OXIDE REINFORCED ALUMINUM COATINGS

by

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June 2021

Thesis Advisor: Co-Advisor: Andy Nieto Troy Ansell

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## CORROSION BEHAVIOR OF COLD SPRAYED ALUMINUM OXIDE REINFORCED ALUMINUM COATINGS

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#### ABSTRACT

The selection of materials in the cold spraying process has a significant impact in corrosion resistance. Recognition of this could provide the opportunity to adapt a wide range of coating deposits for different applications for repair in protection against corrosion. Cold sprayed coatings of pure aluminum and alumina reinforced aluminum were deposited to understand the role of composition on corrosion. Coatings were sprayed with thicknesses varying from 100  $\mu$ m to ~3 mm in order to understand the role of coating thickness on corrosion. A salt fog chamber test helps mimic an austere marine condition for 1000 hours and 2000 hours of continuous exposure. Dimensional changes and mass gain were measured periodically throughout the salt fog exposure testing. The corrosion test revealed that reinforced aluminum is better for protection than pure aluminum having unresolved galvanic vulnerabilities within the coating and delaminating from the substrate. The alumina reinforced coating exhibited greater roughness in thicker coatings, which resulted in higher initial corrosion rates. With additional testing, cold spray could be used for coating protection of parts that are exposed to austere environments.

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# LIST OF ACRONYMS AND ABBREVIATIONS

aluminum
aluminum oxide
additive manufacturing
cold spray
copper nickel
Department of Defense
energy dispersive spectroscopy
high velocity oxygen fuel
optical microscope
polylactic acid
scanning electron microscope
salt fog chamber
X-ray diffraction

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## I. INTRODUCTION

#### A. BACKGROUND

#### 1. Motivation

Technical advances to gas dynamic cold spray (CS) are increasing and are great for specific Department of Defense (DOD) repair applications such as pumps, pipes, seawater cooling tubes, and more. Having the capability to fabricate a part or component rapidly has been found to be extremely useful within many areas of mechanical engineering and marine science across the Navy. In recent years, CS was made portable, allowing repairs to be conducted in the field without the long system down times and extended dock time. Having this capability allows components to be repaired with minimal material and personnel. New notions of in-situ repair paved the way for providing structural improvements, safety, and quality of life for ships and sub-systems. With the belief of CS in providing corrosion protection rising, the objective of this thesis is to move towards engineering aluminum oxide (Al-Al<sub>2</sub>O<sub>3</sub>) reinforced metals to improve the mechanical strength and wear resistance of coatings and to protect the underlying metal substrate from corroding. A deeper understanding of how Al<sub>2</sub>O<sub>3</sub> will play a role in corrosion resistance is needed prior to deploying the technology to marine environments.

#### 2. Thesis Objectives

CS has been recently explored for corrosion protection for several structural and manufacturing applications. Copper nickel alloys are among a unique class of isomorphous alloys, where the two metals have complete solubility in both liquid and solid state with each other. This solubility is due to copper and nickel preferring the same valence state, sharing the same crystal structure, exhibiting similar electronegativity, and having about the same atomic and ionic radii (all these characteristics mainly due to the two metals sitting right next to each other on the periodic table). The selection of copper–nickel in the cold spray process can increase the corrosion resistance of a substrate as the alloy is known for its resistance to corrosion. The purpose of this thesis is to explore two objectives: (a) understand the role that aluminum oxide reinforcements would have on corrosion as compared to pure aluminum, and (b) to understand the role of coating thickness on corrosion resistance of a given coating. The best way to make a one-to-one comparison would be processing the material the same way within this experiment.

## **B.** REVIEW OF THE CURRENT STATE OF THE ART

#### 1. Current Repair Methods

Repair times of parts can have long lead times causing long downtimes for a piece of equipment. Employing CS coatings to components can reduce repair time and cost within industries and the military. CS is a scalable repair technique and is compliant with existing DOD standards for surface repair and corrosion prevention applications. CS machines can be deployed upon ships as a portable CS system and would only require a metal feedstock powder and compressed air to operate.

Another approach to CS is additive manufacturing (AM); using the cold spray technique to build objects by adding layer after layer of metallic (or composite) materials together. Similar processes for repair include flame spray, high velocity oxygen fuel (HVOF) and plasma spray. More common repair processes are solid state welding, block joining, and ultrasonic welding (which were not considered AM traditionally, but since these involve material joining can be considered AM by definition). Thermal spray is a more conventional AM spraying process, which melts the material onto the sprayed surface.

#### 2. What is Cold Spray

CS is a solid-state coating process that uses high speed gas to accelerate powder particles toward a substrate, the particles plastically deform and merge with the substrate at impact. When comparing the cold spray process there are high pressure systems allowing high particle velocity upon impact, enabling the facilitation of heavier and less ductile materials. Then there are low-pressure systems used to process lighter ductile metals which provides low deposition efficiency. Deposition efficiency is key to the CS process, it can be improved by adding harder particles (such as alumina), enhancing the quality of the coating by increasing the bond strength and reducing the porosity. Thus, making it less susceptible to corrosion. Cold spray particles can attach to substrates without melting fully before they impact, due to kinetic energy.

#### **3.** Cold Spray for Corrosion Protection

Hassani-Gangaraj et al. [1]. reviewed the application of cold spray materials for corrosion protection. The authors focused on cold spray deposited material, creation of passive layers, as well as the cathodic protection of the coating. The effects of cold spray parameters were discussed. Industrial applications within the biomedical, naval, and electrical field were examined as well. This review concluded with a critical discussion of the path forward within cold spay applications. In summary:

- High compact coatings with less porosity are crucial in cold spay applications.
- Higher plastic deformation obtains better mechanical properties.
- Corrosion resistances increase with a greater level of plastic deformation, marring pores and reducing porosity.
- Broadening the deposition temperatures and pressure, with finer particles and thicker coatings potentially improves corrosion behavior.
- Rough surfaces decrease corrosion resistance, preventing pit formations within the coating.
- Titanium can be designed against aqueous corrosion, zinc and aluminum provides a sacrificial protection against steel. [1]

#### 4. Al & Al<sub>2</sub>O<sub>3</sub> Cold Sprayed Coatings

(i) Microstructure and mechanical properties

Pure aluminum is soft, ductile, and has high resistance to corrosion. Al is one of the lightest engineering metals, compared to steel and has a higher strength to weight ratio. Al density is a third of that of copper or steel, however, it does not have as high a tensile strength as the other metals. Most metals as well as Al can be reinforced with ceramics to make a stronger composition and microstructure. The reinforced element used in this study

is alumina (Al<sub>2</sub>O<sub>3</sub>), imparting upon aluminum higher tensile strength. In addition, alumina serves as a hard impactor during cold spraying, yielding a coating with less porosity that typically results in greater adhesion strength.

#### (ii) Corrosion

Corrosion is a chemical reaction among a metal or metal alloy and its environment. Corrosion restores the metal to its natural state in chemical compounds that are identical to the mineral from which it was extracted from. Corrosion occurs due to thermodynamics and kinetics; prevention of corrosion is to slow the reactions occurring in a metal.

Toa et al. [2]. investigated the properties of cold sprayed Al- Al<sub>2</sub>O<sub>3</sub> composite coated on AZ91D magnesium alloy. Their objectives were to learn the porosity, microhardness, adhesion, and tensile strength of Al- Al<sub>2</sub>O<sub>3</sub>. They also ran polarization tests which are shown in Figure 1. This shows an anodic polarization curve of pure Al, revealing a passive inclination while the composite coatings show an increase in current density as well as an increase of polarization potential. The results of the experiment showed that the composite coatings had lower porosity, and complex adhesion/ tensile strength than cold sprayed Al coatings.



Figure 1. Polarization curve in 3.5wt% NaCl solution. Source: [2].

Silva et al. [3]. examined the corrosion characteristics of cold sprayed reinforced aluminum composites on carbon steel. This study compared pure Al coating sprayed on the substrate, and Al-Al<sub>2</sub>O<sub>3</sub> sprayed on top of Al coating which was sprayed on top of carbon steel substrate. Mechanical properties of the coatings were improved by the inclusion of alumina particles, as well as all coatings had good adhesion and low porosity. They immersed their samples in a salt solution of 3.5wt% NaCl for up to 3000 hours, the Al-Al<sub>2</sub>O<sub>3</sub> on Al showed higher corrosion resistance then the pure Al on the carbon steel substrate. Their result showed Al coatings can protect against corrosion for long times.

Irissou et al. [4]. investigated Al-Al<sub>2</sub>O<sub>3</sub> cold spray coating formation and properties. They explored the influence of particle size and mass fraction of the powders would have within the coating once sprayed onto a substrate, preventing corrosion. They evaluated the bonds between Al and Al-Al<sub>2</sub>O<sub>3</sub>, and showed these were weak and caused poor construction between the powders. The authors improved the Al powder by adding hard particles, increasing adhesion and surface area of the coating to the substrate. The

conclusion of this study determined inclusion of the alumina products had no unfavorable effects on the corrosion protection of the substrate.

Li et al. [5]. investigated solid-state additive manufacturing and repairing by cold spray. The article focuses on the state-of-the-art and problems using cold spray as an AM and repair technique. In summary the authors state CS has great potential in forming and coating parts for repairs, however several problems limit its application as an additive manufacturing repair technique. To list a few concerns:

- Coatings had low ductility, as well as weak bonding strength.
- The processing parameters when operating should be under a systematic control.
- Nozzle clogging, and the lack of design criteria posed a common struggle.

## 5. Copper Nickel Alloys

Copper-Nickel (Cu-Ni) is a single-phase alloy, it exhibits complete solubility in both liquid and solid states in Figure 2. Cu-Ni is used in countless naval applications, as CS is used to repair damage to metallic components Cu-Ni is an important one to consider.



Figure 2. Copper-nickel equilibrium diagram. Source: [6].

One could superimpose the Pourbaix diagram for copper and nickel to give an idea of how a Cu-Ni alloy will behave in a corrosive environment. Figure 3 infers that each of the two metals behaves independently from one another, showing the preferential dissolution of copper and nickel as well as where both undergo dissolution. Regions of immunity and passivity are extended in Ni alloy, so it makes it better for corrosion resistance. A mixture of the two alloys provides a high corrosion resistance in a multitude of environments.



Figure 3. Pourbaix diagrams of copper (dotted lines) and nickel (solid lines) superimposed. Source: [7].

The German Copper Institute [6] researched copper-nickel alloys and address its properties, processing, and application. The identify the historical discovery of both metals and their phase diagram, identifying phases that occur and coexist at equilibrium. Cu-Ni has good mechanical properties at low and elevated temperatures, and has high electric resistivity making it corrosion/ ware resistant.

### II. EXPERIMENTAL METHODS AND MATERIALS

## A. SELECTION OF MATERIALS

Two powders from Centerline Ltd: pure aluminum (SST-A5001) and alumina (SST-A0050) -45 to + 5  $\mu$ m were used for this study, shown in Figure 4. A 70/30 Cu-Ni substrate was identified as the ground material needed to be protected against corrosion. Al has a low density and high ductility, and Al anodic reaction creates an aluminum oxide film as a corrosion resistance barrier making it an ideal metal for cold spray applications. Al powder is spherical in shape making the particles aerodynamic and allowing easier pick up amongst the flow of gas during CS process. The powders were baked in a Model 40 Lab Oven (Quincy Lab, Inc) at 80 °C, eliminating moisture within to prevent clumping, thereby allowing easy flow through the CS system.



Figure 4. SEM micrograph of (a) SST-A5001 (b) SST-A0050 powders

#### **B.** COLD SPRAYING OF COATINGS

In preparation for cold spray, Cu-Ni substrates were grit blasted with  $\sim 40 \ \mu m \ Al_2O_3$ particulates, then cleaned with acetone prior to cold spraying. The pure Al and Al-Al<sub>2</sub>O<sub>3</sub> were cold sprayed onto the substrate using a low-pressure cold spray system, using nitrogen gas as the propellant. Grit blasting roughened the surface to allow better adhesion of the Al cold sprayed coating. Acetone, a good solvent in dissolving all organic compounds on the surface of the substrates.

CS coatings were sprayed with a temperature of 350 °C, .93 MPa of pressure, transverse speed of 20 mm/s, and a line spacing of one millimeter. The number of passes, standoff distance was varied to obtain different thickness. The feed rate was varied to obtain similar thickness for the two different coating compositions. The standoff distance for the thin coating was 25.4 mm with one pass, where the thick coating needed more passes and a standoff distance of 12.7 mm. The feed rate change to properly process the two powders, Al feed rate is 9.7 g/min, while Al-Al<sub>2</sub>O<sub>3</sub> is 14.8 g/min. The CS parameters are listed in the Table 1.

Table 1.Cold spray parameters

Coating	Temperature (°C)	Pressure (MPa)	Standoff Distance (mm)	Feed (g/ min)	Traverse Speed (mm/s)	Line Spacing (mm)	Number of Passes
Thin	350	.93	25.4	14.8 /*9.7	20	1	1
Intermediate	350	.93	12.7	14.8 /*9.7	20	1	1
Thick	350	.93	12.7	14.8 /*9.7	20	1	*4/5

\* Al coating

# C. CORROSION SALT FOG CHAMBER TESTING

A MX-9204 salt fog chamber (SFC), in accordance with ASTM B117, was used to simulate an austere marine environment by pressurizing a 3.5 wt% NaCl aqueous solution as illustrated in Figure 4. Three-point five weight percent is the average salinity of the ocean, fog/mist is produced into the chamber making a corrosive atmosphere. Respective substrates were placed into three polylactic acid (PLA) trays that are 3D printed at NPS in Figure 5. The trays hold the samples at 20° from the bottom drainage cavity, eliminating water build up. Three sets of samples were immersed in the SFC for testing, totaling 18 samples separated into three thickness groups (thin, intermediate, and thick) for 1000 hours and 2000 hours.

Performance of overall weight and thickness gain were measured weekly, due to the formation of a passive oxide layer. Upon extracting the samples from the SFC, they were dried with a master heat gun (Model HG-301A) for approximately 10–15 minutes. The samples were measured with a Mitutoyo Digimatic 6 Inch Digital Calipers across the length of each substrate at three points (the two end and the middle).



Figure 5. Salt fog chamber



Figure 6. Polylactic acid trays

# **D.** CHARACTERIZATION

In completion of time requirements samples were sectioned and cold mounted with epoxy (Epofix 1, Struers Inc., Ted Pella Inc.) and then cured overnight. Samples were then polished using 320-, 600-, 800- , 1200-grit silicon paper and then finished using a 1  $\mu$ m diamond alumina suspension solution. Polished samples were imaged using a Nikon Epiphot 200 optical microscope (OM) and a Zeiss Neon 40 scanning electron microscope (SEM) was used for microscopy imaging of qualitative characterization of the as sprayed coatings. Elemental mapping of samples was performed in the Zeiss SEM using an attached EDAX electron dispersion spectrometer (EDS). A profilometer (Zygo NewView 7100) was used to determine the roughness of each starting witness samples.

# **III. RESULTS AND DISCUSSION**

#### A. AS SPRAYED MICROSTRUCTURES

#### 1. Roughness

One sample from each coating thickness set was used as a witness or a control sample, dictating the starting requirements. The witness samples for Al are W1, W3, and W5. In addition, the witness samples for Al-Al<sub>2</sub>O<sub>3</sub> are W2, W4, and W6. Roughness measurements of the surface of each witness samples were taken and are displayed in Figures 7 and 8. This measurement allowed a better understanding of the mechanical performance of the sprayed coatings. Roughness can determine irregularities on the surface that may form nucleation sites for corrosion. Al-Al<sub>2</sub>O<sub>3</sub> has lower roughness then Al, which is higher corrosion rate as seen in Tables 2 and 3.



Figure 7. Al witness samples



Figure 8. Al-Al<sub>2</sub>O<sub>3</sub> witness samples

Figures 7 and 8 scale bars next to the images indicates relative heights along the measuring line. The variation in height informs you about the roughness in a sample. Looking back at the images, red regions are higher, green regions are near zero, and blue regions are lower points below the zero mark. Figure 7 shows that the witness samples of Al are rougher, given it has tons of regions with variating color and black regions. Figure 8 that the witness samples of Al-Al<sub>2</sub>O<sub>3</sub> are smoother in roughness given it looks uniformed in color.

Table 2. Roughness of aluminum

Al Coatings	Average (μm) <u>+</u> Standard Deviation
Thin	20.45 <u>+</u> 1.63
Intermediate	21.46 <u>+</u> 2.68
Thick	24.15 <u>+</u> 3.11

Al-Al <sub>2</sub> O <sub>3</sub> Coatings	Average (μm) <u>+</u> Standard Deviation
Thin	$7.79 \pm 0.33$
Intermediate	12.97 <u>+</u> 0.69
Thick	18.70 <u>+</u> 3.84

Table 3. Roughness of alumina

#### 2. Thickness

Micrographs of the witness samples are shown in Figures 9 and 10 of both Al and Al-Al<sub>2</sub>O<sub>3</sub> coatings. In Figure 9, you can see the alumina particles used to reinforce the coating, they are the dark spots in the micrographs. The particles are uniformly distributed throughout the coating, backed by EDS analysis shown in Figure 23. In Table 4, you can see the overall starting thickness of the initial spray. Tables 5 and 6 are the corrosion/ amount loss of the two powdered coatings. These tables state that the thicker coatings have a higher corrosion rate than the other thicknesses. Upon further evaluation of the Al coatings, the thin and intermediate coating have roughly similar corrosion rates. Al-Al<sub>2</sub>O<sub>3</sub> shows a statically significant increase in roughness in the thin and intermediate coatings could be caused by the compaction of aluminum oxide as it is sprayed on the substrate. The thickness of Al was largely higher than Al-Al<sub>2</sub>O<sub>3</sub> because there was no alumina particle compaction when cold sprayed onto the Cu-Ni substrate.



Figure 9. Al micrographs of witness samples (a) thin, (b) intermediate, and (c) thick



Figure 10. Al-Al<sub>2</sub>O<sub>3</sub> micrographs of witness samples (a) thin, (b) intermediate, and (c) thick

As Sprayed	Al (µm)	Al2O3 (μm)
Thin	307.29 <u>+</u> 35.44	$102.25 \pm 10.75$
Intermediate	647.73 <u>+</u> 80.83	460.23 <u>+</u> 21.44
Thick	3012.93 <u>+</u> 117.74	3108.86 <u>+</u> 63.39

## Table 4. As sprayed coatings

#### Table 5.1000-hour corrosion

<b>1000 Hours</b>	Al (µm)	Al2O3(μm)
Thin	274.91 + 61.98	189.59 + 7.24
Intermediate	244.11 + 37.90	364.60 + 47.25
Thick	3706.51 + 1160.66	1728.02 + 122.19

Table 6.2000-hour corrosion

2000 Hours	Al(µm)	Al2O3(μm)
Thin	168.12 + 39.80	93.99 + 14.67
Intermediate	717.33 + 71.65	92.76 +32.77
Thick	2865.49 +14.33	2715.99 + 309.46

#### 3. Microstructure

Figures 11–16 show cross section micrographs of the as sprayed samples. Figure 11 is the thin coating, Figure 12 is the intermediate coating, and Figure 13 is the thick coating of sprayed Al powered. Figures 11b and 12a shows severe breaks within the cross section dictating the powered did not adhere is some places. Figure 13 thick coating adhered better than the intermediate and thin with little to no breaks within the cross section as the powder was cold sprayed onto the substrate. Figures 14 is the thin, Figure 15 is the intermediate, and Figure 16 is the thick coating of the alumina cold sprayed samples. In Figures 14 through 16 you can see the coatings were sprayed without imperfections and remained unbroken.



Figure 11. Al witness samples (a) low magnification, (b) high magnification



Figure 12. Al witness samples (a) low magnification, (b) high magnification



Figure 13. Al witness samples (a) low magnification, (b) high magnification



Figure 14. Al-Al<sub>2</sub>O<sub>3</sub> witness samples (a) low magnification, (b) high magnification



Figure 15. Al-Al<sub>2</sub>O<sub>3</sub> witness samples (a) low magnification, (b) high magnification



Figure 16. Al-Al<sub>2</sub>O<sub>3</sub> witness samples (a) low magnification, (b) high magnification

## **B.** CORROSION TESTING

Figures 17–22 illustrates the cross-sectional micrographs of the corroded samples tested for 1000 hours and 2000 hours. Figure 17 shows Al thin samples; a) you see pitting corrosion and d) you see localized corrosion at the interface. Figure 18 displays the alumina thin coatings which have been corroded away completely. In Figure 19, Al intermediate coatings have pits throughout and localized corrosion where breaks within the interface existed, the breaks were originally seen in the witness sample of sprayed aluminum coating. Figure 20 shows the alumina intermediate sample. In Figures 20a and 20b, coatings did not remain, but Figures 20c and 20d, shows some remanence of the coating remaining intact over the Cu-Ni substrate. Figure 20c for 2000 hours you can see a horizontal crack withing the coating. Figure 21, for the Al thick coating exposed for 1000-hour, the coating detached from the substrate. This is likely due to the presence of residual strain and galvanic corrosion and image c and d of that figure was the only sample through that set which remained intact throughout the all testing. Figure 22, Alumina thick coatings remained unbroken at the interface and in one piece, showing little to no corrosive behavior throughout the testing.



Figure 17. Al Optical micrographs of cross-sections of salt fog tested cold sprayed Al thin coatings, a) low magnification image of Al thin coating after 1000 h, b) high magnification image of Al thin coating after 1000 h, c) low magnification image of Al thin coating after 2000 h, d) high magnification image of Al thin coating after 2000 h



Figure 18. Al-Al<sub>2</sub>O<sub>3</sub> Optical micrographs of cross-sections of salt fog tested cold sprayed Al-Al<sub>2</sub>O<sub>3</sub> thin coatings, a) low magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thin coating after 1000 h, b) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thin coating after 1000 h, c) low magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thin coating after 2000 h, d) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thin coating after 2000 h



Figure 19. Al optical micrographs of cross-sections of salt fog tested cold sprayed Al intermediate coatings, a) low magnification image of Al intermediate coating after 1000 h, b) high magnification image of Al intermediate coating after 1000 h, c) low magnification image of Al intermediate coating after 2000 h, d) high magnification image of Al intermediate coating after 2000 h

2000 h



Al-Al<sub>2</sub>O<sub>3</sub> optical micrographs of cross-sections of salt fog tested cold sprayed Al-Al<sub>2</sub>O<sub>3</sub> intermediate coatings, a) low magnification image of Al-Al<sub>2</sub>O<sub>3</sub> intermediate coating after 1000 h, b) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> intermediate coating after 1000 h, c) low magnification image of Al-Al<sub>2</sub>O<sub>3</sub> intermediate coating after 2000 h, d) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> intermediate coating after 2000 h, d) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> intermediate coating after 2000 h, d) high



Figure 20. Al Optical micrographs of cross-sections of salt fog tested cold sprayed Al thick coatings, a) low magnification image of Al thick coating after 1000 h, b) high magnification image of Al thick coating after 1000 h, c) low magnification image of Al thick coating after 2000 h, d) high magnification image of Al thick coating after 2000 h



Figure 21. Al-Al<sub>2</sub>O<sub>3</sub> Optical micrographs of cross-sections of salt fog tested cold sprayed Al-Al<sub>2</sub>O<sub>3</sub> thick coatings, a) low magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thick coating after 1000 h, b) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thick coating after 1000 h, c) low magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thick coating after 2000 h, d) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thick coating after 2000 h, d) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thick coating after 2000 h, d) high magnification image of Al-Al<sub>2</sub>O<sub>3</sub> thick coating after 2000 h, d) high magnification image of Al-

An Energy Dispersive Spectroscopy (EDS) analysis was performed to determine the elemental composition of the cold sprayed coatings seen in Figure 23. This information confirms the existence of copper, nickel, oxygen, and aluminum within the sprayed coatings. Figures 27–30 confirm weekly testing and observation of corrosion growth, Figures 29 and 30 shows the most extreme case of the cold sprayed coating depleted and Cu-Ni sample corroding. Additional EDS analysis was done on one of the Al thin corroded samples for 2000-hours as seen in Figure 24. The recessed shadow regions are the exposed surface due to oxidization of the coating. The exposure is backed by Figures 24c and 24d detailing the Cu-Ni arrangement. Now, in Figure 25 shows the same sample but a different region and the dark shadowy shape correlates to remanence of the coating. Besides the outer region of the dark area is the Cu-Ni substrate itself, seen in Figures 25c and 25d. X-ray Diffraction was conducted on an Al 1000-hour sample displayed in Figure 26, the graph is showing the passivation layer of the sample. Qualitatively the Al peaks are larger compared to other peaks with Al-Al<sub>2</sub>O<sub>3</sub> present, one can state the Al coating sprayed onto Cu-Ni passivated. The Al layer did not corrode away fully, and after 1000-hours of exposure to a pristine marine environment some of the coating is eaten away, that forms copper passivating layer. The passivation layer of normal seawater is hampered in this study, Al passivation layer is Al-Al<sub>2</sub>O<sub>3</sub> and Cu passivation layer is CuCl<sub>2</sub>.



Figure 22. Electron Microscopy images and elemental mapping of sample



Figure 23. Electron Microscopy image of Al thin 1000-hour sample Area 1



Figure 24. Electron Microscopy image of Al thin 1000-hour sample Area 2



Figure 25. X-ray diffraction of Al cold sprayed phase analysis

Samples were removed weekly to measure changes in mass and thickness as shown in Figure 31. Weight changes are seen over time. This was due to loss of metal and a gain of corrosion products. All samples had a mass increase, the average of the coatings varied. For aluminum, the thin was 496 mg, 708 mg intermediate, and 999 mg for thick coatings. For alumina, the thin was 445 mg, 823 mg intermediate, and 1288 mg for thick coatings. The Al-Al<sub>2</sub>O<sub>3</sub> set of samples for 1000-hour testing remained intact with the coatings as a sacrificial anode for corrosion protection. However, the thick Al set of samples for 1000 began to delaminate from the substrate as early as week four. The same testing was conducted for a continuous 2000 hours, the samples mass gain trend for the remaining weeks are also shown in Figure 31.



Figure 26. Al corrosion samples (a) low magnification, (b) Al-Al<sub>2</sub>O<sub>3</sub> corrosion samples



Week 6

Figure 27. Al corrosion samples (a) low magnification, (b) Al-Al<sub>2</sub>O<sub>3</sub> corrosion samples



Figure 28. Al corrosion samples (a) low magnification, (b) Al-Al<sub>2</sub>O<sub>3</sub> corrosion samples



Figure 29. Al corrosion samples (a) low magnification, (b) Al-Al<sub>2</sub>O<sub>3</sub> corrosion samples



Figure 30. Changes in weight over exposure to austere marine environment (a) Al (b) Al- Al<sub>2</sub>O<sub>3</sub> sample

## **IV. CONCLUSION**

The objective of this study was to investigate the effects of aluminum oxide on the corrosion behavior of cold sprayed aluminum coatings. Cold sprayed coatings of aluminum and alumina reinforced aluminum of varying thickness on Cu-Ni substrates were examined in a simulated austere marine environment. This is intended to provide a scope for future analyses to take place in performing coating repairs of metallic components in applications across the Department of Defense. As the conclusion is not an obvious statement to which coating performed better. The data states in the mass gain charts, the Al-Al<sub>2</sub>O<sub>3</sub> had a negative weight loss, meaning that the coating was considerably deteriorated. While the Al data plateau in the last six weeks, meaning it is protective given that the weight doesn't increase with the oxide formation and corrosion has stopped. Cold sprayed Al onto Cu-Ni exhibited reduced adhesion to the interface allowing delamination of coatings. The Al coatings needs further investigation to determine the optimum spraying parameters to successfully adhere it to a Cu-Ni substrate. Systematic spraying the two powders were not beneficial in this study, the Al coatings require high temperature to enhanced adhesion strength.

Corrosion testing was conducted in a salt fog chamber for a continuous 1000 or 2000-hours to measure the corrosion behavior of the Al and Al-Al<sub>2</sub>O<sub>3</sub> deposits. Measurements were taken weekly, and on average the coatings had a steady increase in mass gain as well as thickness. Conversely, the cross-sectional micrographs showed localized corrosion and pitting throughout the Al coating even gaps within the interface rendering an unsuccessful application.

Cu-Ni is an important alloy used in various marine applications. Cold spray, as a coating and repair technique, could extend the lifetime of components made with Cu-Ni. Reinforcing the metal with Al or Al-Al<sub>2</sub>O<sub>3</sub> provided extended corrosion protection. Additionally, the Al-Al<sub>2</sub>O<sub>3</sub> coating was shown to be an effective composite coating with improved coating density and substrate adhesion. The Navy could use the alumina cold spray coating for long-term repair within the interior or exterior of ships, even inside valves and pumps with reduced maintenance requirements.

# V. RECOMMENDATIONS FOR FUTURE STUDY

- Based on the unexpected delamination of the cold spray coating from the substrate, further research should investigate the cause and if there is a correlation between the cold spray settings and material preparation that could have caused the separation.
- Investigation into the medium used for grit blasting material. There has been some research into coating layer protection of a polished surface as opposed to grit blast surfaces. Initial data shows polished surfaces perform better then grit blasted surfaces. More research should be studied on Cu-Ni and the different types of the alloy and its hardness.
- Generally, Cu-Ni alloys are good at resisting corrosion but when those alloys are exposed to polluted sea water the resistance decreases dramatically. Further research is needed to evaluate different cold spraying coating layers in actual marine environment.
- More research on optimizing cold spray coating onto Cu-Ni. In this research we
  are protecting a Cu-Ni substrate but there needs to be research on how to
  understand the alloy and its effectiveness in critical resistance on ships such as
  piping and tubing that are compromised with polluted sea water systems.

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# APPENDIX A. THICKNESS MEASUREMENTS FOR AL

Weeks	Mass (mg)	Thickness
Thin	$Avg \pm SD$	Avg + SD
1	457 <u>+</u> 131.10	.04 + .24
2	537 <u>+</u> 182.94	.54 <u>+</u> .15
3	615 <u>+</u> 188.12	.54 <u>+</u> .12
4	833 <u>+</u> 199.46	.56 <u>+</u> .09
5	660 <u>+</u> 234.95	.12 <u>+</u> 1.05
6	380 <u>+</u> 179.44	.68 <u>+</u> .20
7	<u>223 +</u> 50.33	.73 <u>+</u> .13
8	<u>263 +</u> 107.86	.68 <u>+</u> .06
9	<u>240 + 34.64</u>	.87 <u>+</u> .20
10	410 <u>+</u> 95.39	.81 <u>+</u> .26
11	620 <u>+</u> 235.16	.86 <u>+</u> .20
12	$163 \pm 60.28$	.61 <u>+</u> .07
Intermediate	$Avg \pm SD$	$Avg \pm SD$
1	<u>582+</u> 222.15	1.7 <u>+</u> .13
2	<u>672 + 209.51</u>	<u>299.7 + .09</u>
3	<u>2285 + 260.18</u>	.52 <u>+</u> 3.9
4	<u>958 + 323.95</u>	.66 <u>+</u> .19
5	<u>952 + 287.79</u>	.76 <u>+</u> .34
6	<u>872 + 506.42</u>	.76 <u>+</u> .52
7	<u>657 +</u> 470.78	.78 <u>+</u> .51
8	<u> 397 ± 125.83</u>	.65 <u>+</u> .62
9	<u>587 + 552.93</u>	.87 <u>+</u> .69
10	<u>603 ± 683.11</u>	.88 <u>+</u> .73
11	760 <u>+</u> 723.81	.94 <u>+</u> .74
12	<u>380 ± 585.06</u>	.85 <u>+</u> .69
Thick	$Avg \pm SD$	$Avg \pm SD$
1	727 <u>+</u> 101.32	.0 <u>+</u> .08
2	<u>827 + 141.49</u>	.16 <u>+</u> .07
3	<u>920 + 1465.93</u>	.016 <u>+</u> .10
4	<u>947 + 1483.62</u>	69 <u>+</u> .44
5	<u>952 + 1616.96</u>	63 <u>+</u> .30
6	<u>898 + 1632.20</u>	-1.31 <u>+</u> .15
7	<u>510 ± 117.90</u>	$-1.60 \pm 1.63$
8	<u>633 ± 170.98</u>	$-1.58 \pm 1.68$
9	$560 \pm 165.23$	$-1.53 \pm 1.65$
10	$667 \pm 106.93$	$-1.51 \pm 1.67$
11	<u>603 + 162.89</u>	-1.59 + 1.64
12	583 <u>+</u> 166.53	-1.47 <u>+</u> 1.7

# APPENDIX B. THICKNESS MEASUREMENTS FOR ALUMINA

Sample/Weeks	Mass (mg)	Thickness
Thin	Avg <u>+</u> SD	Avg <u>+</u> SD
1	325 <u>+</u> 120.95	.25 <u>+</u> .15
2	$380 \pm 136.08$	.49 <u>+</u> .13
3	$667 \pm 158.95$	.38 <u>+</u> .10
4	50 <u>+</u> 861.60	.07 <u>+</u> .03
5	495 <u>+</u> 173.29	.68 <u>+</u> .16
6	916 <u>+</u> 909.43	.51 <u>+</u> .13
7	$180 \pm 121.24$	.67 <u>+</u> .17
8	-97 <u>+</u> 80.83	.63 <u>+</u> .19
9	-250 <u>+</u> 95.39	.53 <u>+</u> .06
10	-280 <u>+</u> 134.54	.45 <u>+</u> .04
11	$-440 \pm 60$	.45 <u>+</u> .17
12	-550 <u>+</u> 36.06	.29 <u>+</u> .13
Intermediate	Av <u>g +</u> SD	Avg <u>+</u> SD
1	319 <u>+</u> 91.51	.20 <u>+</u> .16
2	127 <u>+</u> 385.21	.51 <u>+</u> .33
3	595 <u>+</u> 255.88	.41 <u>+</u> .29
4	492 <u>+</u> 314.94	.08 <u>+</u> .09
5	1036 <u>+</u> 378.25	.64 <u>+</u> .45
6	2809 <u>+</u> 2814.81	.55 <u>+</u> .56
7	1325 <u>+</u> 573.43	.57 <u>+</u> .18
8	798 <u>+</u> 501.61	.58 <u>+</u> .14
9	348 <u>+</u> 257.50	.52 <u>+</u> .24
10	185 <u>+</u> 431.83	.63 <u>+</u> .05
11	148 <u>+</u> 732.06	.63 <u>+</u> .18
12	-548 <u>+</u> 701.04	.47 <u>+</u> .12
Thick	$Avg \pm SD$	$Avg \pm SD$
1	400 <u>+</u> 305.29	14 <u>+</u> .28
2	513 <u>+</u> 412.29	07 <u>+</u> .24
3	973 <u>+</u> 529.14	07 <u>+</u> .26
4	1143 <u>+</u> 457.67	02 <u>+</u> .21
5	<u>1373 +</u> 532.83	.02 <u>+</u> .09
6	<u>2080 + 901.18</u>	.03 <u>+</u> .09
7	1093 <u>+</u> 597.86	.05 <u>+</u> .27
8	<u>226 +</u> 375.81	01 <u>+</u> .19
9	<u>90 +</u> 173.49	03 <u>+</u> .20
10	-170 <u>+</u> 253.16	10.16 <u>+</u> 17.40
11	-37 <u>+</u> 176.16	.10 <u>+</u> .20
12	$-627 \pm 292.63$	$0 \pm .35$

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