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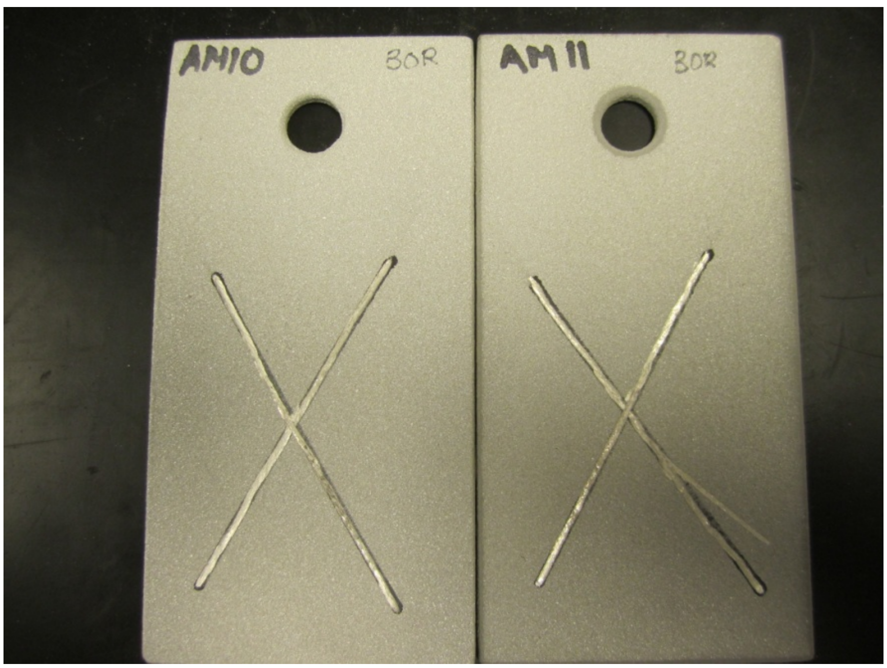
Technical Memorandum No. MERL-2012-14

Laboratory Evaluation of Metalized Coatings for Use on Reclamation Infrastructure



U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Denver, Colorado

May 2012

Mission Statements

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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BUREAU OF RECLAMATION
Technical Service Center, Denver, Colorado
Materials Engineering and Research Laboratory, 86-68180

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Laboratory Evaluation of Metalized Coatings for Use on Reclamation Infrastructure

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Acronyms and Abbreviations

AA	aluminum/aluminum oxide
Al	aluminum
AM	aluminum/magnesium
ASTM	American Society of Testing and Materials
AWS	American Welding Society
BOR	Bureau of Reclamation
cm	centimeter(s)
DFT	dry film thickness
DIFT	deionized immersion flow test
DHS	dilute Harrison solution
DI	deionized
EIS	Electro-impedance spectroscopy
lb/hr	pounds per hour
Mg	magnesium
mg	milligram(s)
mm	millimeter(s)
MMC	metal matrix composite
MWD	Metropolitan Water District
OCP	open circuit potential
psi	pounds per square inch
psia	pounds per square inch absolute (pressure)
QUV	accelerated weathering test
Reclamation	Bureau of Reclamation
SCE	saturated calomel electrode
scfh	Standard cubic feet per hour (flow rate)
SSPC	Steel Structures Painting Council
TSC	thermal spray coatings
USACE	U.S. Army Corps of Engineers
UV	ultraviolet
V	volt(s)
VOC	volatile organic compound
Zn	zinc

EXECUTIVE SUMMARY

Metalized/thermal spray coatings (TSCs) were investigated by the Bureau of Reclamation's (Reclamation) Materials Engineering and Research Laboratory. The goal of this study was to evaluate the feasibility of using TSCs for corrosion protection on Reclamation equipment. The focus of this study was on thermal spray materials that are anodic (corrode preferentially) to steel. This study includes a literature review of metalizing by others as well as laboratory test programs that evaluated five thermal spray alloys and two sealer systems.

The best use of metallizing at Reclamation is on radial gates, partially exposed trash racks and other equipment subjected to a fluctuating immersion environment. Although metallizing has an initial cost premium of 30-40% over a comparable polymer coating system, it has the potential to be less expensive from a life cycle standpoint. Other applications where metallizing should be considered include severe atmospheric service environments such as bridges and above ground piping.

The lab tests were intended as accelerated weathering tests and included the following: Prohesion, BOR and Immersion. The Prohesion test consisted of alternating salt spray and ultraviolet (UV) light exposure. The BOR test consisted of alternating salt spray, UV light exposure, and immersion testing in a corrosive mixture known as a "Dilute Harrison Solution" (DHS). Immersion testing took place in either DHS, deionized (DI) water solution, or a high-velocity DI solution (DIFT). Following testing, each system was evaluated for coating performance.

Testing revealed that alloy composition and exposure condition significantly affect corrosion protection performance. Of the systems tested, the pure aluminum system is believed to offer the best combination of corrosion protection and expected service life in immersion or fluctuating immersion. The system works well as long as the water has a pH between 4.0 and 8.5. In addition, aluminum is easy to apply, relatively low in cost, and exhibited greater adhesion strengths compared to the other alloy systems.

The zinc system provided the highest level of corrosion protection performance, but experienced rapid deterioration during immersion testing in DHS. Use of zinc metallizing should therefore be avoided when frequent or prolonged immersion in corrosive environments is expected.

The 85/15 Zinc-Aluminum system offered good corrosion protection as well as a more stable oxide that was not easily damaged or removed. However, the system experienced blistering during prolonged immersion in both DHS and DI water solutions and is therefore not recommended.

90% aluminum+10% aluminum oxide (AA) and 95% aluminum+5% magnesium (AM) systems are variations of the pure aluminum TSC that are intended to provide increased abrasion resistance and increased galvanic protection. Neither of these systems is recommended. The AA system experienced more extensive oxide formation than other systems, and both AM panels blistered in the BOR test. In addition, locating feedstock for both of these systems was difficult. The AA system was not readily available in wire form, so a powder was mixed and applied using a combustion system.

The use of a polymer seal coat over the TSC system appeared to offer little in terms of increased corrosion protection unless the material was applied in greater thickness, in which case it is considered to be more of a topcoat.

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INTRODUCTION

Metalizing is a technology used to provide corrosion protection to steel and concrete engineering structures. It offers several advantages over conventional coating technology.

Advantages include:

- No cure time. The structure can be placed in service immediately following the conclusion of the application.
- No production of volatile organic compounds (VOCs).
- Good impact resistance (compared with epoxy).
- Good ultraviolet (UV) light resistance (compare with epoxy).
- No temperature restrictions for application.
- No humidity restrictions for application.
- Potential for long service life with less downtime for coating maintenance.

Disadvantages include:

- Not compatible with impressed current cathodic protection systems found on many structures such as buried pipe.
- Higher initial cost (30–40 percent).
- Metallizing heats the substrate which may be unacceptable in certain situations. The surface temperature will be dependent on the process and parameters used.
- Fast-flowing water can, as some studies have shown, decrease coating life (Bureau of Reclamation [Reclamation], 1966).
- Service life in immersion can vary significantly depending on water chemistry and coating material.

Metalizing is not a new technology. It has been in use since the 1930s. Although it has seen limited use in comparison with conventional coatings, this is primarily due to economics. In past years, application rates for metalized coatings have been slow, making the process an expensive alternative to conventional coatings.

However, the technology has fostered advances in equipment that result in faster production times due to greater reliability and greater material deposition rates. The average spray rate has increased from 7.5 pounds per hour (lb/hr) to 35 lb/hr for aluminum (Rogers, 1997).

In the polymeric coatings industry, local, State, and Federal regulations are driving changes in the coatings industry by reducing the VOC limits in many States. Facility owners are searching for alternatives to coating systems such as vinyl resins, which were once commonplace in applications that required corrosion protection in fluctuating immersion. Furthermore, coatings are becoming more expensive to purchase and apply. Old coatings systems, such as lead-based paints, were surface tolerant. Modern coating systems have more stringent surface preparation requirements that frequently require a near white metal blast. Plural component systems may require expensive plural component equipment. Not only are these newer coatings systems more expensive to apply, but there is greater chance of applicator error and, hence, premature failure. Many of the newer systems have expected service lives that are much shorter than the coating systems historically used. For example, coal tar enamel, lead-based paint, and vinyl systems have been known to last in excess of 50 years. In contrast, an epoxy system typically has an expected service life of 15–20 years. All of these factors mean metalizing is becoming a more attractive option for corrosion protection.

The report provides a general introduction to the metalizing process, including literature regarding various aspects such as process parameters, surface preparation, and materials selection. Examples of metalizing use in industry, as well as laboratory and field studies on metalized coating service life are also presented. These studies are discussed within the context of the current research project; results and discussion from the current laboratory study are presented. Finally, the report provides a summary of the findings and recommendations for incorporating metalizing into the construction and maintenance of Reclamation facilities.

SUMMARY AND CONCLUSIONS

Five thermal spray alloys and two sealers were investigated using laboratory test methods that included immersion, accelerated weathering, adhesion, and electro-impedance spectroscopy. All the coating systems tested appear to offer some degree of corrosion protection to the steel substrate; the un-scribed and undamaged areas of all of the plates remained corrosion free throughout the test. However, there were problems noted with some systems, such as blistering, application difficulties, and excessive weight loss during testing. The following conclusions from this study are offered:

- Metalized coatings provide a significant life-cycle cost advantage over polymer coatings on equipment subject to fluctuating immersion such as radial gates, stoplogs, and partially exposed trashracks. Conventional polymer coatings have a shorter service life in fluctuating immersion environments. Metalized coatings are superior to polymer coatings when rapid return to service is needed, during cold weather applications or where VOC emissions are restricted. Note that metallizing is not compatible with impressed-current cathodic protection systems.

- The service life of all metalized coating systems will depend heavily on the factors related to the service environment, such as immersion duration and frequency, as well as water chemistry. Avoid using zinc or aluminum in immersion environments with extreme pH (below 6 or above12) values. The use of zinc should also be avoided in flowing water.

- Of the systems tested, the pure aluminum system is believed to offer the best combination of corrosion protection and expected service life in immersion or fluctuating immersion. In addition, aluminum is easy to apply, relatively low in cost, and exhibited greater adhesion strengths compared to the other alloy systems.

- Zinc provides better galvanic protection than aluminum, but is expected to exhibit the shortest service life in corrosive environments (especially environments with high flow rates) due to the high consumption rate of oxide reactants.

- Aluminum systems appear to offer good general corrosion protection to steel but reduced cathodic protection to areas where the coating is damaged especially in water with low levels of conductivity i.e. reservoirs fed by snowmelt .

- Further research and evaluation is needed to accurately determine an expected service life, determine ease to repair defects, and determine a method to deal with crevice corrosion. Another research area would be to investigate a molten aluminum dipping process, similar to galvanizing, to investigate the corrosion protection.

- 85/15 Zn/Al and 95/5 Al/Mg systems are not recommended for use on equipment where immersion is likely. Unsealed panels of Zn/Al experienced blistering in tests that involved immersion. Al/Mg samples blistered in the BOR test which involves immersion cycling.

- Specialized application equipment and expertise is required when applying the Zn/Al system. During application, the Zn/Al system exhibited the tendency to produce an unstable arc. This is believed to be due to oxidation of the wire surfaces.

- Zn/Al appears to produce an oxide that is more stable than that of pure zinc. The samples lost no weight during testing, and visible corrosion was less than what was observed in the other unsealed panels. These results warrant investigation into a modified Zn/Al alloy that produces a stable oxide without blistering in immersion.

- The AA samples produced significant amounts of oxidation reactants that tended to be dispersed randomly on the plate rather than uniformly.

- Both sealants offer increased corrosion protection when applied with sufficient DFT. However, both sealants are susceptible to degradation from UV light. In addition, the use of a sealer removes some of the advantages associated with TSC such as immediate return to service, fast application, and less restrictions on environmental conditions.

BACKGROUND AND EXISTING LITERATURE

Metalizing is fairly well understood, and there are several resources that provide detailed information for the facility owner which specify information such as surface preparation, materials selection, application parameters, and health and safety. The following information comes from several sources, including the U.S. Army Corps of Engineers (USACE) report: Thermal Spraying: New Construction and Maintenance (1999).

Surface Preparation

There is a general agreement that metalizing requires a very clean surface prior to application. This surface should be specified as a SSPC-SP5 white metal blast (Cunningham, 1996). Typically, steel grit or aluminum oxide is the abrasive that is used. The minimum surface profile is 2 mils (Rogers, 1997). Cunningham (1996) recommends using a 3 mil profile.

Thermal Spray Materials for Corrosion Protection of Steel

The most common materials used are aluminum, zinc, 85/15 Zn/Al, and 90/10 aluminum/aluminum oxide metal matrix composite (MMC). These materials are typically found in wire or powder form. The 90/10 Al MMC is only available in powder form. Zinc is more active on the galvanic series and therefore offers greater cathodic protection than aluminum in freshwater. Aluminum with aluminum oxide offers increased resistance to abrasive wear. Sometimes magnesium is added to aluminum (Sampson, 1997). New alloys are continuously being investigated.

Application Methods

Thermal spray is accomplished using either flame spray or electric arc. Arc spray has typically produced a higher deposition rate than flame spray. The nozzle is typically held between 6 and 12 inches from the substrate and moved at a velocity of 1.75 feet per second. The spray band is between 0.5 – 1 inch wide. There is an optimal thickness for maximum service life for aluminum (3–6 mils), with excessive thickness resulting in blistering (American Welding Society [AWS], 1974). Arc spray has higher adhesion (up to 7,000 pounds per square inch [psi]) versus flame spray (up to 4,000 psi). American Society of Testing and Materials

(ASTM) C633 is the test that is typically used to measure adhesion. Adhesion values will vary depending on the test method used. Arc spray has less porosity and greater density, which is due in part to the kinetic energy imparted to each individual particle. Greater impingement particle velocities will result in a coating that has greater density and less porosity.

Coating density and porosity are important factors in corrosion protection. If the coating is too porous and has inadequate thickness, it will offer little barrier protection and will function mainly as a sacrificial anode. Hence, coating life will be significantly reduced. Porosity will typically vary from 3 to 18 percent depending on the application process and parameters used (Cunningham, 1996). For example, increasing the standoff distance will increase porosity. A less porous coating is desirable. Other factors that may play a role in coating morphology include spray angle, travel speed, substrate temperature, etc. Porosity is best measured by metallographic examination of a representative cross section. Alternatively, a dye can be applied to the coated surface to identify any exposed substrate.

The USACE also studied the effects of application parameters on coating quality (A.D. Beitelman, et al., 2001). The alloys investigated included 85/15 Zn/Al, Al, Zn, 90/10 Al/AlO_2 as well as an 85/15 Zn/Al pseudoalloy in which zinc and aluminum wires are fed simultaneously to produce the alloy. The variables included surface profile depth, surface profile shape (round versus angular), standoff distance, spray angle, current, and air pressure. The USACE found that adhesion values are not necessarily a good indication of physical performance expected from a coating. They state that there is a need for a field inspection technique that can accurately determine porosity and oxide content. This sentiment is echoed by other researchers who state that nondestructive evaluation methods for thermal spray are lacking. Currently, the best way to characterize thermal spray coatings (TSCs) is destructively by using metallography. The metallographic method involves removing a section of material and mounting a cross section in a plastic mould. The sample is then polished and etched for microscopic evaluation. Examination under a microscope reveals a lamellar structure that is created by the deformation of individual droplets. Voids are periodically created between droplets where there is no material. These voids are readily visible during microscopic examination.

Others have performed similar studies (Varacalle, et al., 1998) and have investigated the effects of process parameters such as standoff distance, current, pressure, and nozzle type on 85/15 Zn/Al and 70/30 Zn/Al. The panels were evaluated for corrosion resistance using a salt spray procedure for 1,000 hours. Porosity and oxide analysis were also conducted. The two alloys were found to behave in a similar fashion.

Metalized Coating Testing

The goal of the current project was to examine the service life of metalized coatings. This section attempts to provide some context for this project within the existing literature.

Perhaps the most referenced study involving thermal spray corrosion protection of steel is the AWS 19-year report. The report details the findings of field tests conducted using metalized panels under a variety of exposure conditions over an exposure period of 19 years. The panels tested were flame-sprayed zinc and flame-sprayed aluminum applied at a variety of thicknesses ranging from 3 to 15 mils. Several surface preparation techniques were also tested. The substrates were tested with and without a seal coat. The seal coats tested are no longer available, but the nonsealed results are useful. The exposure conditions included immersion in stagnant ocean water, immersion in flowing saltwater, severe marine atmosphere, mild marine atmosphere, and industrial atmosphere. The study concluded that aluminum metalized panels with a coating thickness of 3 to 6 mils were protected without a seal coat in immersion conditions for the 19-year duration of the study. Unsealed zinc-sprayed panels required at least 12 mils to achieve complete protection for the entire test duration. The study also concluded that thicker coatings of aluminum were more likely to develop pitting. Since the coatings were applied in the 1950s, application equipment has undergone changes. Electric arc spray is now a commonplace method used in applying TSCs, which can result in a denser, less porous coating that is more corrosion resistant.

Other similar long-term field studies have been conducted as well. ASTM published a report detailing the results of a 34-year test of metalized panels in the marine atmosphere environment and determined that the coating offered adequate protection (Kain, et al., 1987).

The results of these studies have been considered when developing standards for metalizing that are still in use today. For example, the Canadian Standards Association and British Standards Association specify the expected service life of TSCs under various service environments (CSA, 1966), (British Standards Institution, 1977). However, caution must be used when applying the results to the freshwater environment. A 1966 study conducted by Reclamation noted rust after just 6 months in flowing freshwater (Reclamation, 1966). The coating ultimately failed after 3 years in service. This result contrasts sharply with the conclusions of the AWS report, which conducted their tests in flowing seawater. Table 1 summarizes several additional field and laboratory studies which have been performed over the years.

Metalizing Case Studies and Examples

Although metalizing is far less common than polymeric coatings, it has a documented track record of use in multiple exposure conditions.

Atmospheric Exposure

Many entities use metalizing on bridge structures such as the New York Throughway and other transportation agencies. Metalizing is also popular in Europe on bridge structures. In addition, metalizing has been used in lieu of galvanizing on radio towers. While these applications show that metalizing can be competitive from a life-cycle cost standpoint, the exposure conditions are not directly relevant to Reclamation's needs. Reclamation is looking for a coating to provide corrosion protection in the freshwater immersion and fluctuating freshwater immersion environment.

Table 1.—Summary of selected studies on TSCs

Reference	TSCs tested	Application parameters	Sealers tested	Test conditions and duration	Results
(AWS, 1974)	Flame-sprayed aluminum and zinc	Various thicknesses Various surface preparation methods	Wash primer Aluminum vinyl Clear vinyl Chlorinated rubber	Field test of samples for 19 years: Industrial atmosphere Salt air Severe marine Seawater	Aluminum protected for 19 years with and without a seal coat for thicknesses of 0.003 to 0.006 mil.
(Varacalle, et al., 1998)	Twin-wire electric spray 85/15 Zn/Al 70/30 Zn/Al	Various standoff distance, nozzles, pressure, current	None	Lab test: Salt spray for 1,000 hours	The two alloys provided similar corrosion resistance. Corrosion resistance increased with porosity. *This observation conflicts with other studies.
(Fischer, Thomason, Rosbrook, and Murali, 1994)	Aluminum with sealer	Unknown	Silicone	8 years immersion/ splash zone in seawater	After 8 years, the coatings were in good condition.
(Greene, Long, Badinter, and Kambala, 1995)	Unknown	Unknown		Case histories of pile corrosion	Localized corrosion can result from oxygen concentration.

Table 1.—Summary of selected studies on TSCs

Reference	TSCs tested	Application parameters	Sealers tested	Test conditions and duration	Results
(Kuroda and Takemoto, 2000)	Zinc, aluminum, and zinc/aluminum (Arc spray and flame spray)	Varying thicknesses	Yes	Seawater immersion	All of the coatings were in good condition after 5 years. Zinc coatings with and without seals were experiencing degradation in immersion after 7 years. Aluminum and Zn/Al held up well after 7 years.
(Kain and Baker, 1987)	Al, Zn/Al	Unknown	Unknown	Field test: 34 years in marine atmospheric exposure	Aluminum worked for 34 years.
(Brenna, Hays, and Masson, 1995)	Aluminum flame spray	Unknown	None	Field test: Marine atmosphere – 5 years	Good performance was observed.

Table 1.—Summary of selected studies on TSCs

Reference	TSCs tested	Application parameters	Sealers tested	Test conditions and duration	Results
(Brenna, Hays, and Masson, 1995)	Aluminum and Zinc Arc and flame spray	Unknown	Epoxy topcoat on some panels	1-year lab test: Immersion (unspecified water) Splash spray Severe marine atmosphere	Both zinc and aluminum provided superior protection compared with painting alone. Unsealed aluminum and zinc panels had high corrosion rates. No difference between flame spray and electric arc. Aluminum was observed to provide barrier protection, while zinc corroded by dissolution.
(Irving, 1993)	Aluminum		N/A	Bridges – Marine atmosphere	Zinc is being successfully applied to concrete bridges to cathodically protect the rebar.
(Race, Hock, and Beitelman, 1989)	Aluminum-bronze (Arc spray) Stainless steel (Arc spray) Zinc-aluminum (Flame spray) Zinc (Flame spray)	No attempt was made to vary the process parameters; average coating intended thickness was 10—15 mils	SSPC paint 27 for Zn and Zn/Al For aluminum/bronze and stainless steel: 3 coats vinyl Epoxy 1 coat vinyl	Field test: Freshwater immersion on gates in the Ohio River for 9 months (Zn, Zn/Al) and 20 months (stainless, aluminum/bronze)	Defects were observed in the aluminum/bronze and stainless steel after just 9 months. Zinc and Zn/Al provided protection to the structure.

Table 1.—Summary of selected studies on TSCs

Reference	TSCs tested	Application parameters	Sealers tested	Test conditions and duration	Results
(Lieberman, Clayton, and Herman, 1984)	Zinc, aluminum, 15/85 (Zn/Al), and duplex layered zinc-aluminum. Flame sprayed and electric arc sprayed	No attempt was made to vary the process parameters	None	Lab test: Immersion in 3% NaCl Immersion in natural seawater	Arc-sprayed coatings yield less porous and more dense coatings than flame spray.
(Shaw, Leimkuhler, and Moran, 1986)	Aluminum , Zinc, 85/15 Zn/Al, 15% Zn/Al prealloyed wire, 15% Zn/Al pseudoalloyed wire	Materials applied with Department of Defense standard 2138	None	1-year field test: Marine atmosphere Seawater spray Seawater immersion 40% of panels were scribed through the coating	Aluminum oxide provides a good barrier protection. Blistering on duplex.
(Race, 1992)	Aluminum and zinc		Various	Lab test: 2 years Freshwater (tap) immersion Seawater immersion	Seawater was the more aggressive environment, causing more damage to the samples. Several systems were found to be acceptable for freshwater use, while no acceptable sealer systems were found for seawater.

Immersion/Fluctuating Freshwater Immersion

Reclamation has limited experience using metalizing (primarily zinc with various topcoats) on hydraulic infrastructure, including:

- *Blue Mesa* (Gunnison, Colorado): In 1988, 8 mils of zinc were applied to radial gates via the electric arc method. Two coats of epoxy were applied over the metalized surface as a topcoat. The upstream side of the gates is typically in immersion for 9 months per year (Johnson, 2000).

- *Glen Canyon* (Paige, Arizona): In 1991, 8 mils of thermal-sprayed zinc was applied to the upstream side of the radial spillway gates. The zinc was topcoated with a high-build epoxy urethane mastic. Exposure conditions on the upstream gate surface vary due to fluctuating water levels, with some portion of the surface typically in immersion. Since then other equipment, including the stairs and internal structures, have been metalized with 3–5 mils of pure zinc (Johnson, 2000).

- *McClusky Canal* (near Wilton, North Dakota): In 1991, 8 mils of pure zinc was flame sprayed and sealed with a primer (MIL-P-15328d) and topcoated (aluminum vinyl) on two radial gates (Johnson, 2000).

Reclamation's experience has been mixed. Each of the systems was inspected in the spring of 1999 after 8 to 11 years of service, and the performance varied, with poor results at Glen Canyon Dam and good performance elsewhere. The radial gates at Glen Canyon Dam exhibited blisters on the upstream side. Johnson attributes the variation to potential compatibility issues that exist between the metalized zinc and the topcoat and states the need for further investigation in this area.

USACE and others, such as the Salt River Project, have used metalizing on hydraulic equipment in the fluctuating immersion environment with good results:

- *Belleville Lock and Dam* (Parkersburg, West Virginia), 1986–1987: Test site for USACE. Materials sprayed included aluminum-bronze, stainless steel, zinc-aluminum, and pure zinc. Aluminum-bronze and stainless steel showed signs of failure after 9 months of exposure, and zinc and zinc-aluminum successfully protected the structure (Race, et al., 1989). A subsequent report revealed cohesive failures in 85/15 coatings after 8 years of service (USACE, 1999).

- *Racine Lock and Dam* (West Virginia): Tainter gates were metalized with 3–5 mils of 85/15 Zn/Al in 1993.

- *Morris Shepard Dam* (90 miles west of Dallas, Texas): Gates were slated to be metalized as of 2006.

- *St. Andrews Lock and Dam* (Lockport, Manitoba, Canada): Dam was metalized in cold weather conditions.

- *Mormon Flat Dam* (Phoenix, Arizona): Gates were metalized in 1970 with zinc at 7–10 mils. Gates are in continuous immersion with a water line that fluctuates daily. After 22 years of exposure, there is no evidence of any significant consumption of the zinc coating (Brodar, 1995).

Metropolitan Water District (MWD) in southern California has successfully deployed zinc metalizing (no seal) on radial gates under fluctuating freshwater immersion. Southern California is subject to severe restrictions on the use of VOCs. For MWD, metalizing offers an attractive zero VOC coating that is durable, resistant to UV light, and allows for a fast return to service.

Seawater Immersion

In addition to freshwater use, TSCs are used extensively in the marine industry and various navies to protect ship structures and machinery from corrosion (Brenna, et al., 1995). The life of a zinc or aluminum coating in seawater is likely to be different than in freshwater immersion.

Factors Affecting Service Life of Metalized Coatings in Immersion

The service life of a metalized coating will vary depending on multiple factors, including:

- Alloy used. Common alloys include aluminum, zinc, 85/15 Zn/Al, and 90/10 Al/Al_2O_3, and, on occasion, 95/5 Al/Mg.

- Water chemistry (Rahrig, 2003).

    - pH

        - Aluminum has an optimal pH range from 4 to 8.5 (varies from source to source up to 11). This is a range in which a passive aluminum oxide film is most stable.

        - Zinc has an optimal pH range from 6 to 12. This is the range where a passive zinc oxide film is most stable.

    - Presence of dissolved minerals (hard water). Soft water is more aggressive to zinc than hard water. This is due to the fact that in hard water, carbonates can be deposited on the surface which can slow the corrosion process.

    - Dissolved oxygen increases corrosion.

    - Salinity: The presence of chlorides in excess of 50 milligrams per liter accelerates corrosion in zinc.

- Temperature: Corrosion rates are increased with temperature.

- Exposure to mechanical damage: Erosion, abrasion.

    - Zinc, aluminum, and their alloys will form a protective metallic oxide film that inhibits corrosion.

    - Erosive forces can destroy or inhibit the formation of this protective film, causing corrosion to accelerate:

        - Erosion will be accelerated in rapidly flowing or turbulent water

        - Erosion will be accelerated in water carrying abrasive media (i.e., hard particulates).

    - Abrasion damage may be accelerated by floating debris or ice.

    - Susceptibility to mechanical damage will depend on the type of coating.

- Coating condition:

    - Porosity: A more dense coating will create a superior corrosion barrier.

    - Coating thickness: Increasing thickness increases the level of protection. However, too much thickness can sometimes result in cracking and reduced protection. This was one of the findings of the AWS 19-year report.

    - The presence of a seal coat is reported to protect the TSC and extend the life of the structure.

There are mixed results for field tests of metalized equipment. For example, the metalized radial gate coatings at Blue Mesa and Mormon Flats Dams have performed well, while the Glen Canyon Dam coating system showed blisters after 8 years. This may have been due to compatibility issues between the zinc and the topcoat. The Steel Structures Painting Council (SSPC) predicts a service life of 23–35 years for tainter gates using a 85/15 Zn/Al system (Sulit, 2002). At a Shasta Dam test program to evaluate coatings in penstocks, metalized coatings showed early signs of failure, whereas SSPC estimates a service life of 30–40 years in penstocks using a 85/15 Zn/Al system (Sulit, 2002). Metalizing has the potential to reduce life-cycle costs, but additional research was needed to ensure the best system is used.

METHODOLOGY

For the current study, 3 by 6-inch mild steel panels were selected as the substrates to be coated. Five thermal spray systems were selected for evaluation in this study:

- 100% Zn
- 100% Al
- 85/15 Zn/Al
- 95/5 Al/Mg
- 90/10 Al/Al_2O_3

Aluminum, zinc, and 85/15 (Zn/Al) are common alloys used for thermal spray, and wires were obtained easily. The desired Al/Mg alloy was eventually located in wire form, and the aluminum/aluminum oxide alloy was created manually by combining powders to achieve the proper ratio. Table 2 summarizes the materials used and their respective procurement costs.

Table 2.—Materials tested

Alloy	Designation	Form	Unit cost (per pound)
Aluminum	A	1/16” diameter wire spools	$4.54
Zinc	Z	2-mm diameter wire spools	$3.70
85/15 Zn/Al	ZA	2-mm diameter wire spools	$5.84
95/5 Al/Mg	AM	1/16” diameter wire spools	$7.18
90/10 Al/Al_2O_3	AA	Aluminum powder + Al_2O_3 powder	$10.00

Reclamation's laboratory does not currently have thermal spray capabilities; therefore, the surface preparation and application was originally contracted out to Nevada Thermal Spray, Inc. Prior to thermal spray application, the panels were first solvent cleaned and then blasted to obtain a 4–5 mil profile. Nevada Thermal Spray experienced difficulties in applying the 85/15 wire with their equipment. Consequently, Midwest Thermal Spray was contracted to apply that system. Twin-wire electric arc systems were utilized for all wire systems. The Al/A_2O_3 system required the use of a powder-fed combustion unit. Table 3 summarizes the parameters used in the application of each system.

Table 3.—Thermal spray application methods and parameters

	Zn	Al	Zn/Al	Al/Al2O3	Al/Mg
Process and equipment used	Twin-wire electric arc (Praxair Tafa 9000)	Twin-wire electric arc (Praxair Tafa 9000)	Twin-wire electric arc (Thermion)	Combustion (Metco 6P)	Twin-wire electric arc (BP400)
Primary pressure	60 psia[1]	60 psia	70 psi	N/A	60
Secondary pressure	30 psia	30 psia	N/A	N/A	N/A
Spray distance	6”	4–6”	6”	6”	4-6”
Current	200 ampere	200 ampere	100 ampere	N/A (34 scfh fuel, 34 scfh oxygen used)[2]	165 ampere
Feed rate	40 lb/hr	12 lb/hr	N/A	6 lb/hr	N/A
Console voltage	21 volts	30 volts	32 volts	N/A	29 volts
Spray angle	90 degrees	90 degrees	N/A	90 degrees	90 degrees
Travel speed	N/A (Manual)	N/A (Manual)	N/A	N/A (Manual)	N/A (Manual)
Passes	4	8	N/A	8	8
Layers	4	5	N/A	3	3
Target thickness	10 mils	10 mils	10 mils	10 mils	10 mils

[1] Pounds per square inch absolute (pressure).
[2] Scfh = Standard cubic feet per hour (flow rate)

Sealers

Two sealer systems were chosen to test: PPG Amercoat 240 and Sultzer-Metco Metcoseal URS. Amercoat 240 is a two-part epoxy system that is commonly used for corrosion protection on Reclamation structures in immersion service. In order to use the product as a sealer, the viscosity was reduced with a thinner. The target viscosity was 35 +/- 5 seconds with a #4 Ford Cup viscometer.

The URS system is marketed as an all-purpose, low-VOC sealer for corrosion protection. It is a single-component, moisture-cure urethane system.

The sealers were brush applied to both sides of each test panel. During application, it was noted that small bubbles were forming on the Metco-sealed panels after the sealer was applied. This is thought to be caused by gas bubbles escaping from the porous structure of the metalized coating. However, no issues of out-gassing were encountered with the Amercoat 240.

The purpose of the sealer is to penetrate down into the pores of the TSC to reduce porosity and prevent the electrolyte from reaching the substrate. It is not necessary to build up a thick coat; the target dry film thickness (DFT) of each system was in the range of 1–2 mils. The aluminum, zinc, and 85/15 coated systems ended up a bit thicker at approximately 3–4 mils for both sealers. The difference was noticeable in that the surface texture of the metalized coat is still slightly visible with the thinner coats. The thicker seal coats resulted in a smoother surface, which completely covered the asperities of underlying TSC.

Test Program

The current study involved testing several state-of-the-art metalized coating systems with and without sealers. Scribed and unscribed panels were immersion-tested in a dilute Harrison solution (DHS) and deionized (DI) water solution. A group of samples were rotated between the accelerated weathering test (QUV) and salt fog test chambers. This test is referred to as the Prohesion program. A second group known as the BOR group was rotated between QUV, salt fog, and immersion testing as follows: QUV-FOG-IMMERSION-FOG. Both groups were rotated at 1-week intervals. The test matrix is presented in Table 4.

Metalized coating is unlikely to be affected by UV light; however, the seal coat could be susceptible to degradation. The results from this test provide a direct comparison to the corrosion performance of traditional coatings tested by Reclamation. The most similar study is the one conducted by the USACE in 1992, which performed laboratory testing on seal zinc and aluminum metalized panels in freshwater and saltwater immersion. The current study includes additional exposure conditions, additional thermal spray alloys, and modern sealing systems.

Table 4.—Test matrix

Group	Panels	QUV	Salt fog	Immersion (dilute Harrison)	Immersion (deionized water)
DI	1 scribed 1 unscribed				X
DHS	1 scribed 1 unscribed			X	
PRO	2 scribed	X	X		
BOR	2 scribed	X	X	X	
DIFT	2 scribed				X (Flowing)
Adhesion	1 unscribed				

Testing

The panels were each tested for approximately 5 months (5,040 hours) starting in March or April 2011 and concluding in October or November 2011. On May 31, 2011, each scribed panel was re-scribed in order to ensure bare metal exposure.

The test was interrupted periodically to examine and weigh the immersion samples. The samples in Harrison immersion, deionized immersion, and high-flow immersion were each inspected, dried, and weighed periodically during the test. The BOR and Prohesion samples were cycled and inspected on a weekly basis but not weighed. Prohesion samples were rotated between a salt spray cabinet and a UV light weathering cabinet. For the BOR samples, immersion in the Harrison solution was included every 4^{th} week (QUV, FOG, IMMERSION, FOG, repeat).

The Harrison immersion samples were also tested with electro-impedance spectroscopy periodically to assess the rate of water uptake. During the testing, several of the panels developed corrosion nodules on the surface, which prevented the gasket from forming a complete seal and thereby prevented further testing.

Electro-Impedance Spectroscopy

Electro-impedance spectroscopy (EIS) was utilized to evaluate the coating performance periodically throughout the test for DHS samples. One sample from each sealed metalized coating set was placed in an immersion tank filled with dilute Harrison's solution (DHS—0.35 wt% $(NH_4)_2SO_4$ and 0.05 wt% NaCl).

The samples were removed periodically to perform EIS measurements. A rubber *O*-ring and a 4-centimeter-diameter cylindrical glass cell were clamped to the sample to create an immersion surface area of 12.6 cubic centimeters. DHS is added to the glass cell along with a saturated calomel electrode (SCE) and platinum mesh to serve as the reference and counter electrodes, respectively. The working electrode is connected to the sample's steel substrate. The tests were performed within a Faraday cage to minimize electromagnetic interference. Figure 1 illustrates the experimental setup for EIS.

Figure 1.—Experimental setup for EIS.

EIS measurements are performed using a 15 mV perturbation around the sample's free corrosion potential, also known as the open circuit potential (OCP). The frequency range is 10^5 to 10^{-2} hertz at a rate of 10 points per decade. The measured surface area is constant for all tests and samples; therefore, impedance values are not corrected for area. The OCP was recorded for 100 seconds prior to the start of the EIS measurement. These data are also included within this report. Details on EIS theory are included in appendix B.

RESULTS

The samples were dried, weighed, and photographed at the conclusion of the test program. Before and after photo documentation is included in appendix A for each sample. Tables 5, 6, and 7 provide a summary of the observations following testing.

Table 5.—Observations after testing unsealed samples

Panel	Test	Observation
Zinc	DI	Light, uniform oxide layer, light rust on scribe.
	DHS	Slightly heavier oxide layer, variable thickness.
	DIFT	Rust on sample, rust in scribe.
	PRO	Very heavy zinc oxide layer all over and in scribe, small blister on scribe.
	BOR	Slightly less oxide buildup than Prohesion samples, zinc oxide in scribe.
Aluminum	DI	Uniform darkened appearance, some rust on scribe.
	DHS	Some Al_2O_3 scattered on both plates, no rust in scribe.
	DIFT	Some rust in scribe, rust around edge.
	PRO	Al_2O_3 adjacent to scribe, rust in scribe.
	BOR	Al2O3 scattered on plate, rust in scribe.
85/15 Zn/Al	DI	Significant blistering ranging in size up to 16 mm in diameter scattered on front of the plate. A few small blisters on the back of the scribed panel.
	DHS	The entire panel has a uniform, dark gray appearance. Scribed panel has no blisters, unscribed panel has several blisters. More on the front than on the back. Blisters are hollow.
	DIFT	Blistering on scribed side. Rust spots on edge where coating is missing.
	PRO	Very heavy oxide layer present on the front of the panel.
	BOR	Moderately heavy oxide layer on front. Multiple blisters of various sizes on back (both panels). One panel has blistering on both sides.
90/10 Al/Al_2O_3	DI	No damage (unscribed panel). Rust in scribe (scribed panel).
	DHS	Very minor rust in scribe. Oxide is scattered – heterogeneously dispersed. Metalized coating has blistered and fallen off.
	DIFT	Rust in scribe, no damage elsewhere.
	PRO	Rust in scribe. Scattered oxidation on panel.
	BOR	More rust in scribe combined with oxidation. Oxide buildup on panel is similar to sealed panel.
95/5 Al/Mg	DI	Not too much damage except for rusting on top edge. No damage on unscribed panel.
	DHS	Unscribed – some oxide present on patches. Scribed some minor oxide present in patches and adjacent to scribe.
	DIFT	Rust in scribe, no damage elsewhere.
	PRO	Oxide adjacent to scribe, rust in scribe. Looks better than Amercoat panel and comparable to Metco.
	BOR	Some oxide present adjacent to scribe. Minor oxide on upper areas (close to water line). Large ruptured blister on one sample about 1 cm diameter.

Table 6.—Observations after testing Metco sealed samples

Panel	Test	Observation
Zinc	DI	No damage to coated area, rust in scribe.
	DHS	Oxide in scribe, tiny bubbles scattered, tiny zinc oxide nodules present where seal coat is thin.
	DIFT	No damage to coated area, rust in scribe.
	PRO	Zinc oxide in scribe, minor discoloration, zinc oxide nodules where sealer in thin.
	BOR	Zinc oxide in scribe, minor discoloration, zinc oxide nodules where sealer in thin.
Aluminum	DI	Tiny bubbles in sealant. Some rust in scribe.
	DHS	Tiny bubbles adjacent to scribe. No rust.
	DIFT	Very minor rust in scribe. Rust around edge.
	PRO	Al_2O_3 in scribe, rust in scribe, minor seal discoloration, Al_2O_3 on edges where seal is thinner and at a couple of localized spots.
	BOR	Scattered Al_2O_3 (worse than on PRO). Heavy Al_2O_3 buildup in scribe, minor rust in scribe. Undercutting is worse than PRO.
85/15 Zn/Al	DI	Minor rusting in scribe.
	DHS	No damage.
	DIFT	No damage.
	PRO	Oxide is coming through seal coat. No scribe rust. Some undercutting occurring at the scribe.
	BOR	Less oxide coming through coating compared to PRO.
90/10 Al/Al_2O_3	DI	Rust in scribe, minor oxide adjacent to scribe.
	DHS	Oxide coming through metco seal. Note that seal is thin. Similar to Amercoat seal.
	DIFT	Rust in scribe, no damage elsewhere.
	PRO	Similar to Amercoat seal. Less severe than BOR Metco.
	BOR	Minor rust in scribe, significant oxide buildup through coating and on scribe.
95/5 Al/Mg	DI	No damage.
	DHS	Oxide present in patches. Note that seal coat is thin. Coating is blistered and oxide is coming through coating on backside.
	DIFT	Rust in scribe, no damage elsewhere.
	PRO	Less oxide next to scribe. Oxide coming through scattered randomly on front face.
	BOR	Heavy oxidation adjacent to scribe. Lots of oxide coming through coating (both sides).

Table 7.—Observations after testing Amercoat Sealed Samples

Panel	Test	Observation
Zinc	DI	Rust in scribe.
	DHS	Oxide in scribe, no damage to seal coat.
	DIFT	Rust in scribe.
	PRO	Zinc oxide in scribe, moderate discoloration.
	BOR	Zinc oxide in scribe, moderate discoloration.
Aluminum	DI	Seal coat is in good condition, rust in scribe.
	DHS	Very minor undercutting adjacent to scribe. Roughened surface where sealer is thin.
	DIFT	Minor rust in scribe.
	PRO	
	BOR	Al_2O_3 and rust in scribe minor undercutting of sealer. Looks better than Metco. Al_2O_3 spots on back where sealer was applied thin.
85/15] Zn/Al	DI	Some minor rust on scribe.
	DHS	Some minor rust on scribe.
	DIFT	No damage.
	PRO	No damage.
	BOR	Some oxide coming through sealer.
90/10 Al/Al_2O_3	DI	Rust in scribe.
	DHS	Oxide coming through Amercoat seal. Note that the coating is fairly thin.
	DIFT	Rust in scribe.
	PRO	Rust in scribe, oxide buildup around scribe. Less severe than BOR test.
	BOR	No scribe rusting, significant oxide buildup through seal coat and on scribe.
95/5 Al/Mg	DI	No damage
	DHS	Coating is blistering due to oxidation close to scribe. Note that coat is thin.
	DIFT	Rust in scribe.
	PRO	Oxidation is adjacent to scribe. Rust in scribe. Coating failure near center of scribe.
	BOR	Heavy oxidation adjacent to scribe. Some oxide is coming through the coating.

In general, the BOR and Prohesion tests proved to be the most aggressive, with the BOR test being slightly worse in terms of the amount of corrosion observed on the TSC (oxidation). Nearly all of the samples exhibited this type of corrosion to some degree. Systems with thick seal coats fared better, but systems with thin seal coated experienced significant damage. These tests seem to suggest that a thin "seal" type coat does little to prevent damage under cyclic test conditions.

Immersion in deionized water (both static and flowing conditions) as well as immersion in a DHS resulted in less corrosion when compared to the cyclic exposure of the BOR and Prohesion tests.

Weight Loss

Sample weights were measured before and after testing. Immersion samples were periodically dried overnight and weighed during testing to track weight change trends. Of particular interest was the unsealed coating systems, which relied entirely on the metalized coating for protection and would therefore be expected to experience the greatest degree of degradation.

Prior to weighing, each sample was rinsed and lightly cleaned to remove any loose scale accumulation. Most of the oxidation remained visible on the surface. The samples were then dried in an oven and weighed. The results are shown in Figure 2. It should be noted that a minor correction was applied to the DHS, DI, and DIFT samples to account for the re-scribing. The average correction was 0.131 gram. It was not possible to apply a correction to BOR and PRO samples since intermediate weights were not recorded.

Most of the samples actually gained weight during testing, with the zinc metalized panels being the exception. For zinc, the most severe weight loss occurred when samples were immersed in the Harrison solution. This resulted in over 12 grams of metal loss, which was approximately one-third of the overall coating weight. At this rate, the coating was expected to last no longer than 15 months. The BOR test produced some weight loss as well, which was likely due to the samples being placed in immersion 25 percent of the time. In contrast to the BOR samples, the Prohesion samples each gained weight during the test. DI water immersion of the zinc panels resulted in minor weight loss, while the high-flow test was more severe.

One goal of the project was to test the effect of flowing water on the metal consumption rate. For zinc, the static deionized plates lost 0.194 gram, (0.06 percent of the total sample weight), which was 0.6 percent of the coating weight. The DIFT samples lost 0.559 gram (0.5 percent of the total sample weight), which was 4.6 percent of the coating weight. Direct comparison does not account for the fact that the side of the DIFT sample, which was fastened to the

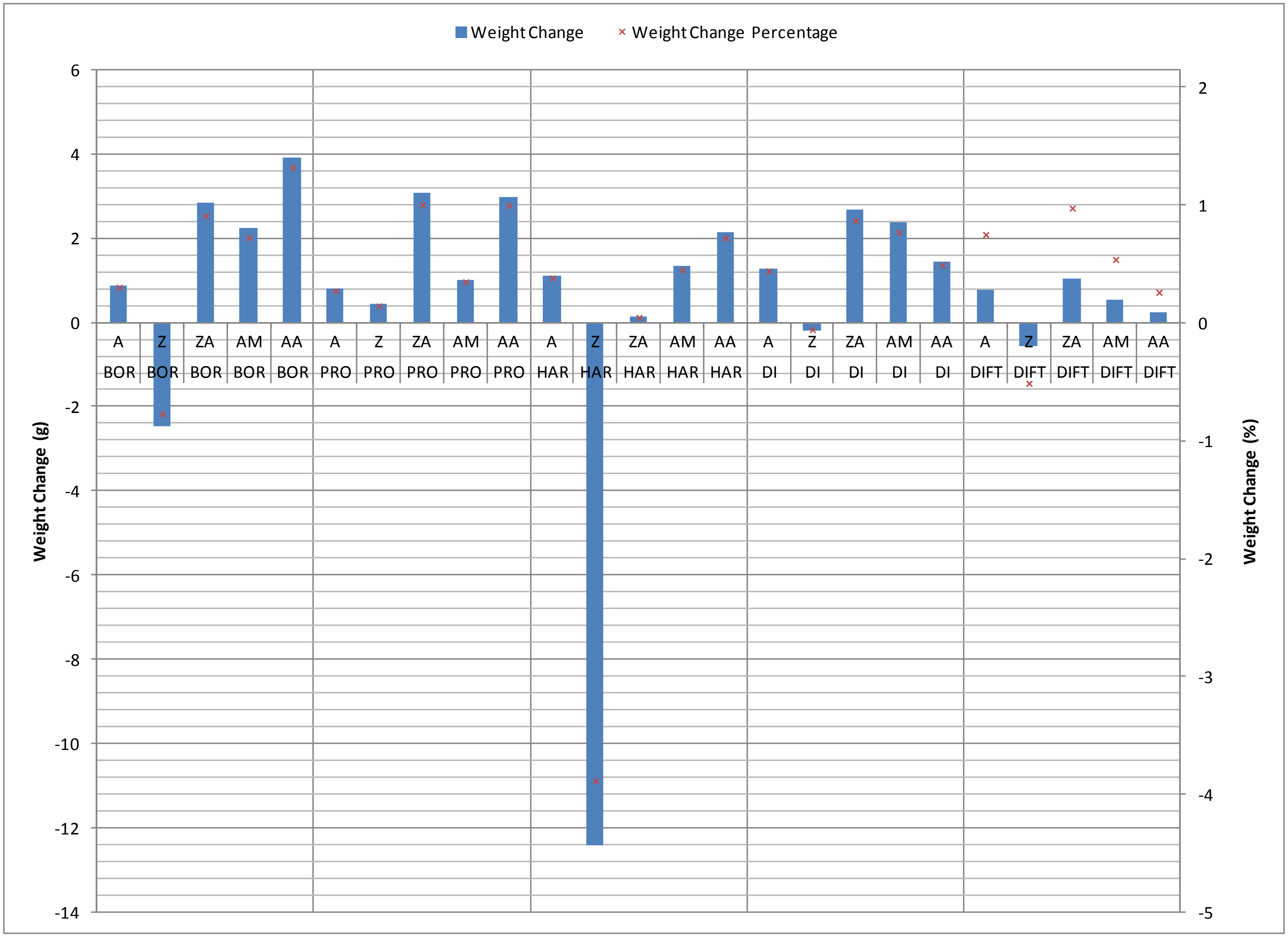

Figure 2.—Weight loss data for unsealed samples.

mounting substrate, was not exposed to high flows. Had both sides been exposed, one could expect the weight loss to nearly double. Clearly, the flowing water immersion is a more aggressive environment for zinc metalizing, but water chemistry plays a more important role. Figure 3 shows the weight change as measured during the test.

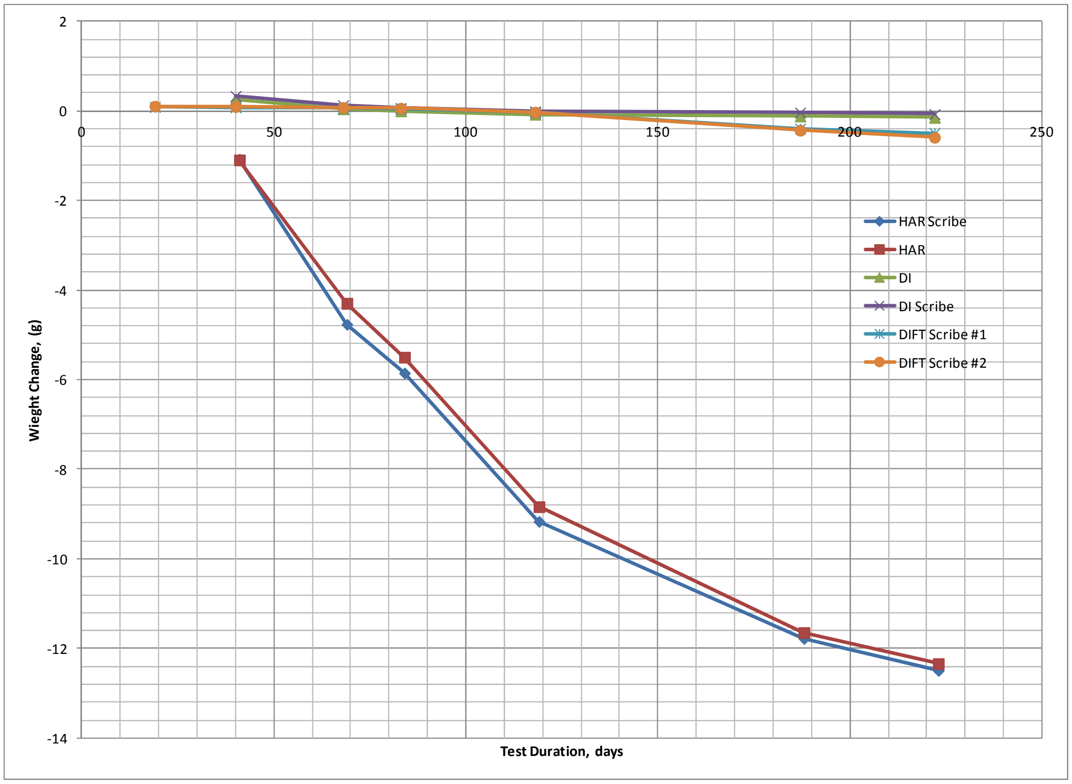

Figure 3.—Weight change versus time for unsealed zinc metalized panels in immersion.

The weight gain of the remaining samples can be explained by the oxidation process in which the aluminum and zinc are transformed into heavier oxygen-containing molecules. Oxidation was still visible on all of the samples (including zinc). Weight could reasonably be expected to increase initially during the corrosion process and then begin to decrease as the oxidation is removed from the surface. Weight gain would therefore indicate that aluminum oxide is more stable and difficult to remove even under high flows. It was interesting that the 85/15 samples also gained weight in every test as well, which suggested that the oxide formulation is significantly different than the oxide formed by pure zinc. Given these results, one would expect superior performance and longevity for 85/15 compared to zinc. However, the blistering that was noted in immersion is problematic.

Adhesion Test Results

Each plate was tested for pull-off adhesion strength in accordance with ASTM D 4541. The results are presented on Figure 4.

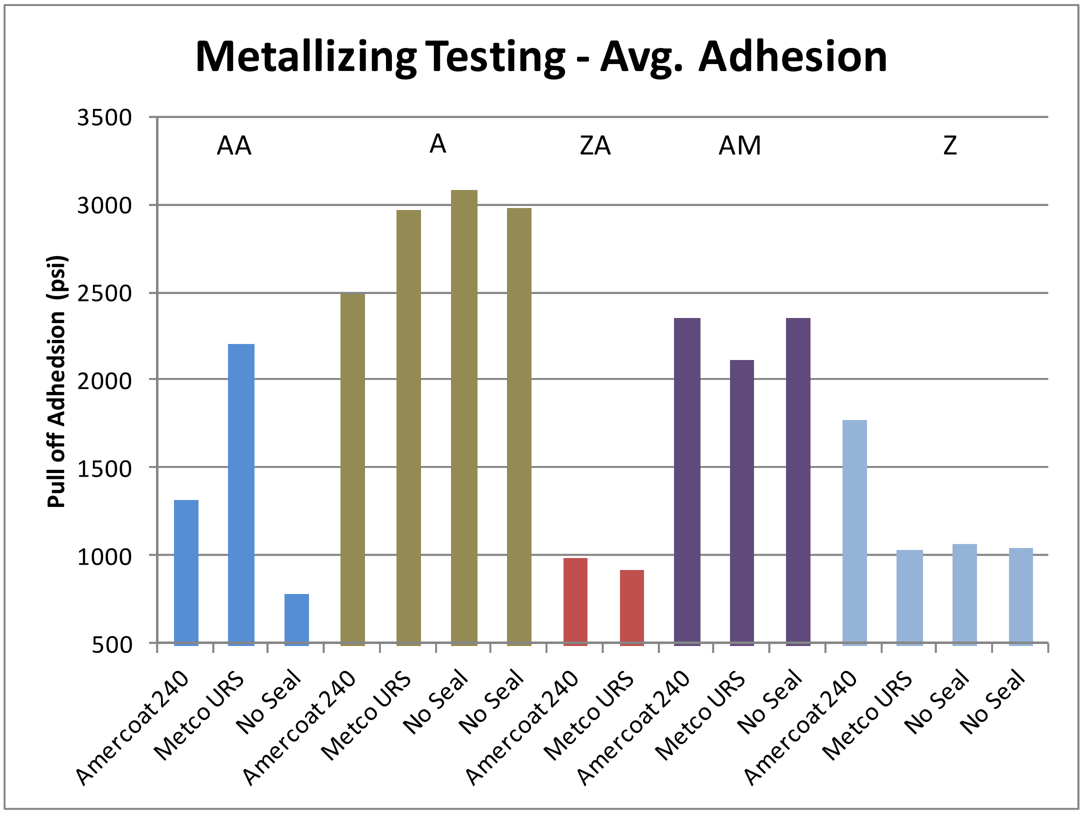

Figure 4.—Pull-off adhesion data for thermal spray systems prior to testing.

The results from the data show that aluminum metalized samples produced the highest adhesion strengths, while zinc based alloys showed much lower adhesion strengths. Note that no adhesion testing was performed on unsealed 85/15 panels. These values meet or exceed the adhesion requirements set by the SSPC paint manual: 500, 700, and 1,000 psi for zinc, 85/15, and aluminum respectively. MWD indicates that 450–650 psi adhesion for zinc is typical (Drooks, 2012).

Electrochemical Experiments

Electrochemical measurements were performed with EIS to characterize the sealed metalized coatings by their barrier properties as well as their ability to provide cathodic protection to the substrate. The ideal coating system should have a stable contribution by both of these mechanisms. The metalized coatings were exposed to immersion conditions in DHS to accelerate the rate of coating degradation without altering the mechanisms. The experimental results were used to rank relative coating performance.

Low-frequency impedance results are provided on
Figure 5 for all sealed metalized coatings examined in this experiment. There are two distinct regions on the graph. Above 10^7 Ω, the coating exhibits very good barrier properties and mitigates corrosion by greatly slowing the diffusion of corrosion reactants to the substrate. Below 10^7 Ω, water and ions are transported through the coating at greater rates.

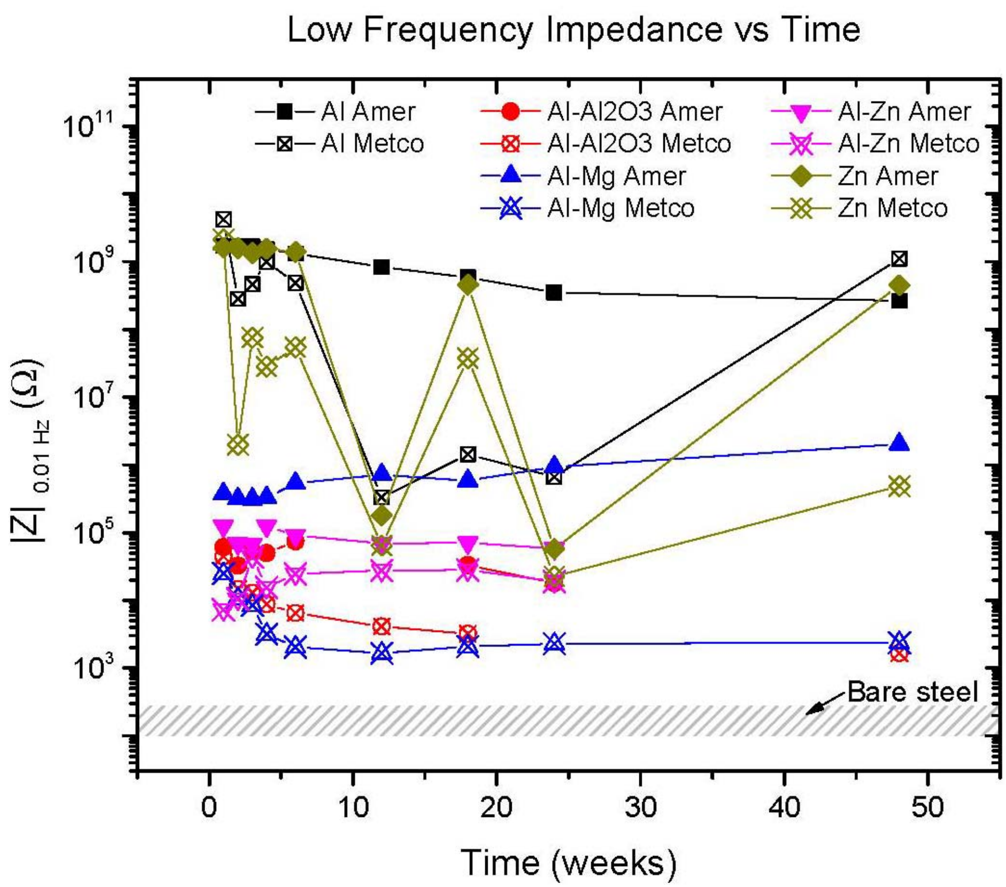

Figure 5.—Low-frequency impedance versus immersion time for sealed metalized coatings.

For all metalized coatings, the Amercoat seal recorded higher impedance measurements, suggesting that it has superior barrier properties compared to Metco. In most cases, this difference is greater than one order of magnitude. The aluminum and zinc metalized coatings show the highest impedance values throughout this experiment. Aluminum TSC with Amercoat seal was the most stable throughout the testing, with a slow decrease from 2.7 x 10^9 to 1.7 x 10^8 Ω over the course of the 48-week exposure period. The zinc coating impedance values decrease by three orders of magnitude at 12 and 24 weeks, while high impedance is measured at all other times. This is likely due to the growth of a semi-impermeable oxide layer (high impedance) followed by its breakdown due to the solution washing away these oxides (low impedance).

All coatings tested showed higher impedance than bare steel, which is approximately 1.0 to 2.0 x 10^2 Ω. This may be due in part to the anodic electrochemical reaction products that have a passivating effect on the steel substrate. This is most pronounced for Al-Mg TSC with Amercoat seal in which a steady increase in impedance occurred over the 48-week test period; the initial and final impedance values were 3.8 x 10^5 and 2.0 x 10^6 Ω. The Bode plot for this coating shows a clear capacitive effect evolving with time. Bode plots are provided in Appendix B for all sealed metalized coatings for the interested reader.

Corrosion potential results are provided on Figure 6 to supplement the above EIS results. These measurements provide a clear indication of whether or not cathodic protection is occurring in a system that employs a galvanic couple. The corrosion potential of bare steel was measured in DHS for both abrasive blasted steel and one with a layer of mill-scale. The resulting region of corrosion potentials is shown on Figure 6 as a shaded region. All corrosion potentials below this region are the result of a galvanic coupling between the steel substrate and subsequent metalized coating system, hence active cathodic protection. The ideal polarization for a cathodic protection system is approximately 0.1 to 0.5 volt (V) below the cathode material. Overpolarization and cathodic disbondment are concerns for sustained polarizations larger than this (Zhu, 2011; Leidheiser, et al.1983).

With the exception of Zn/Amercoat and Al/Metco, all sealed metalized coatings appear to provide cathodic protection to the steel substrate for the first few weeks of immersion in DHS. Both of these coatings fluctuate between cathodic protection and free corrosion of the steel substrate. This is consistent with the growth and breakdown of oxides explanation provided in the above EIS discussion. The Al-Al_2O_3/Amercoat coating has a low level of cathodic protection, which appears to cease within 25 weeks of immersion as it reaches -0.7 V versus SCE. Following 48 weeks of immersion, Al/Amercoat, Al-Mg Amercoat, and Al-Al_2O_3 Metco continue to afford consistent cathodic protection to the steel substrate at approximately -0.9 to -1.0 V versus SCE. Extending the length of this experiment would provide further insight to the service lifetime in which these metalized coatings would be expected to provide cathodic protection.

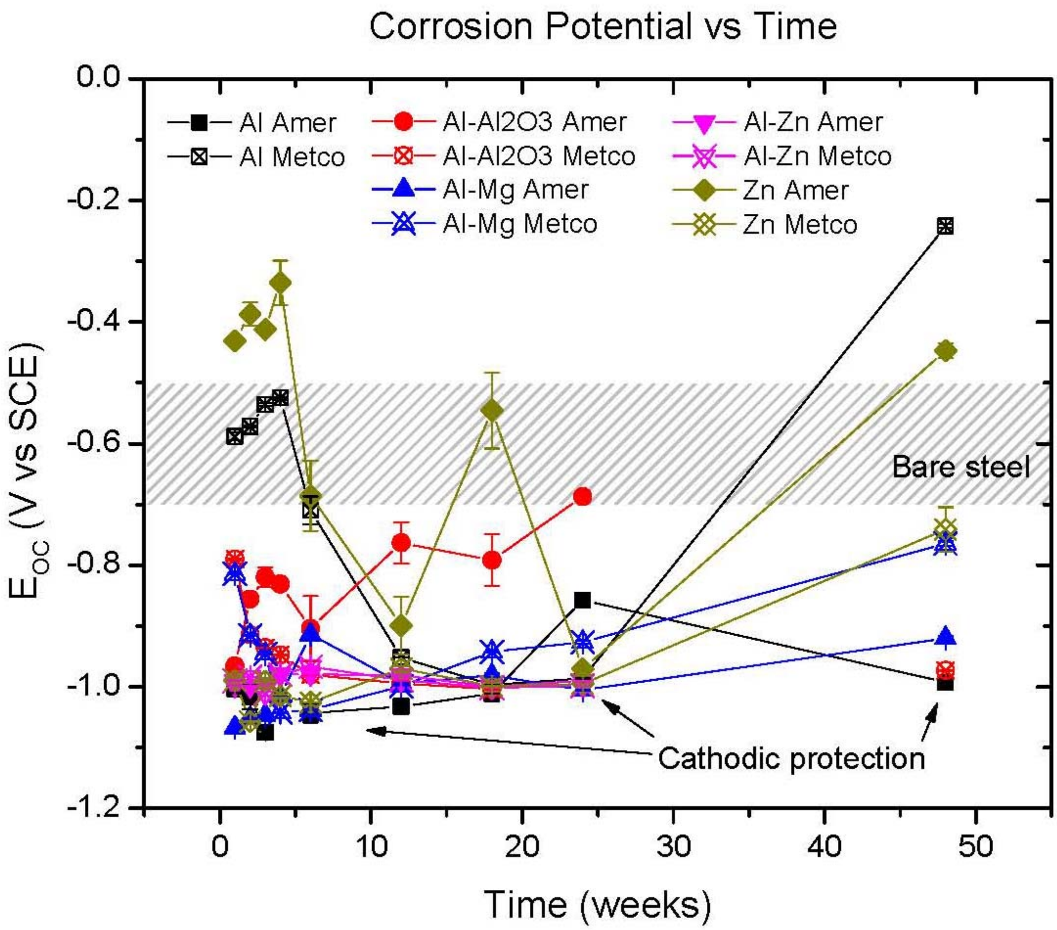

Figure 6.—Corrosion potential versus time for sealed metalized coatings.

DISCUSSION

Substrate Protection at Coating Defect

One benefit of TSCs is that they offers passive cathodic protection when substrates are coated with metals that are more active on the galvanic series (aluminum, zinc, and magnesium in the case of steel). This effect enables localized protection to the steel where the coating becomes compromised. To evaluate the effectiveness of this protection, the scribed areas of each panel were examined. Cathodic protection is evident when no red (iron oxide) rust was present inside the scribe.

Effect of Test Type

The Harrison immersion test produced no rust in any of the panels. There was, however, visible oxidation present on each panel. In contrast, the other tests all tended to produce some degree of rusting on all of the panels. The deionized test seemed to result in more rust and less coating oxidation, whereas the cyclic tests produced increased amounts of both rust as well as coating oxidation (depending on the sample). The BOR test appeared to be slightly more severe than the Prohesion test. These results are expected since immersion in DHS would give the highest level of conductivity to the electrolyte that facilitates cathodic protection. DI water would offer little to no conductivity, reducing or eliminating the effect of cathodic protection. The cyclic tests would fall somewhere in between these two extremes.

Effect of Alloy

While EIS showed all of the alloys offer some degree of cathodic protection, the galvanic series suggests that zinc materials will provide superior cathodic protection compared to the aluminum-based materials. Visual inspection of the post-test samples supports this hypothesis. For example, the BOR and Prohesion tests produced far more rust in the unsealed aluminum versus the unsealed zinc. The scribed zinc panels contained mostly oxidation and a very small amount of iron rust. This oxide to rust ratio was slightly lower in the Zn/Al samples, which is most likely due to the increased aluminum content in the coating. The AA samples were about the same the aluminum samples.

The purpose of testing the AM system was to investigate whether the addition of magnesium would offer enhanced cathodic protection over that of pure aluminum since magnesium is lower on the galvanic series. Visual observation of post-test samples appears to support this hypothesis. For example, the AM samples contained slightly less rust in the BOR and Prohesion tests versus the pure aluminum or AA samples.

It is also notable that the oxide to rust ratio is lowered when the zinc alloy is placed in flowing water. This indicates that some of the oxide product is being removed by the high-velocity flowing water. This effect is much less pronounced on the 85/15 alloy.

Effect of Seal Coat

The seal coat did not appear to negatively affect the TSC’s ability to cathodically protect the scribe. Using the BOR test as the benchmark, there was no noticeable decrease in either the amount of oxide present in the scribe or the oxide:rust ratio.

General Corrosion Protection

Metalized coatings protect the substrate from general corrosion via cathodic protection and by functioning as a barrier to break the electrolyte path (i.e., not allowing the formation of a corrosion cell). The primary function of the coating is that of a barrier. Only when the electrolyte reaches the substrate should any cathodic protection begin to take place. Sometimes the metalized coating will corrode autogenously when placed in a corrosive environment, eventually reaching a state of passivation once a protective oxide layer has formed, preventing further corrosion from occurring. Visual inspection of the panels can give an indication of how much corrosion has occurred and provides insight into how long a particular coating could be expected to last before eventually becoming consumed entirely.

Effect of Test Type

In general, the immersion tests appeared to produce less oxidation than the cyclic testing. The BOR and Prohesion samples were similar in appearance at the test conclusion.

Effect of Alloy

The zinc alloys tended to produce a more uniform layer of oxidation; in contrast, the aluminum samples contains more variable and localized oxidation. Zinc oxidation was finer and more easily removed from the panels with a fingernail or brush. However, it was not possible to remove a large fraction of the material manually since the particles tended to become entrenched in the surface asperities.

Effect of Seal Coat

The presence of a thick seal coat appeared to prevent the oxidation of the underlying coat. This was most evident for the zinc-based systems (Figure 7). However, some chalking and UV degradation was observed on both systems.

However, on systems where the seal coat was applied with a lower DFT, there was no significant performance advantage realized. Figure 8 shows slightly increased oxide deposits in the areas immediately adjacent to the scribe and significant deposits elsewhere on both sealed and unsealed systems.

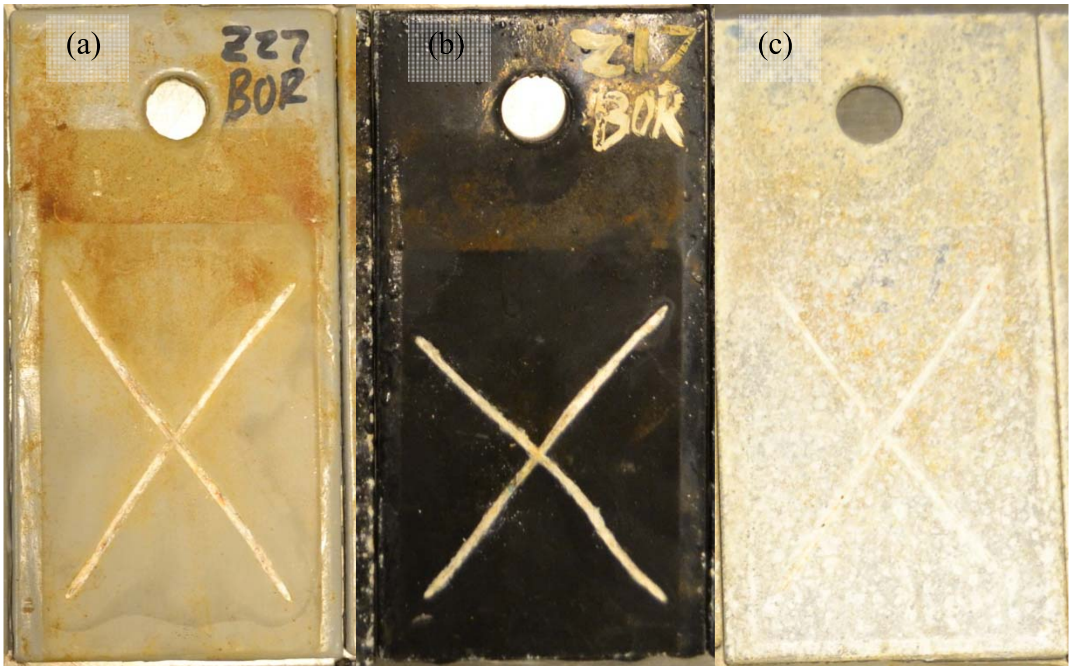

Figure 7.—Effect of thick seal coat: Zinc systems tested in the BOR cycle after 5,040 hours. (a) Amercoat seal, (b) Metco seal, (c) unsealed.

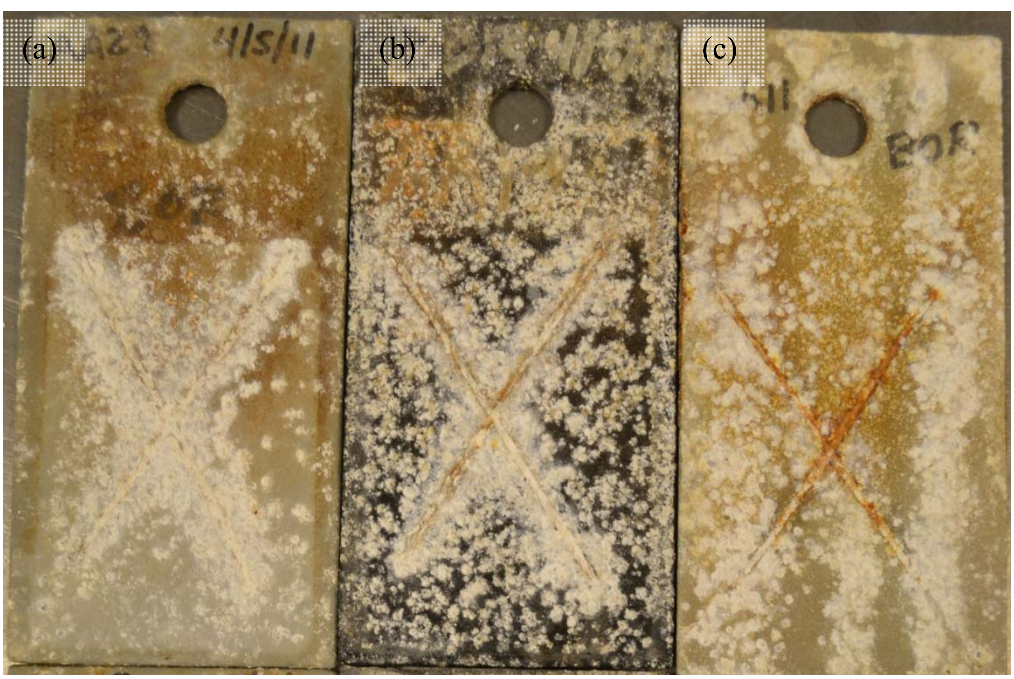

Figure 8.—Effect of thin seal: Aluminum/Al_2O_3 systems tested in the BOR cycle after 5,040 hours. (a) Amercoat seal, (b) Metco, (c) unsealed.

Blistering

Several coating systems experienced blistering during testing. The ZA unsealed panels experienced unacceptable levels of blistering in all tests except for the Prohesion test (i.e., any test where immersion service was encountered). The blisters were hollow inside, which suggests that they could be caused by formulation of lower-density oxides within the coating. Similar results were observed by MWD during laboratory testing of 85/15 Zn/Al TSC panels in raw and treated water (Drooks, 2012). USACE has also observed cohesive failures of a flame sprayed, vinyl sealed 85/15 Zn/Al system after 8 years in service at the Belleville locks and dam (USACE, 1999). The authors noted that the failures are likely due to blister formation as a result of expanded oxide formation. The BOR test cycle also produced blistering in the Al/Mg samples, which most likely eliminates the system from consideration.

Other Considerations

Other factors such as ease of application, cost, and availability of materials should also be considered when selecting a TSC system. For example, one of the applicators experienced difficulties applying the 85/15 material. This is believed to be due to oxidation that occurs on the wire surface, which can have a destabilizing effect on the arc. Specialized thermal spray equipment is therefore required to apply the 85/15 material. The aluminum/aluminum oxide material was not readily available in wire form and cost significantly more to obtain as a powder. Given the lack of any observed performance advantage, it makes little sense to select this material over pure aluminum wire.

Another aspect to consider when specifying a thermal spray process is the potential difficulties in metalizing complex structures. The physical size of the gun can make it difficult to coat interior crevices and other recessed areas with electric arc spray. One potential solution is to use a soldering process known as the hot bar method. In this process, a zinc bar about ¾” x ½” x 6” in size is melted onto substrate in areas that are inaccessible to the spray gun. Alternatively, a zinc-rich coating could be used to cover those areas.

Safety

MWD frequently uses metalized coatings on radial gates and other structures with infrequent/alternating immersion. Metalizing does present a potential fire hazard, and care should be taken to avoid spraying in proximity to flammable chemicals (i.e., solvents used for cleaning). However, the electric arc generates significantly less heat than flame spray, which results in a much cooler substrate. Sales representatives have been known metalize cardboard for demonstration purposes using this process, whereas flame spray would ignite the substrate. In addition, conventional plastic sheeting can be used for containment where necessary. Common sense should be exercised. Air-supplied respirators are recommended. Other personal protective equipment similar to what is worn during welding is required.

RECOMMENDATIONS FOR FUTURE WORK

- Further investigation is warranted to identify additional alloys which offer similar corrosion protection as the 85/15 Zn/Al alloy without experiencing blistering in immersion conditions. The desired alloy produces a dense and stable oxide layer that doesn't expand during the oxidation process.

- Further research and evaluation is needed to determine an expected service life, determine ease to repair defects, and determine a method to deal with crevice corrosion. Because the service life of metallizing coatings is highly dependent on localized conditions such as water chemistry, it is recommended to perform a small field trial using the results from the current study as a basis.

- There is a need to develop a non-destructive technique for examining thermal spray coatings *in situ*, specifically to determine porosity which is highly dependent on application parameters.

- It is also recommended to investigate a molten aluminum dipping process, similar to galvanizing, to investigate the potential for corrosion protection.

FURTHER READING

(Rogers, 1997): Assesses the feasibility of thermal spray for commercial ships. He states that arc spray is more tolerant of surface cleanliness compared to flame spray. Thermal spray coatings applied using arc spray tend to adhere with greater strength (3–4 times greater). Deposition rates have increased, making thermal spray more economical.

(Sampson, 1997): Overview of thermal spray process.

(Cunningham 1996): Thermal spray aluminum coatings can provide 34 years of corrosion protection in a marine environment. Dry film thickness can be measured using magnetic DFT gauges.

(Neville, 1996): Corrosion behavior studies for stainless steel substrates coated with cement coatings (86WC-10Co-4Cr, 50WC-50Ni-Cr-B-Si). The authors conducted laboratory testing in seawater and water with low total dissolved solids. Both coatings were shown to be susceptible to corrosion after a short period. For immersion purposes, it makes sense to choose a coating that is anodic to steel. This way, the coating will provide barrier protection as well as cathodic protection where the coating is damaged.

(Brenna, 1995): Details naval experience with thermal spray on ships. Mentions that Ti was sprayed on seawater piping flanges. Most other thermal spray was done with zinc or aluminum.

(Sulit, 2002): Steel Structures Painting Council guide to thermal spray coatings. Overview of the equipment and operation procedures used in thermal spray. Details on surface preparation, coating thickness, and sealers.

(Tucker, 1994): General writeup of thermal spray processes. Porosity can range from 2–15 vol%.

(U.S. Army Corps of Engineers, 1999): Thermal Spraying: New Construction and Maintenance. This document offers a generalized and comprehensive writeup on metalizing, including coatings selection, surface preparation, application parameters, and sealing systems.

(American Welding Society [AWS], 1993): Guide for the Protection of Steel with Thermal Sprayed Coatings of Aluminum and Zinc and their Alloys and Composites. Covers important information for specification writers such as standards that the coating must meet for adhesion, porosity and morphology, interface contamination, and other quality control procedures. This document includes practical information on coating procedures such as material selection, deposit efficiency for flame spray and arc spray, and coverage data. Service life is discussed extensively:

Reference corrosion tests:

- AWS 19-year report (AWS, 1974)
- ASTM report (Kain, et al., 1989)
- Canadian Standards Association Report (CSA, 1966, Reaffirmed in 1980)
- Accelerated laboratory tests for MMCs and zinc-aluminum alloys (85/15 Zn/Al), which were introduced in the 1970s and 1980s

The optimal thickness is described to be 12–14 mils for aluminum and Al MMC thermal spray coatings in saltwater.

(Kuroda, 1998): A literature review on the structure and physical properties of metalized coatings is presented. Consideration is given to thermal stresses developed during the spray process and the effect of substrate temperature.

(Sobolev, 1997): Gives an in-depth look into the factors that influence bond strength between the substrate and coating.

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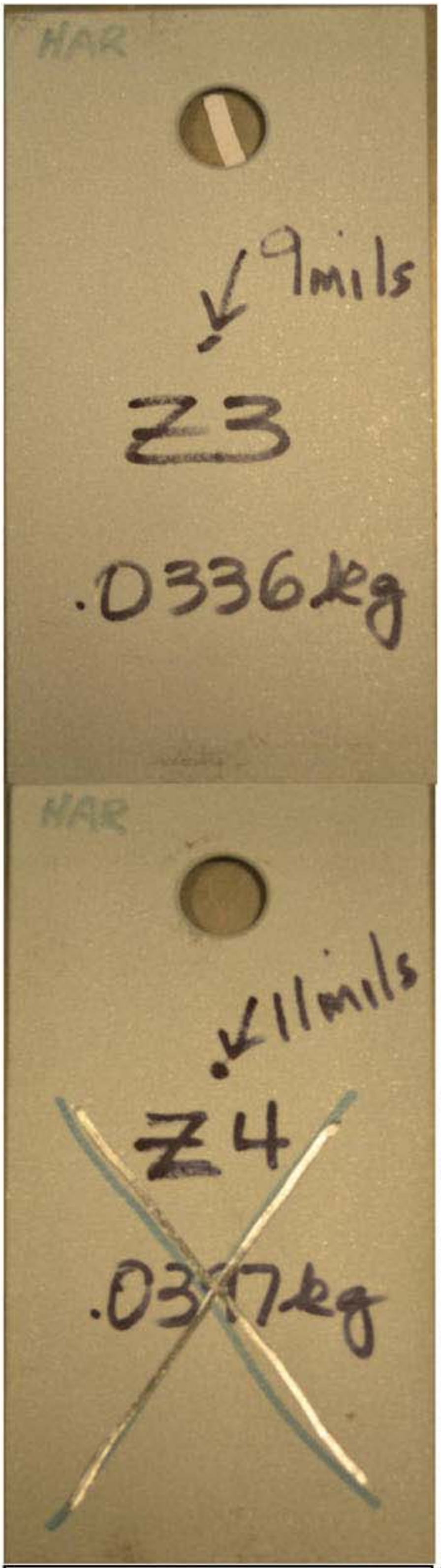
Appendix A

Photo Documentation

Aluminum – HAR
Before Test

Aluminum – HAR
After Test (5040 hrs)



Zinc – HAR Before Test	Zinc – HAR After Test (5040 hrs)

Zn/Al (85/15) – HAR
Before Test

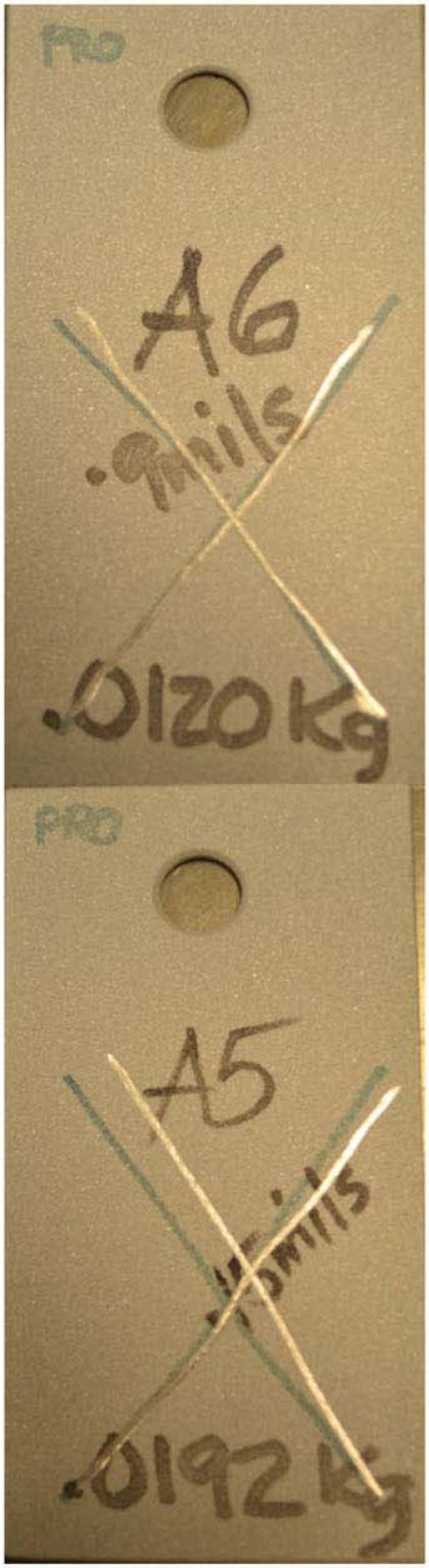
Zn/Al (85/15) 85/15 – HAR
After Test (5040 hrs)

Al/Al_2O_3 90/10 – HAR
Before Test

Al/Al_2O_3 90/10 – HAR
After Test (5040 hrs)

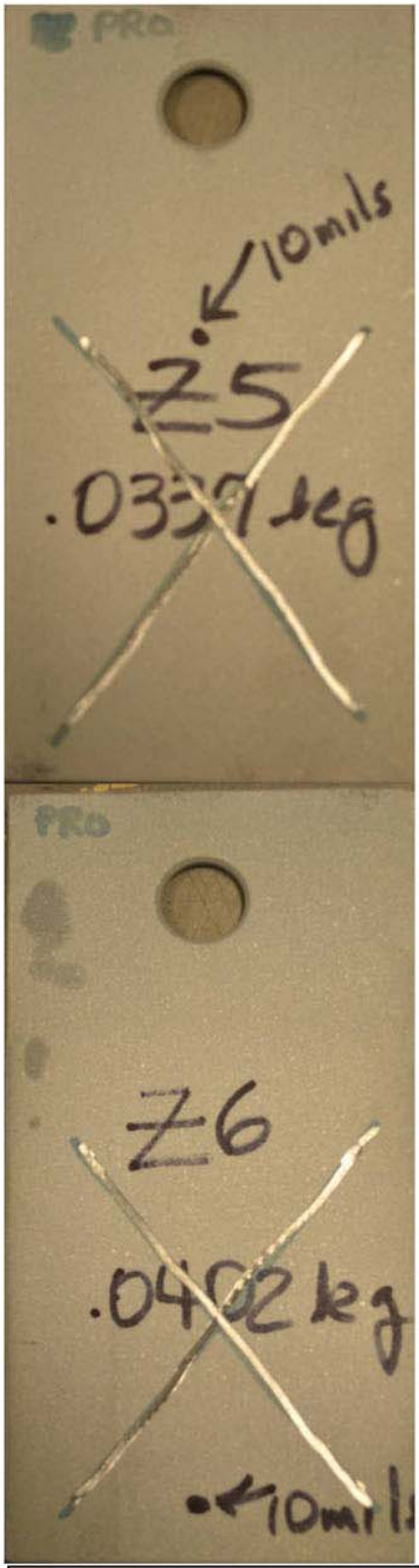
Al/Mg (95/5) – HAR
Before Test

Al/Mg (95/5) – HAR
After Test (5040 hrs)



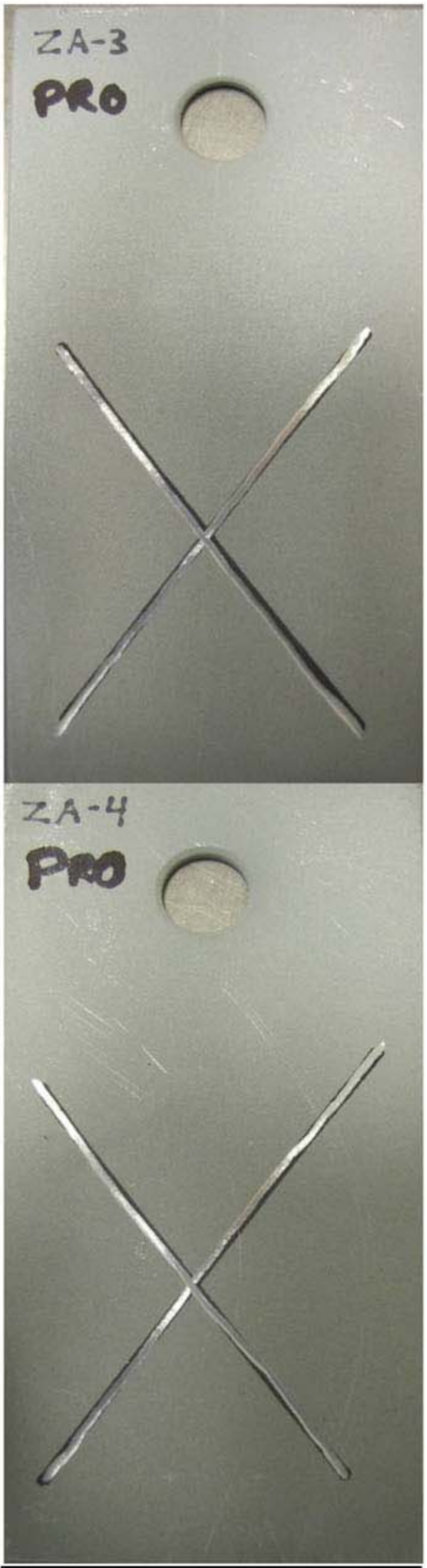
Aluminum – PRO
Before test

Aluminum – PRO
After test (5,040 hours)



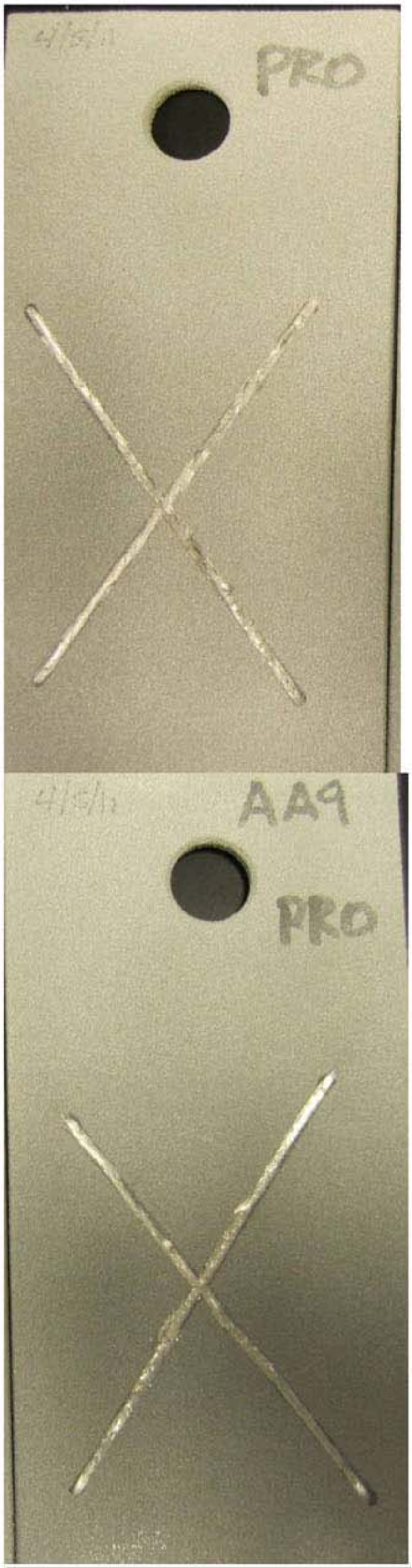
Zinc – PRO
Before test

Zinc – PRO
After test (5,040 hours)



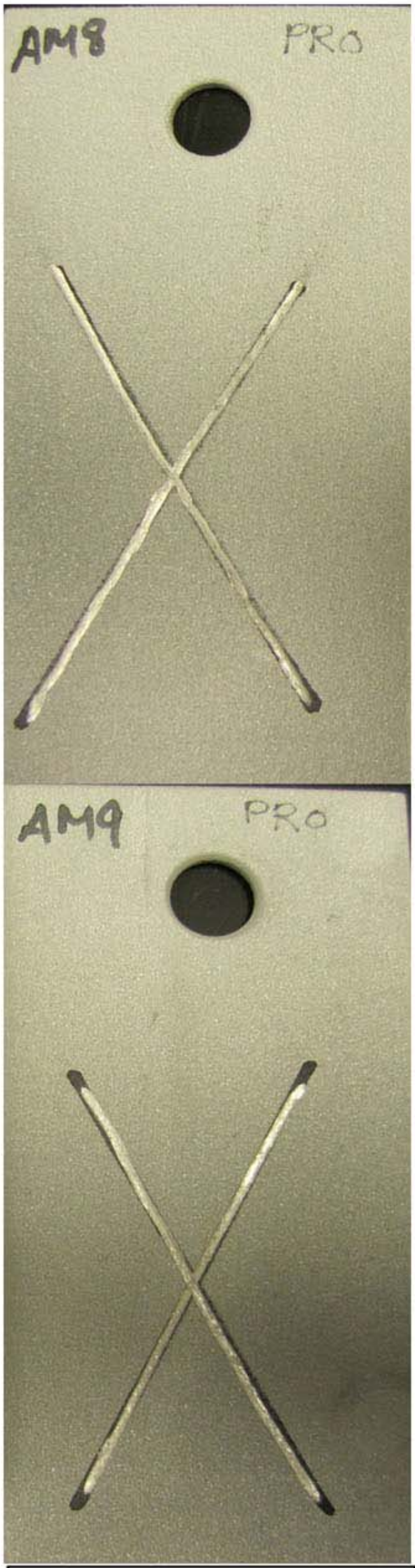
Zn/Al (85/15) – PRO
Before test

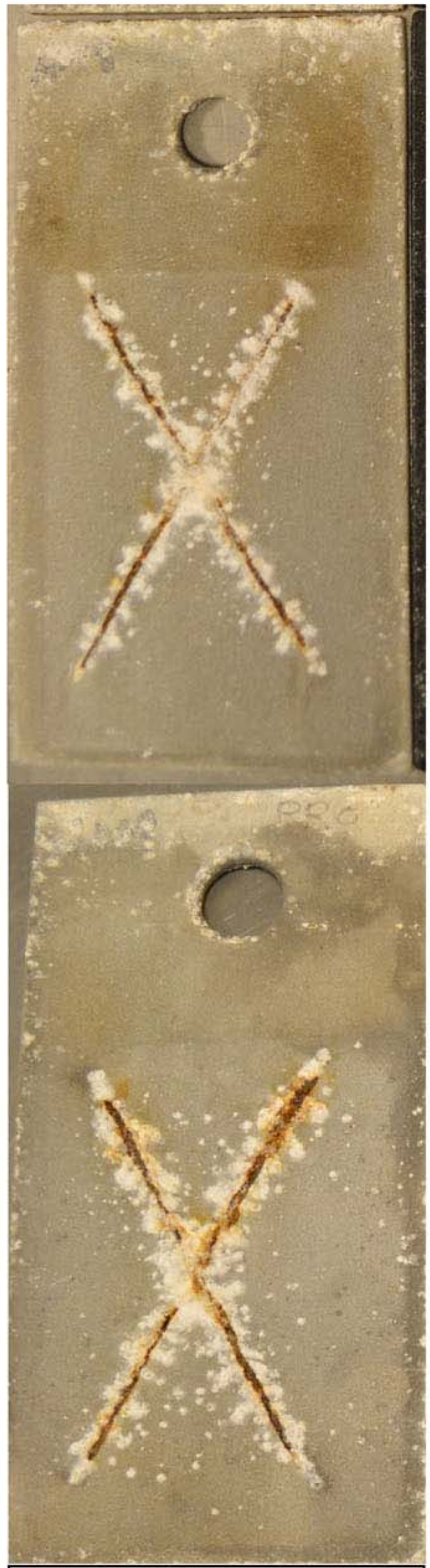
Zn/Al (85/15) – PRO
After test (5,040 hours)



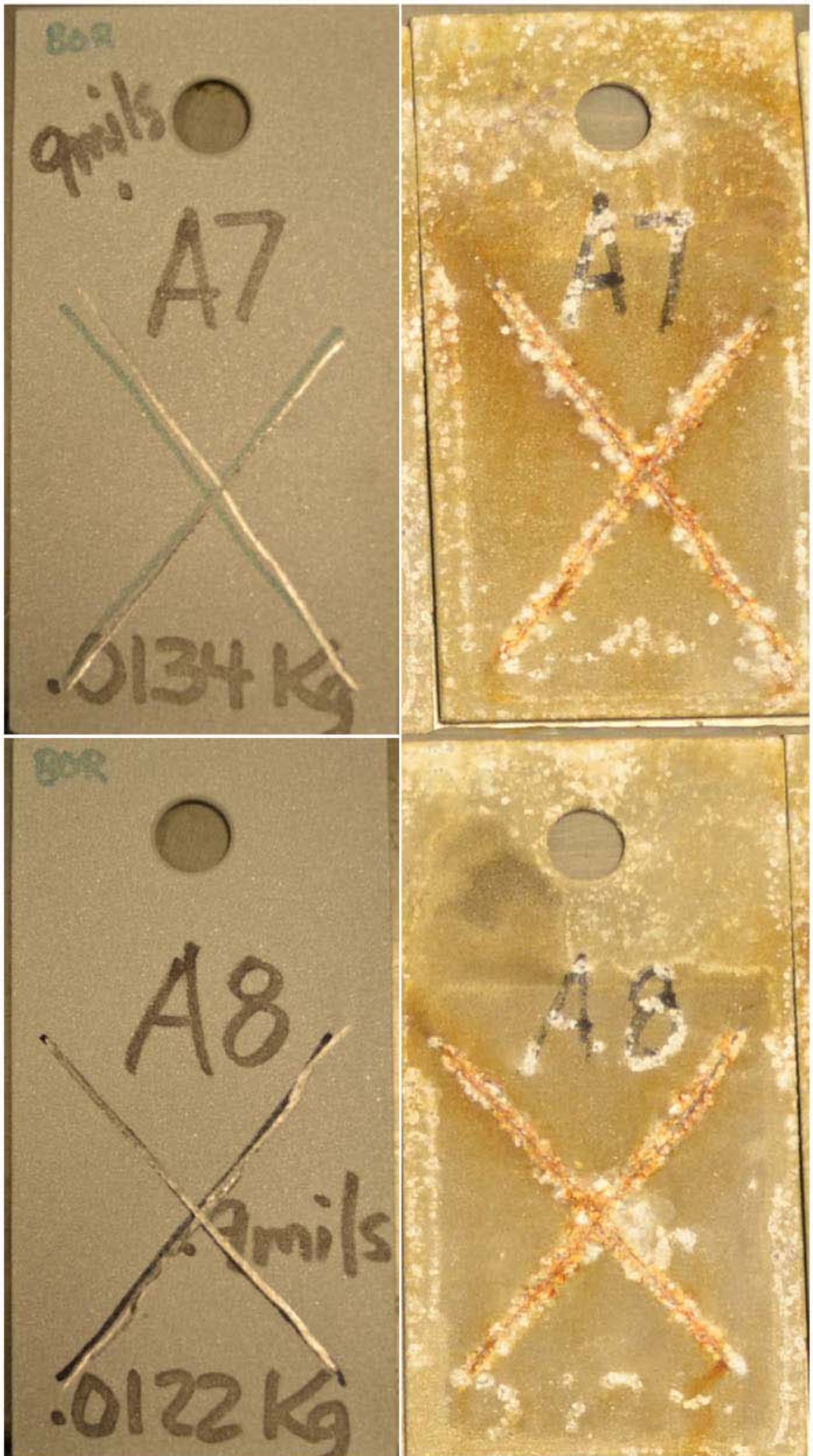
Al/Al_2O_3 90/10 – PRO
Before test


Al/Al_2O_3 90/10 – PRO
After test (5,040 hours)

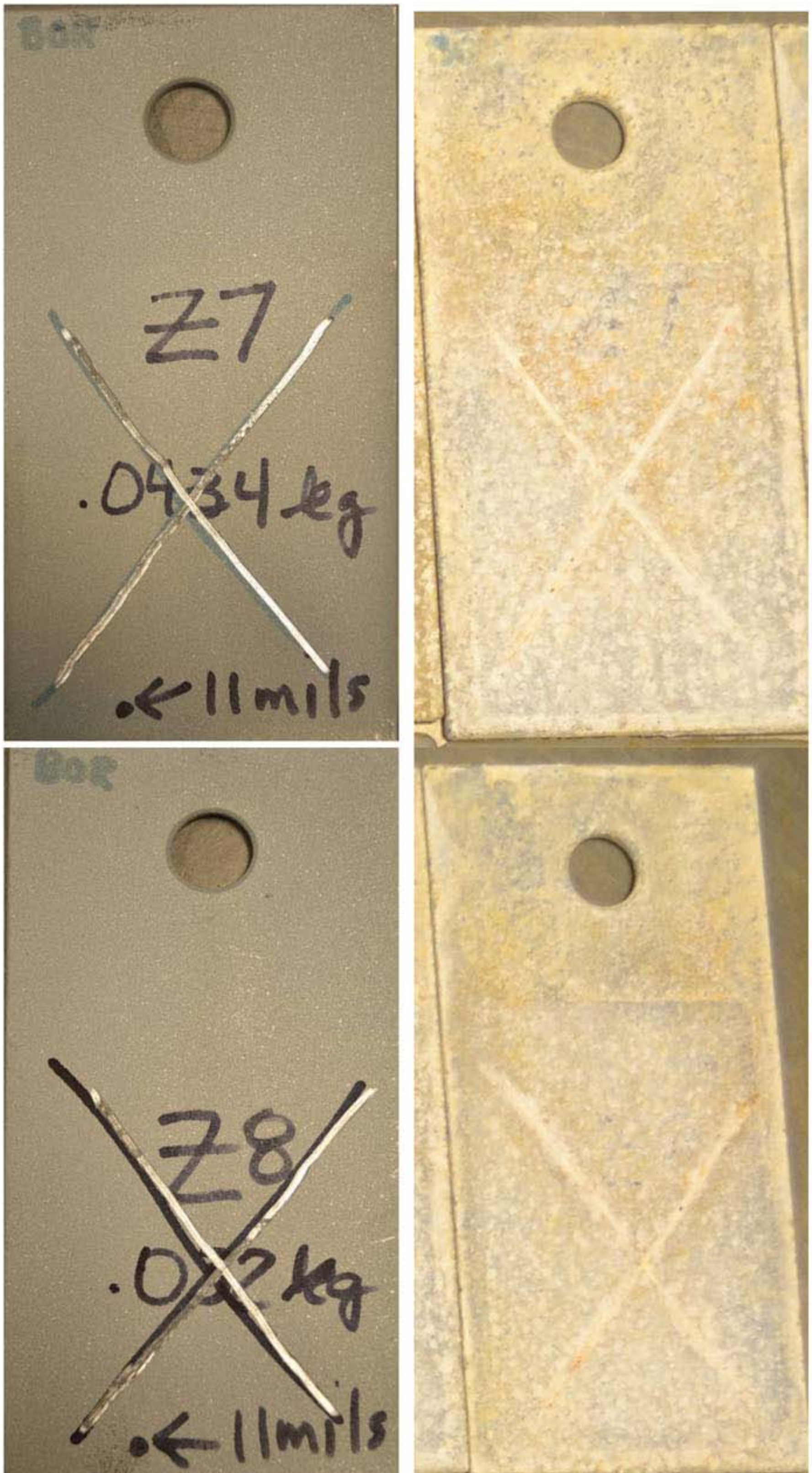




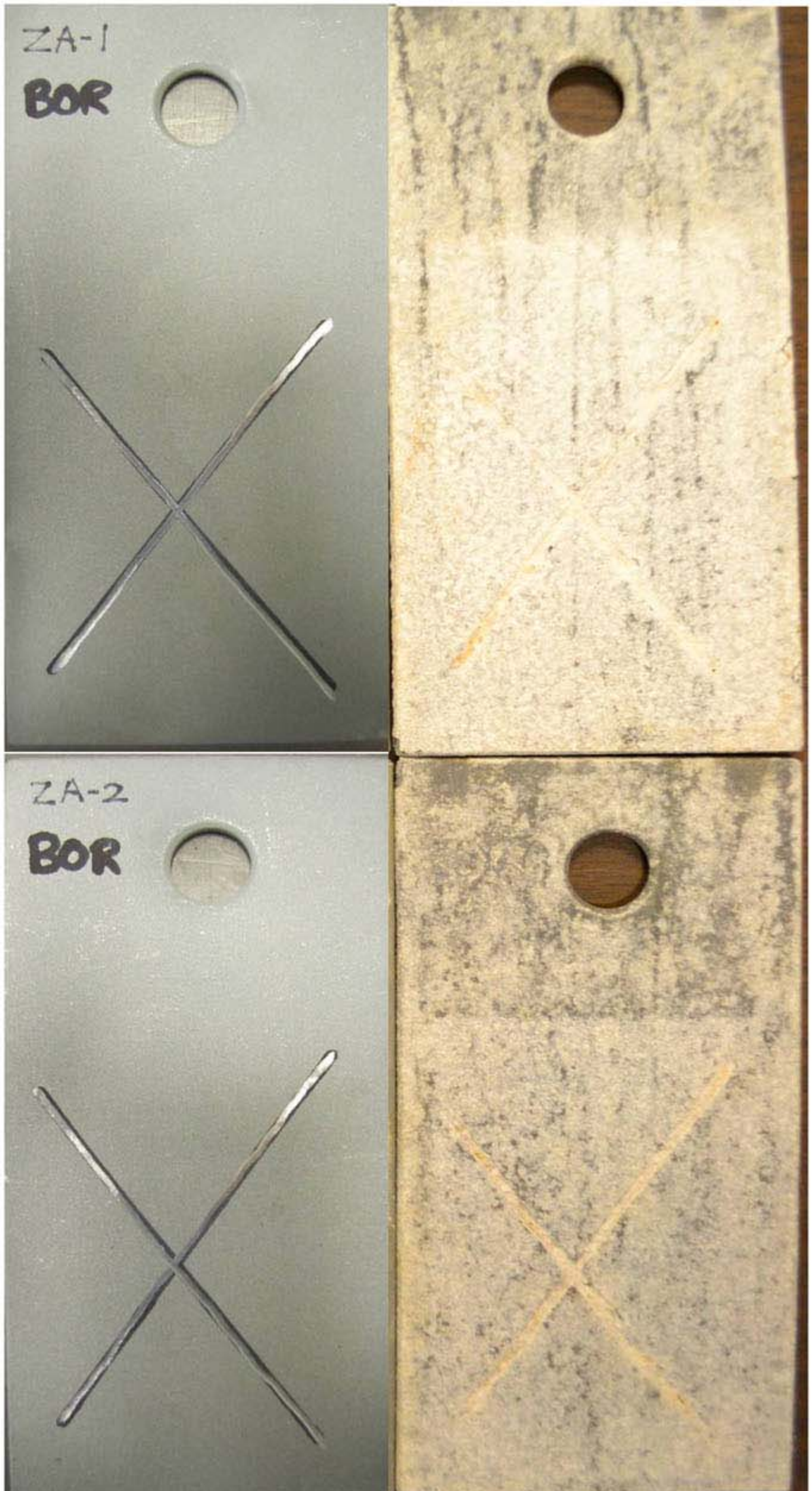
Al/Mg (95/5) – PRO Before test	Al/Mg (95/5) – PRO After test (5,040 hours)



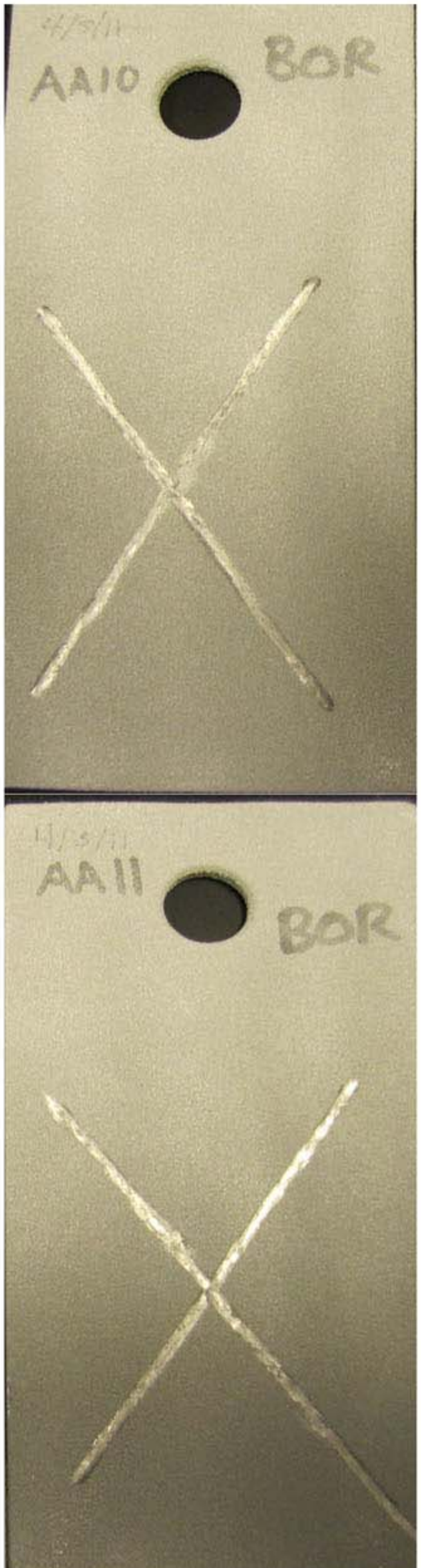
Aluminum – BOR Before test	Aluminum – BOR After test (5,040 hours)



Zinc – BOR Before test	Zinc – BOR After test (5,040 hours)

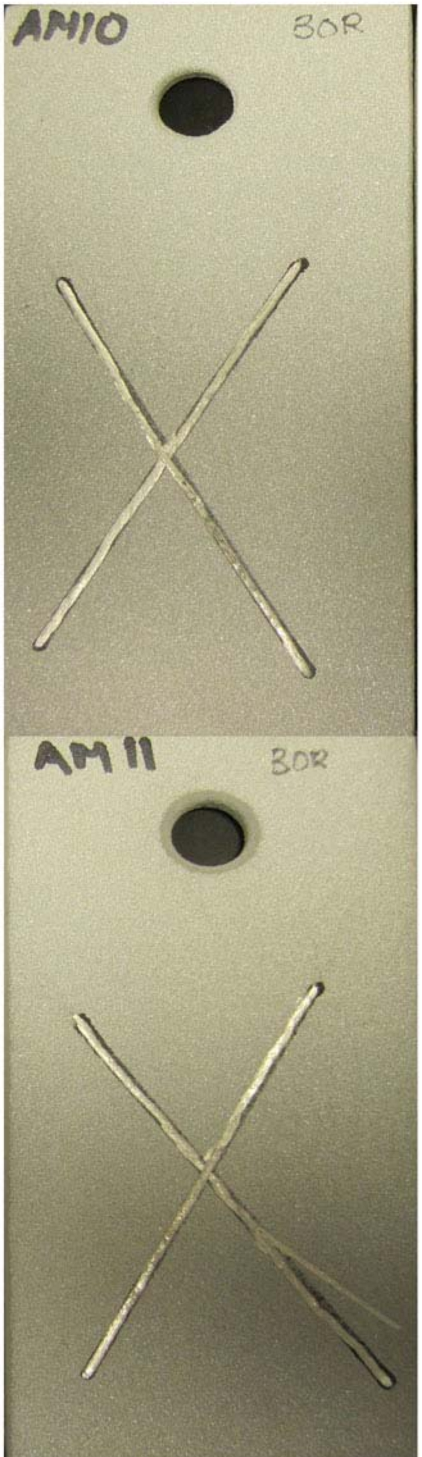


Zn/Al (85/15) – BOR Before test	Zn/Al (85/15) – BOR After test (5,040 hours)



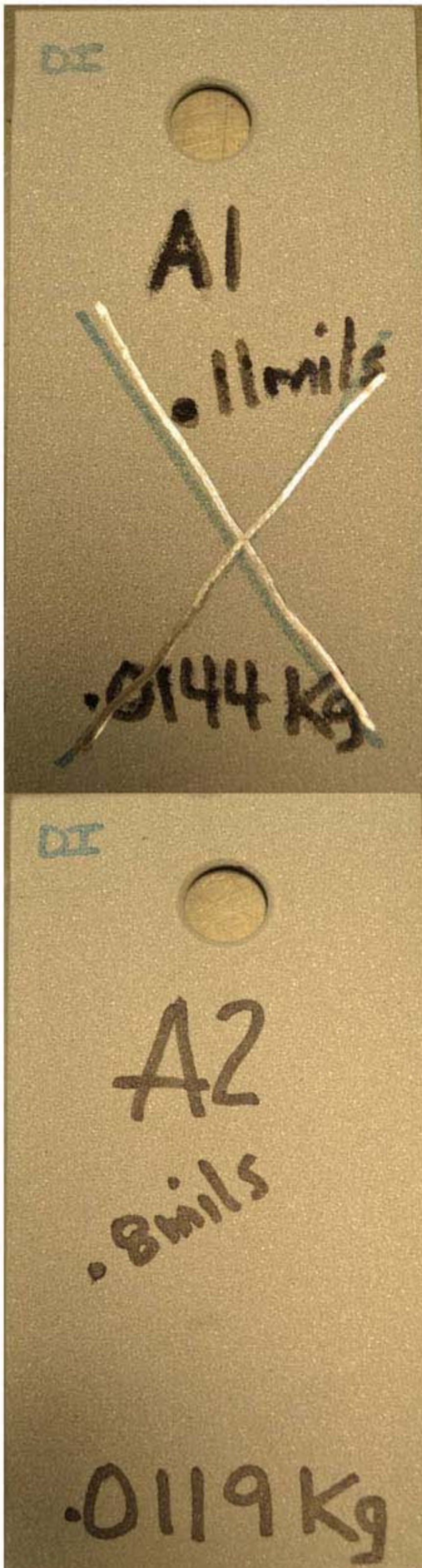
Al/Al_2O_3 (90/10) – BOR
Before test

Al/Al_2O_3 (90/10) – BOR
After test (5,040 hours)

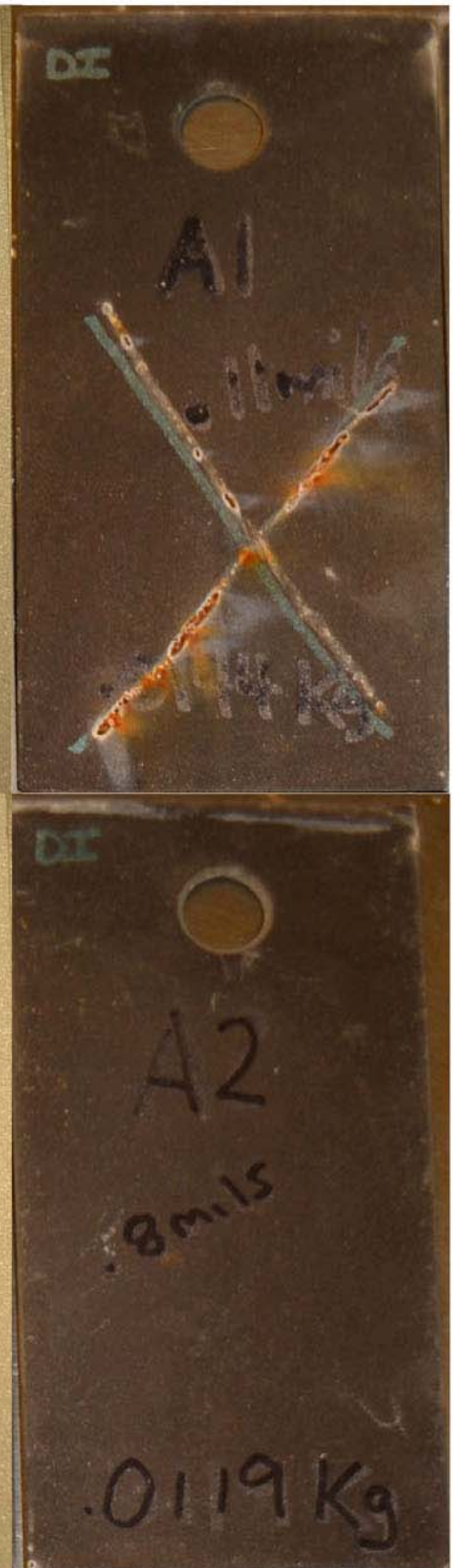


Al/Mg (95/5) – BOR
Before test

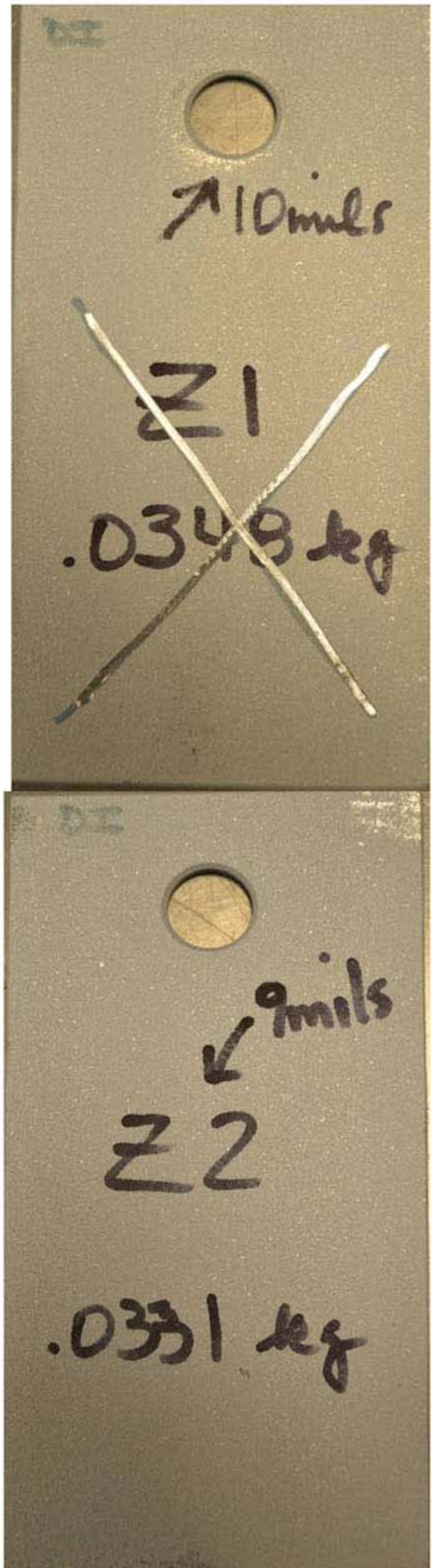
Al/Mg (95/5) – BOR
After test (5,040 hours)



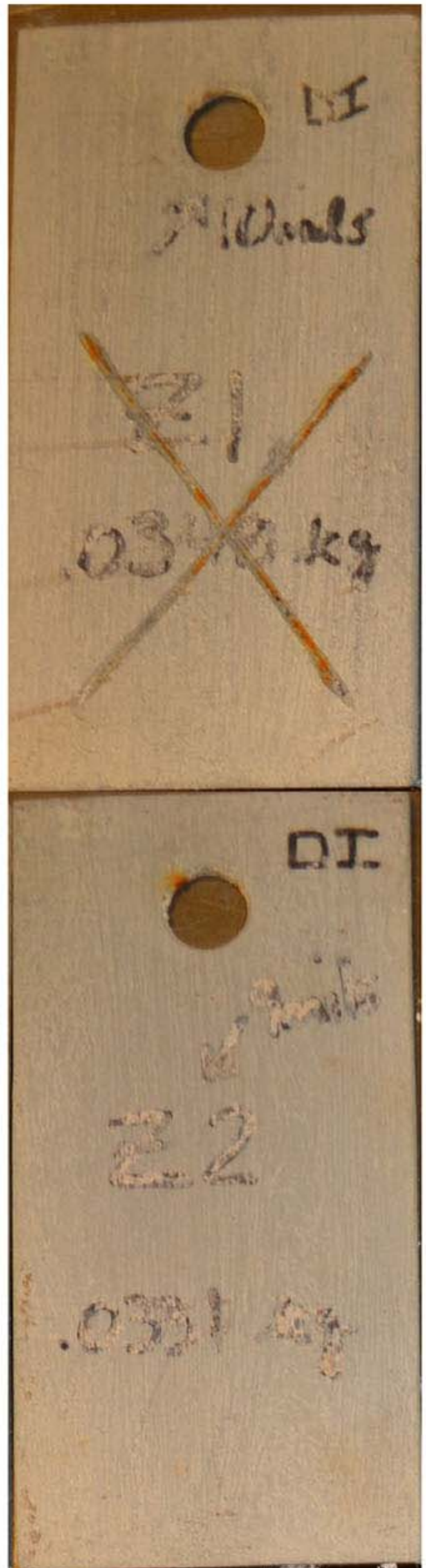
Aluminum – DI
Before test



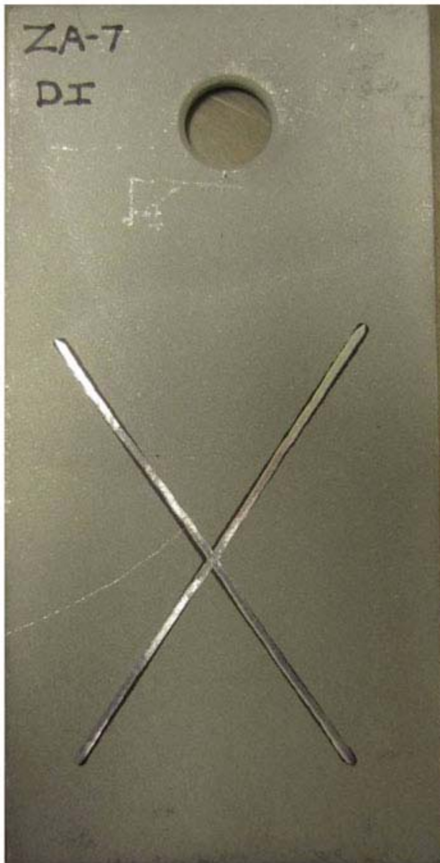
Aluminum – DI
After test (5,040 hours)



Zinc – DI
Before test

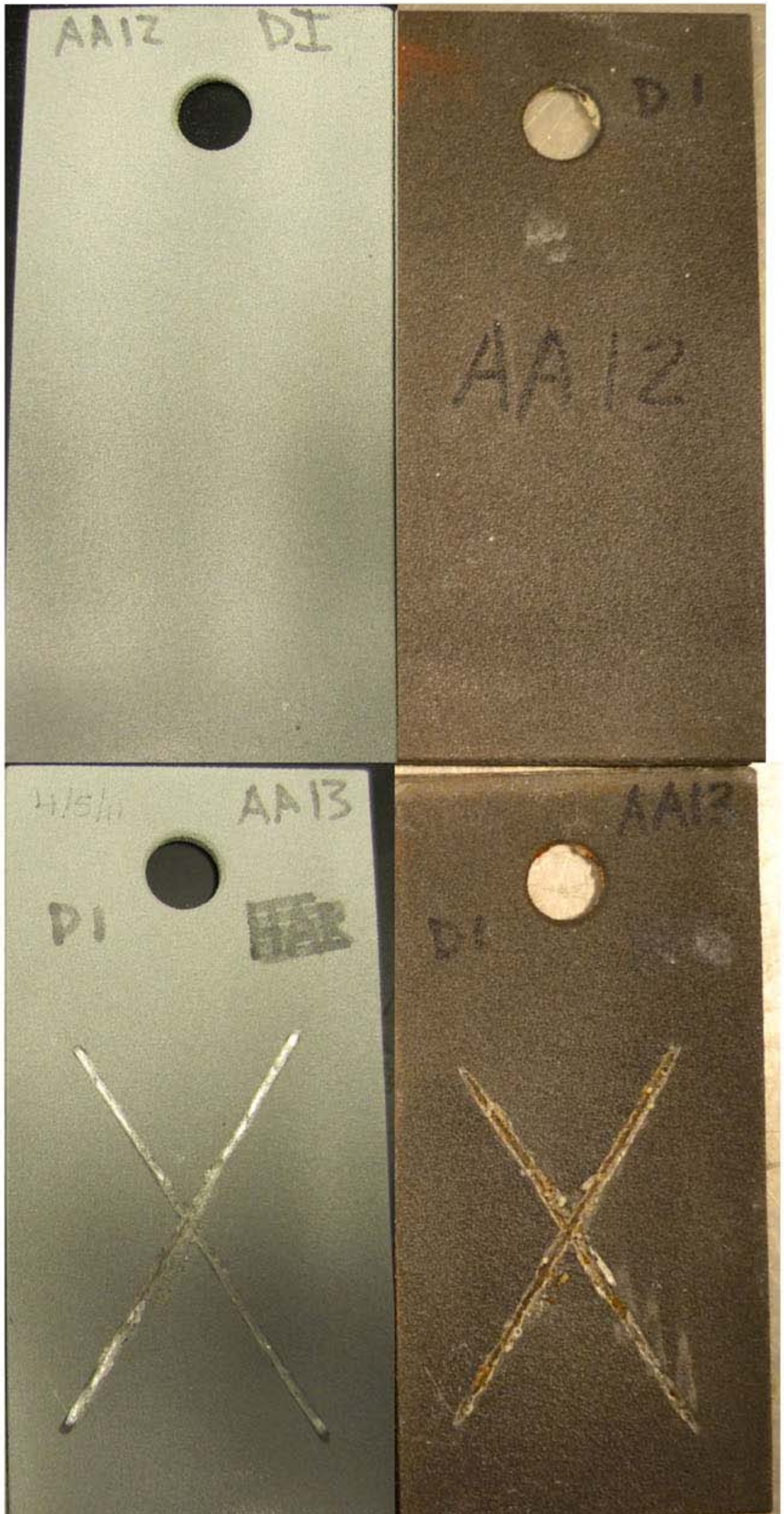


Zinc – DI
After test (5,040 hours)

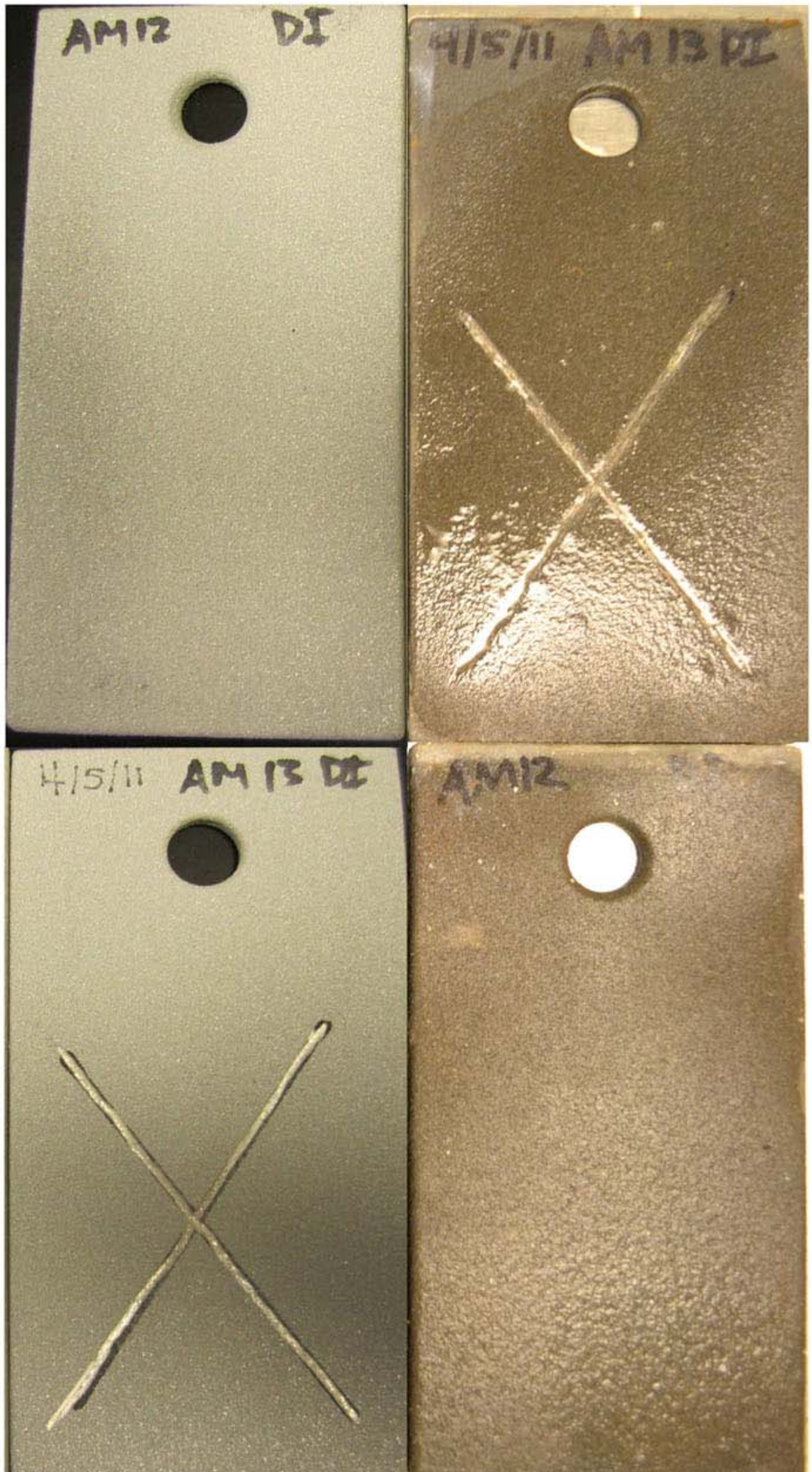


Zn/Al (85/15) – DI
Before test

Zn/Al (85/15) – DI
After test (5,040 hours)



Al/Al_2O_3 (90/10) – DI Before test	Al/Al_2O_3 (90/10) – DI After test (5,040 hours)



Al/Mg (95/5) – DI Before test	Al/Mg (95/5) – DI After test (5,040 hours)

Aluminum - DIFT
During test (888 hours)

Aluminum - DIFT
After test (5,040 hours)

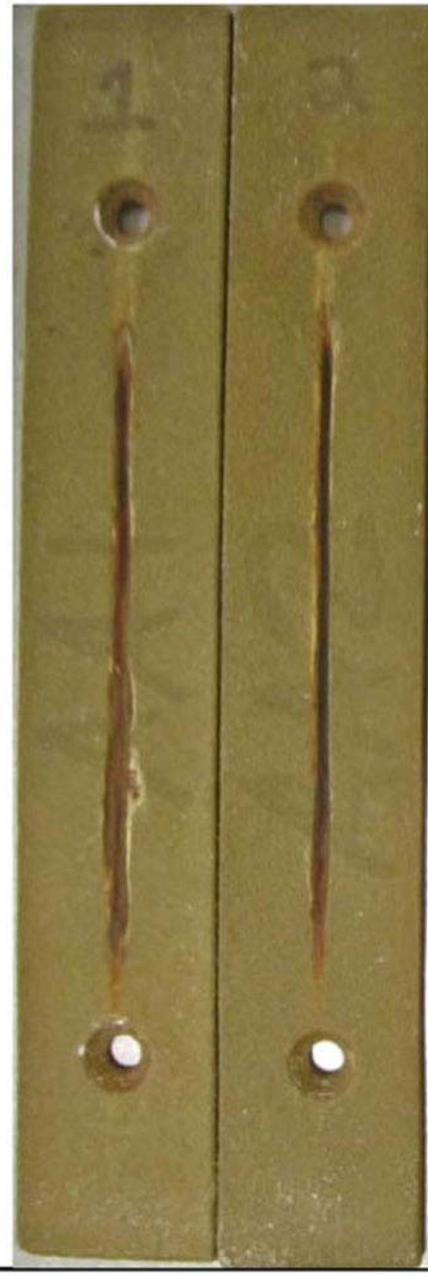
Zinc - DIFT
During test (888 hours)

Zinc - DIFT
After test (5,040 hours)

Zn/Al (85/15) - DIFT
Before test

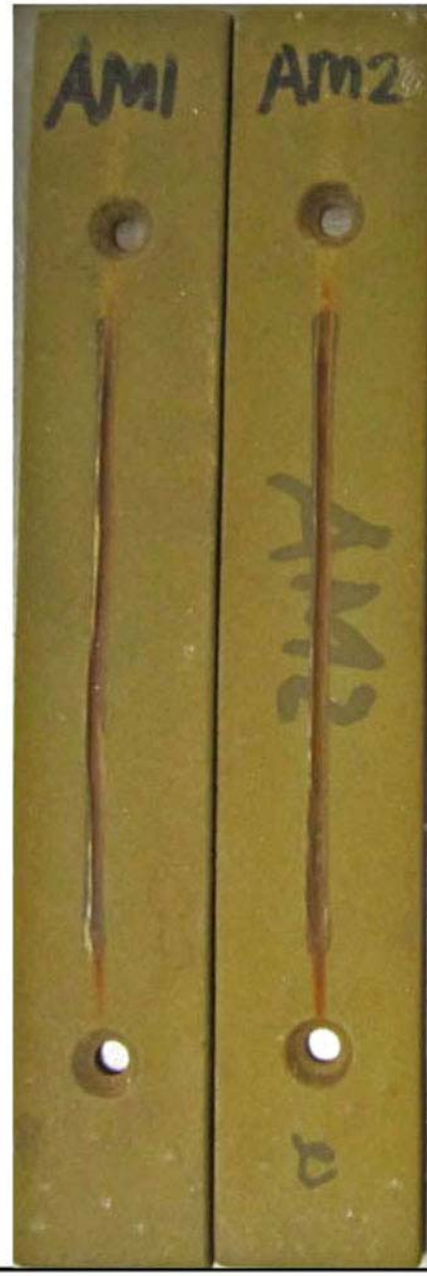
Zn/Al (85/15) - DIFT
After test (5,040 hours)

Al/Al_2O_3 (90/10) - DIFT
Before test



Al/Al_2O_3 (90/10) - DIFT
After test (5,040 hours)

Al/Mg (95/5) - DIFT
Before test



Al/Mg (95/5) - DIFT
After test (5,040 hours)

Appendix B

Electro-Impedance Spectroscopy

ELECTRO-IMPEDANCE SPECTROSCOPY METHODS AND THEORY

The sealed metalized coating samples were measured by electro-impedance spectroscopy (EIS) periodically to determine the electrochemical characteristics of the coating system. This was achieved by applying small sinusoidal perturbations and measuring the current response. The experiment gives insight to the dielectric properties of the sealed metalized coating. As water and ions penetrate the sealed coating, the insulating, capacitive properties give way to more resistive measurements. EIS measurements are used to observe these changes over time and to understand the methods of coating protection and degradation. Ohm's law is the governing equation for this measurement:

$$R = V/I \qquad \text{Eq. B-1}$$

where V is the applied voltage, I is the current, and R is the resistance. The electrical impedance, Z, is substituted into Ohm's law as an equivalent to resistance:

$$Z = V/I \qquad \text{Eq. B-2}$$

Impedance data are most often reported in the form of a Bode Plot, which provides both impedance magnitude, $|Z|$, and phase shift, θ, of the current signal. This graph clearly displays the frequency at which a given measurement was taken (Mansfield, 1996). The relationship between impedance magnitude and phase shift is provided in the following equation:

$$|Z| = V/Ie^{j\theta} \qquad \text{Eq. B-3}$$

The impedance at low frequency is often used to represent the total impedance of the coating system. This is in part due to a capacitor having near infinite impedance, revealing the coating's barrier properties or resistance to ionic transport (Kittel, 2003; Loveday, 2004). This is reported as the impedance magnitude at 0.01 Hz, $|Z|_{0.01\ Hz}$ versus sample immersion time.

The open circuit potential (OCP) was also recorded to observe the mixed corrosion potential of the steel substrate and corresponding metalized coating. When the measured OCP is more negative than that of the steel substrate, ideally by 100 to 400 millivolts, cathodic protection is occurring. Metalized coatings can be classified as a sacrificial method of cathodic protection. Oxidation reactions occur at the surface of the metal coating, and the substrate surface is preserved as the site of reduction reactions. The corresponding reactions are given in equations B-4 and B-5, respectively.

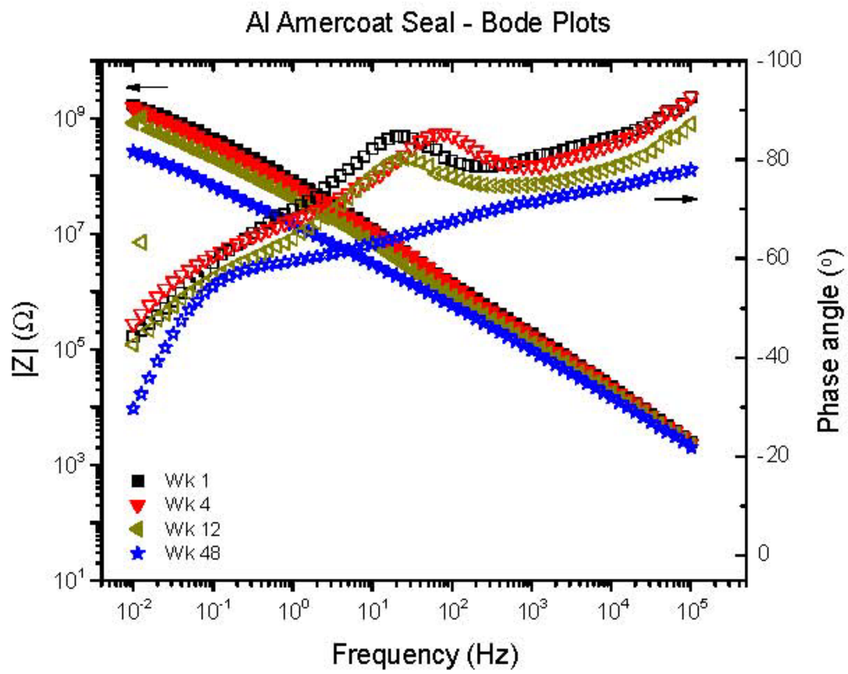
$$M_{coat} \rightarrow M_{coat}^{n+} + ne^{-} \qquad \text{Eq. B-4}$$

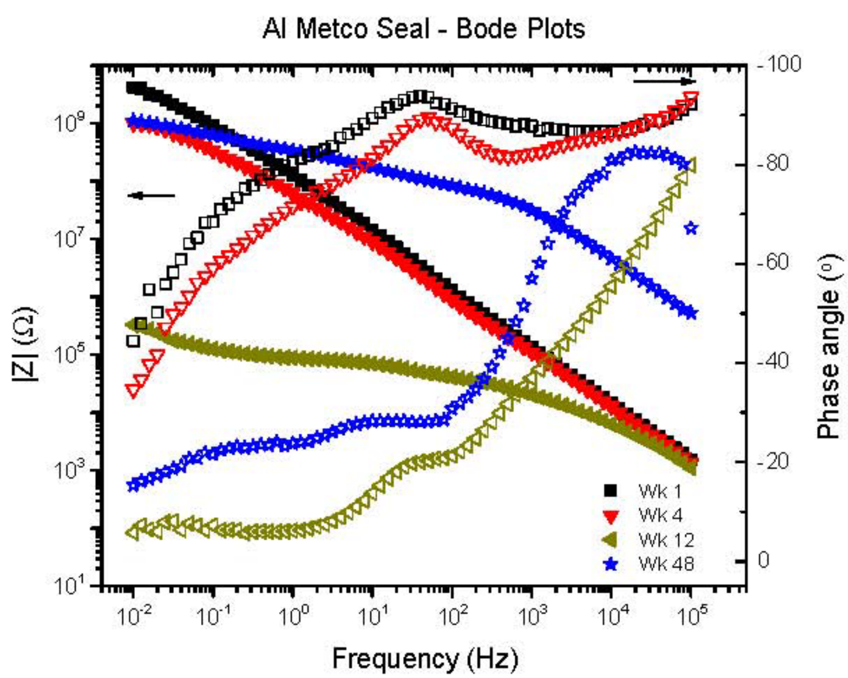
$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad \text{Eq. B-5}$$

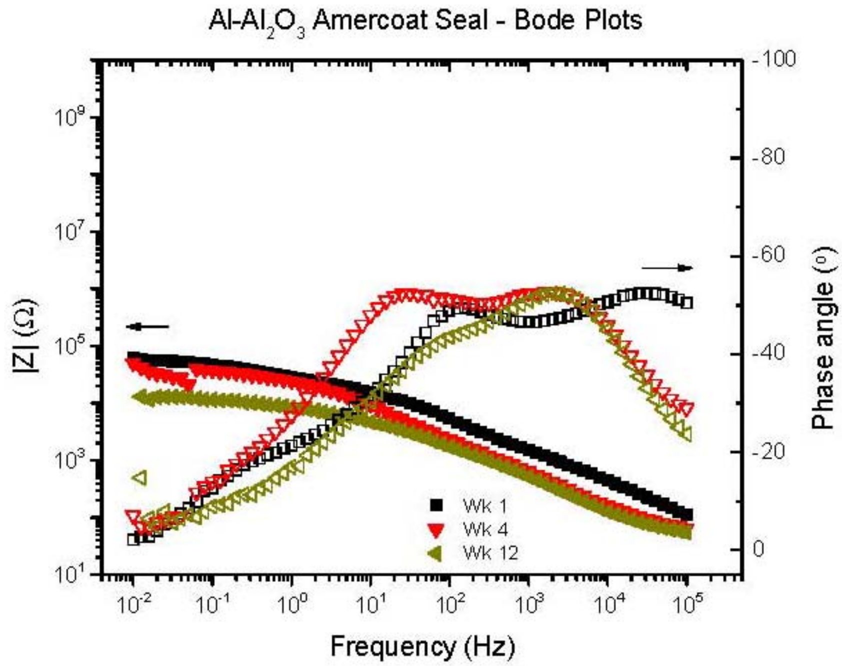
Experimental testing can be used to measure the intrinsic corrosion potential of each metal. This is easily done using a bare steel panel and the setup given in Figure 1. The metals and alloys chosen as coatings for this experiment have corrosion potentials of approximately -1.00 to -1.15 volts versus saturated calomel electrode. Therefore, it is expected that the metalized coatings will provide cathodic protection to steel. The OCP is an effective method of identifying cathodic protection in a system (Felix, 1993). Sacrificial metalized coatings could serve as a useful means of corrosion protection for metal substrates over long service times.

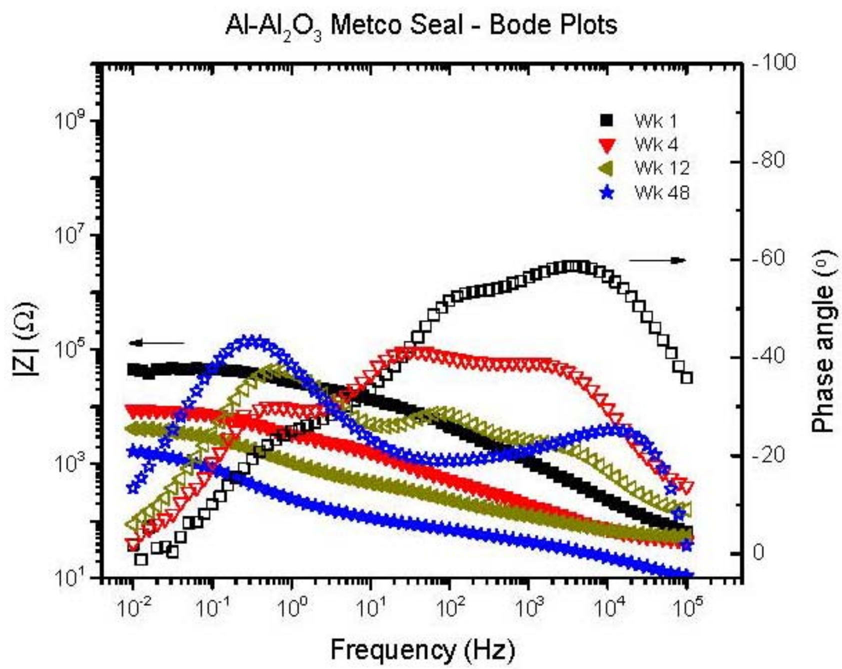
Figure 1.—Experimental setup for EIS.

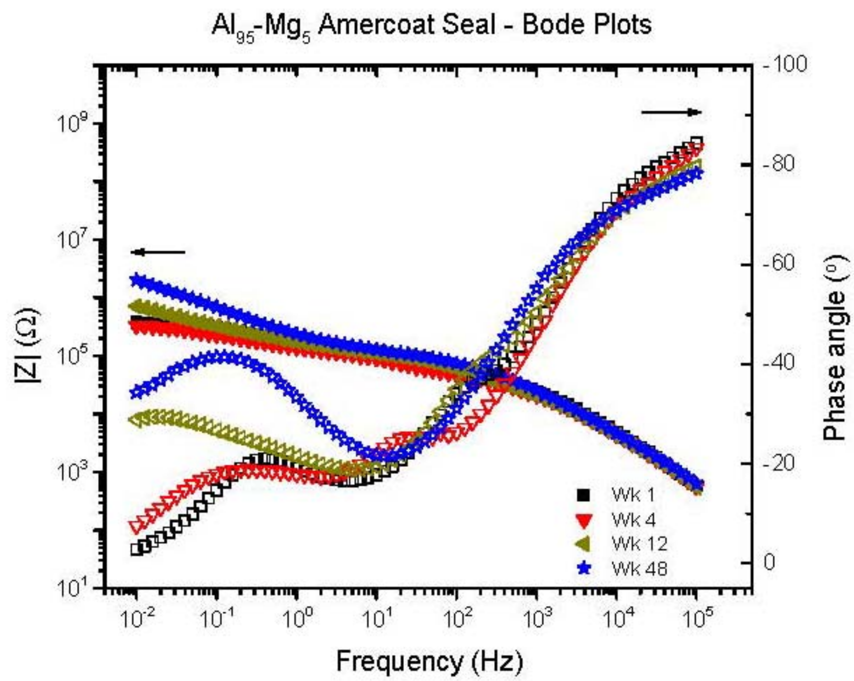
EIS Results as Bode Plots

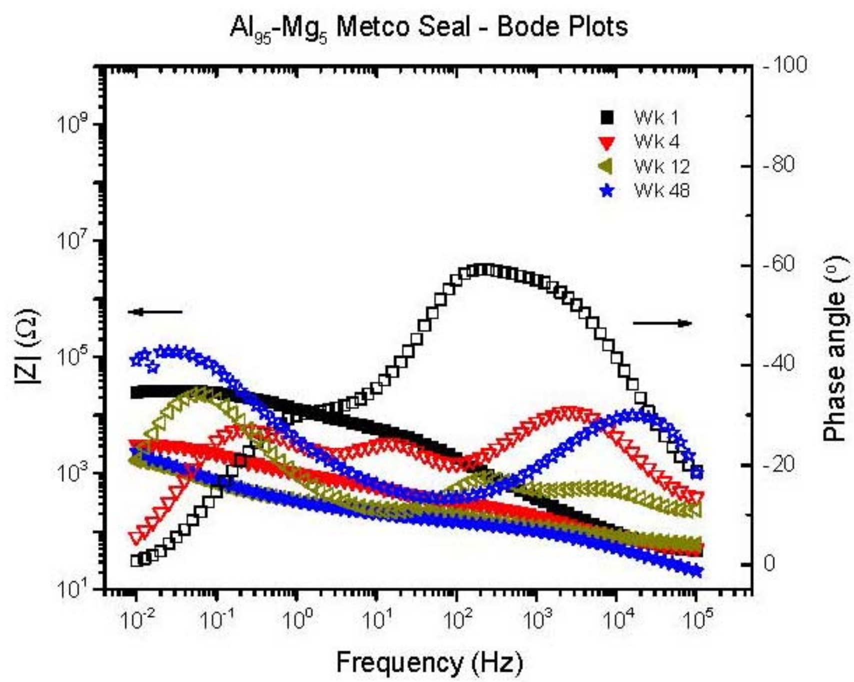




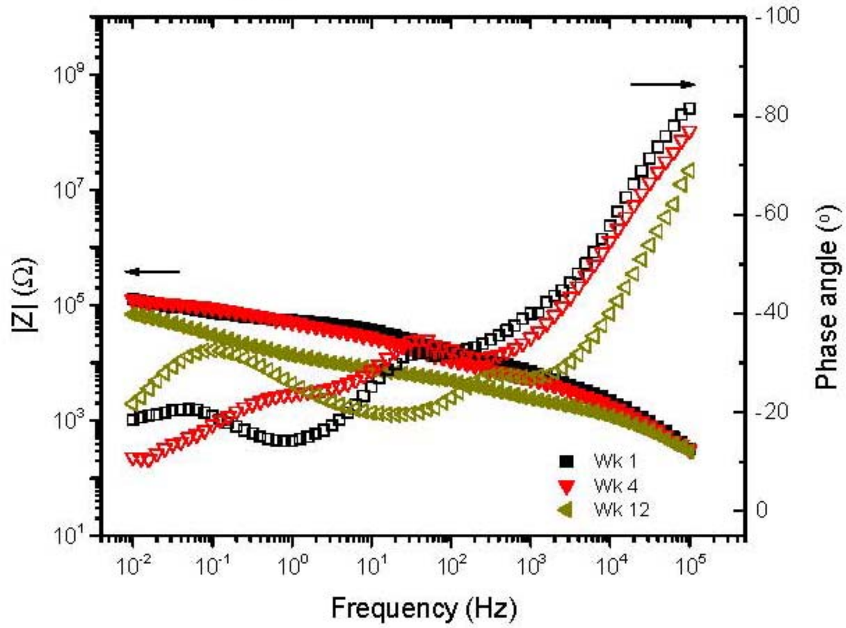

Al-Al2O3 Amercoat Seal - Bode Plots
|Z| (Ω)
Phase angle (°)
Frequency (Hz)
Wk 1
Wk 4
Wk 12


Al-Al2O3 Metco Seal - Bode Plots
|Z| (Ω)
Phase angle (°)
Frequency (Hz)
Wk 1
Wk 4
Wk 12
Wk 48

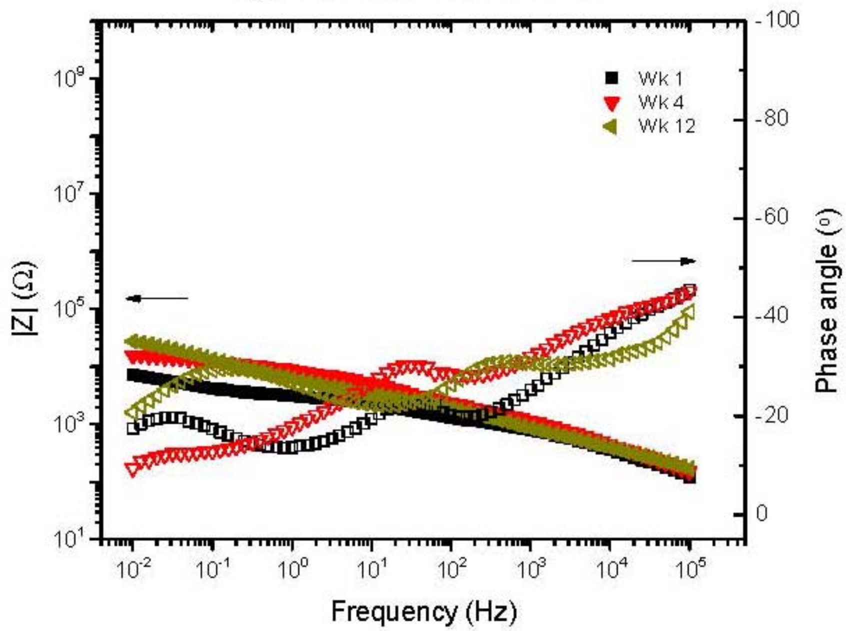

Al95-Mg5 Amercoat Seal - Bode Plots
|Z| (Ω)
Phase angle (°)
Frequency (Hz)
Wk 1
Wk 4
Wk 12
Wk 48

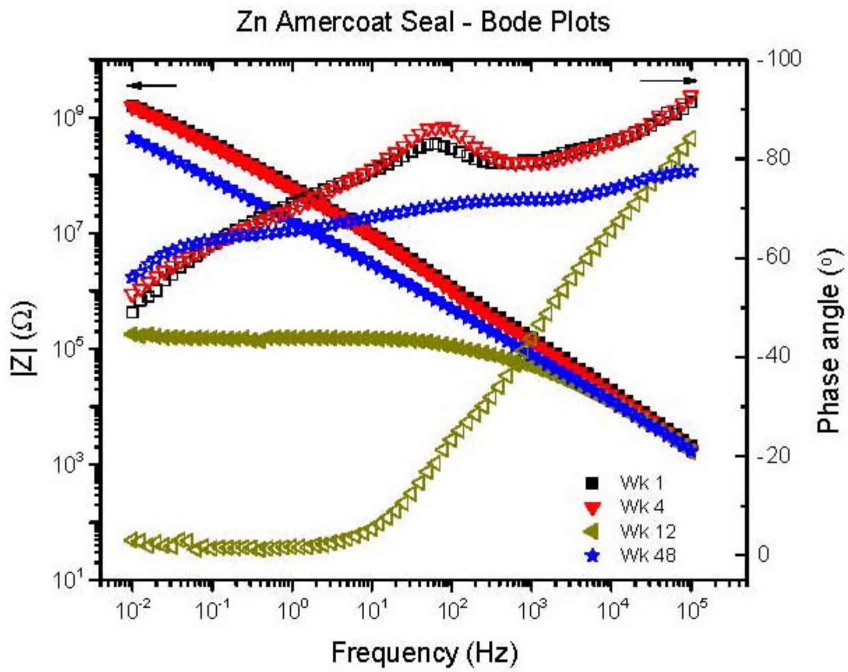

Al95-Mg5 Metco Seal - Bode Plots
|Z| (Ω)
Phase angle (°)
Frequency (Hz)
Wk 1
Wk 4
Wk 12
Wk 48

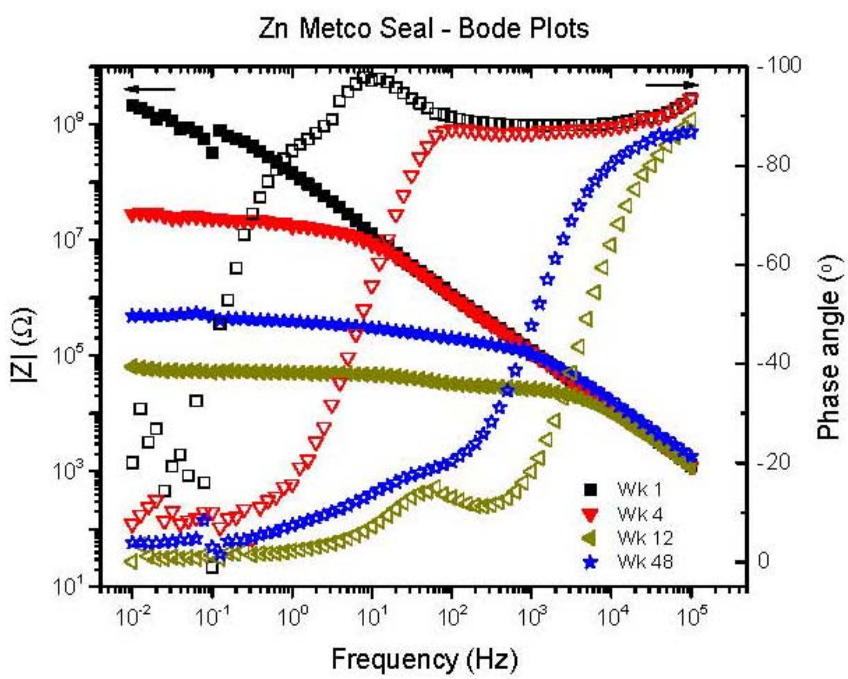
$Al_{85}Zn_{15}$ Amercoat Seal - Bode Plots



Al_{85}-Zn_{15} Metco Seal - Bode Plots




Zn Amercoat Seal - Bode Plots
|Z| (Ω)
Phase angle (°)
Frequency (Hz)
Wk 1
Wk 4
Wk 12
Wk 48


Zn Metco Seal - Bode Plots
|Z| (Ω)
Phase angle (°)
Frequency (Hz)
Wk 1
Wk 4
Wk 12
Wk 48