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A STUDY OF ZN/SN EMI-SEAL MATERIAL

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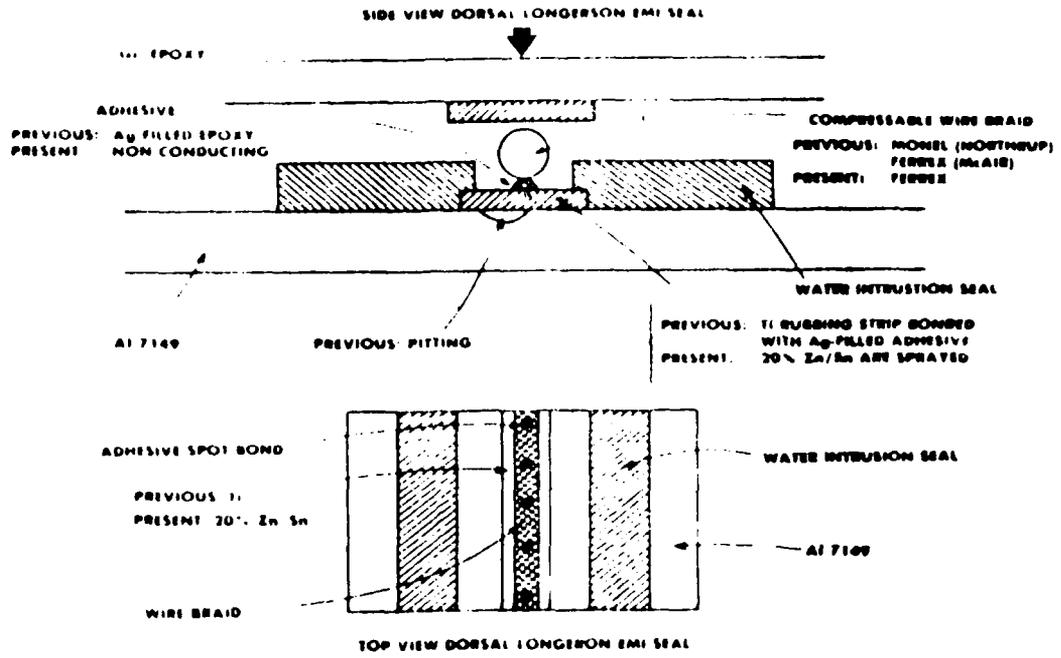
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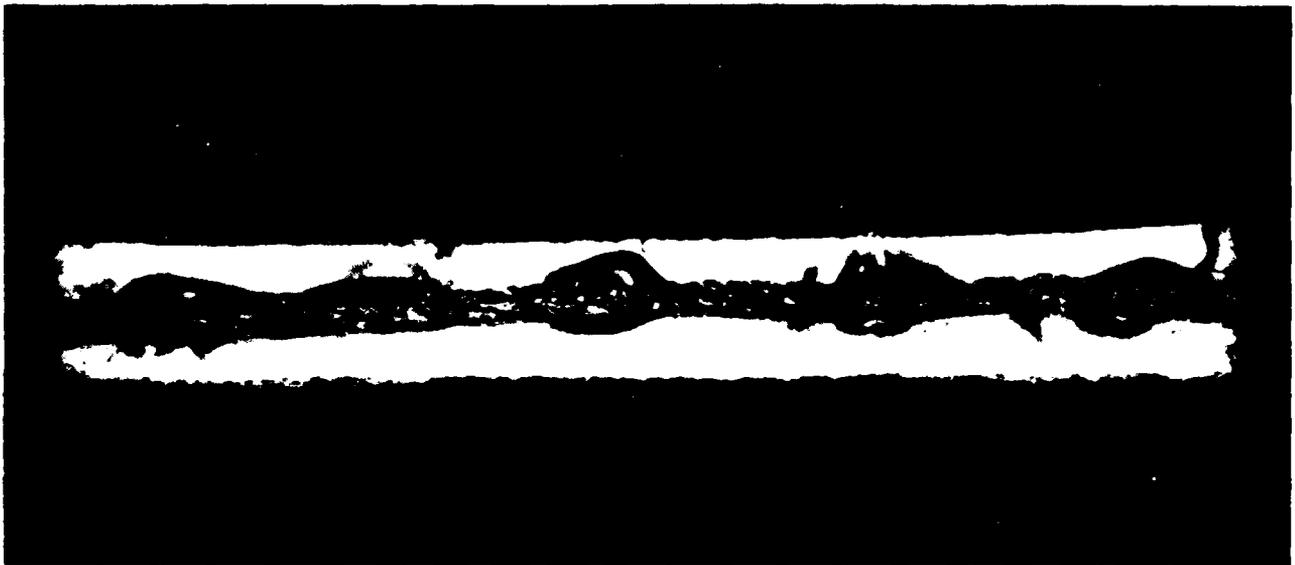
INTRODUCTION

Electromagnetic interference (EMI) seals are required for the Navy's F/A-18 aircraft because of the high electromagnetic environment present on aircraft carriers. These seals prevent the reception as well as broadcast of the electromagnetic energy. They are vital for the proper functioning of avionics and for lightning strike protection. Poor designs and galvanic incompatibility of earlier seals, such as silver-filled epoxy (adhesive material) and Ferrex braid system with aluminum alloy structural materials, have been the major reasons for excessive corrosion damages. Due to the severity of the carrier environment, the corrosion damages have been reported to be beyond the means of simple corrective maintenance efforts. During an Age Exploration Program Depot (AEPD) inspection in 1984, extensive corrosion and pitting, pits up to 70 mils deep (the maximum correctable depth is 10 mils), were found in the aluminum alloy structural materials. A quick solution was instituted to replace the silver-filled epoxy in the EMI seal with a 20% Zn/Sn arc-spray coating. Schematic diagrams of both the old and new seal designs and an unexposed Zn/Sn/Ferrex seal are shown in Figure 1. The 20% Zn/Sn coating was designed to protect the structural aluminum alloy cathodically. However, after three to six months of carrier exposure, structural corrosion damages associated with the new EMI seal were reported (1,2). Figure 2 shows an example of corrosion under the EMI seal and water intrusion on the F/A-18 Radar Nosedome Bulkhead (part number Y128). Additionally, the combination of corrosion and aircraft vibrations caused corrosive wear (dark areas in Figure 2) of the Zn/Sn coating. The formation of corrosion products may also reduce the effectiveness of the EMI seal since most oxides are insulators and create a non-conductive path. Thus, a study of the 20% Zn/Sn coating material was made and its corrosion behavior with respect to the substrate metal (i.e. Al alloy) was evaluated. Recently, a corrosion inspection of F/A-18 aircraft (AEPD, Dec 1985) was performed after one carrier deployment (3). It was reported that the Dorsal Longeron/EMI installation of the F/A-18 revealed large accumulation of powdery residue, a corrosion product. Corrosion pits were noted in the areas that were covered by the metal spray coating. The deepest pits measured were about 0.020 to 0.035 inches. The inspection report concluded that, one year after the application of the Zn/Sn coating and one carrier deployment, the new EMI installation did not perform as well as expected.

F/A-18 EMI SEAL



SCHMATIC DIAGRAM OF SEAL



UNEXPOSED SPECIMEN

Figure 1 - Schematic of the F/A-18 EMI-seal and a photograph of the specimen used.



Figure 2 - Corrosion under the EMI-seal area in the F/A-18 Radar Nosedome Bulkhead (Y128).

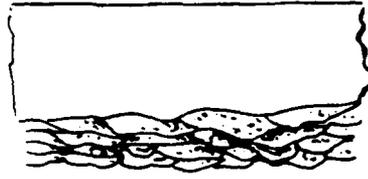
BACKGROUND

Thermal or metal spraying is a process through which metallic substances are deposited onto a substrate to form a coating. The material used for this spray process is usually in the form of wire, rod or powder. Most materials can be thermally sprayed onto a properly prepared substrate surface. Figure 3 shows a schematic of the coating process. After the coating material is melted, a gas jet transfers the molten material into an atomized spray which deposits onto the substrate by impact. A method for depositing the Zn/Sn coating is electric arc-spray; a schematic is shown in Figure 4.

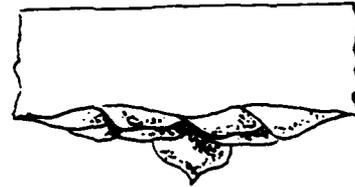
Metal coatings deposited using different thermal spray techniques are very similar in structure and properties. A high quality, dense, well bonded coating can be produced by these processes. However, changes in processing parameters may cause an increase in coating porosity (voids) and oxide content (4). Figure 5 shows a schematic of a cross sectional view of such a coating with possible defects.

Although processing parameters can be altered to affect the coating structure and properties, there will be always some porosity left in the thermal spray coating. The amount of porosity in a typical coating can range from 10 to 15% of the total volume of the coating. Researchers have shown that porosity can increase corrosion susceptibility of a coating and also of the substrate (4,5). Methods to reduce porosity are either through increase of coating thickness or thermo-mechanical treatment after spraying. A technique used to reduce porosity is glass bead blasting of the coated surfaces. However, there is an inherent danger of coating de-adhesion and increase in corrosion susceptibility of the substrate with this process. Another common method to counteract coating porosity problems is to apply a sealant to the coating which covers coating defects and reduces interfacial breakdowns due to corrosion. However, candidate sealants must be conducting to allow EMI protection. In this work, pre-treatments like glass bead blasting and a corrosion preventative compound, MIL-C-81309, were tested for corrosion control.

COATING



SUBSTRATE
IMPACT



MOLTEN
PARTICLE
ACCELERATION



HEAT SOURCE
(ELECTRIC OR
GAS)



FEEDSTOCK
(SOLID OR
POWDER)

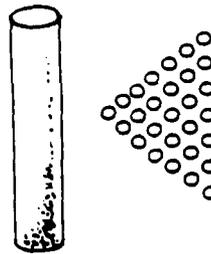


Figure 3 - Schematic of thermal spray process.

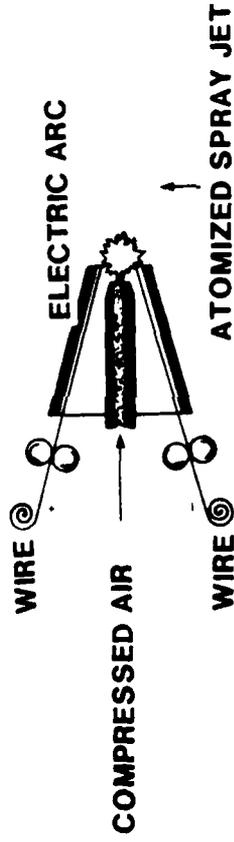


Figure 4 - Schematic of electric arc-spraying process.

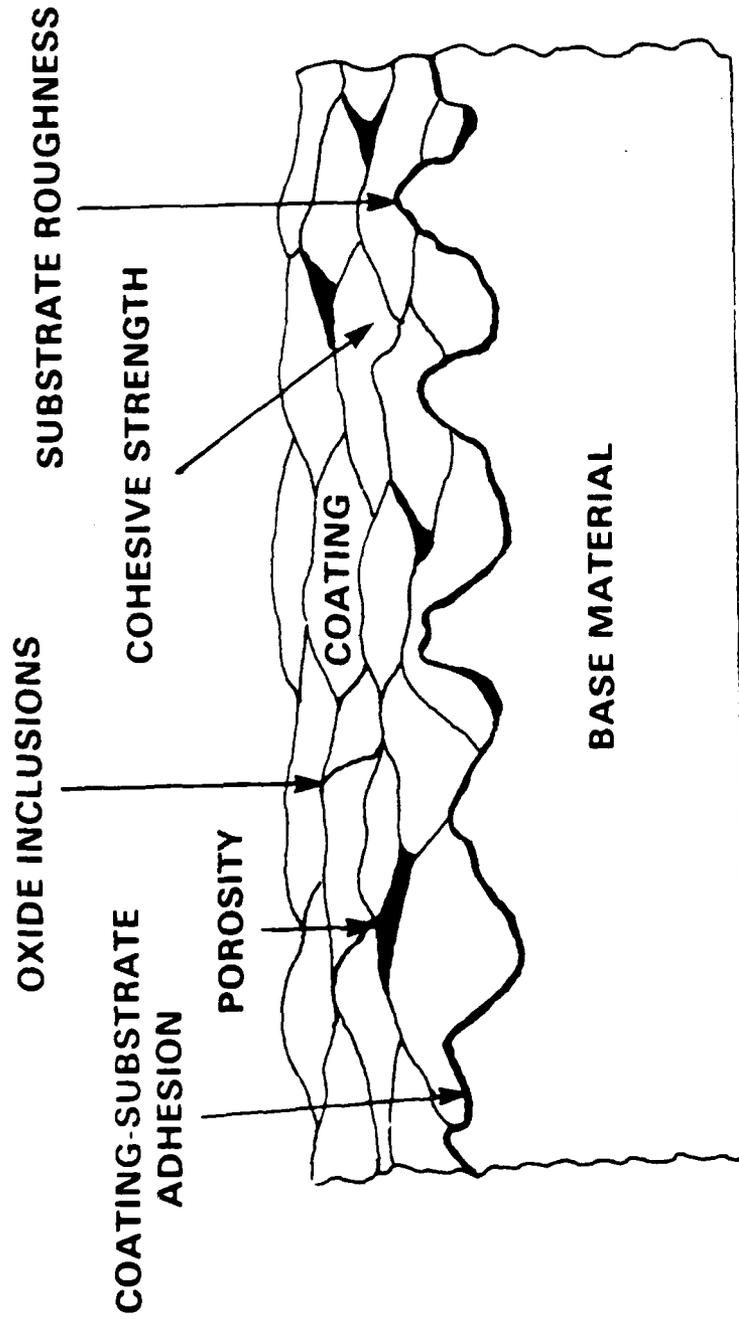


Figure 5 - Cross sectional view of the metal spray coating.

MATERIALS

The materials used were: Al 7075-T6 panels, 20% Zn/Sn wire and arc-sprayed chips, pure Sn and Zn metal sheets, and Zn/Sn coated 7149 Al panels. The Zn/Sn materials and EMI seal assemblies used in this study were provided by McDonnell Aircraft Corporation as tasked by the Corrosion Action Team.

TESTS

A shipboard exposure test of the 20% Zn/Sn arc-sprayed coating was performed by exposing a number of specimens to the carrier environment on the USS CONSTELLATION for six months. Salt spray (5% NaCl/SO₂) tests were performed on both the Zn/Sn/Monel and Zn/Sn/Ferrex braid EMI seal assemblies, as shown in Figure 1. Also tested were 7149 Al panels with a 20% Zn/Sn coating pretreated with (1) a glass bead blast, (2) a coating of MIL-C-81309, (3) a combination of (1) and (2) and (4) no pretreatment. A chemical analysis of the corrosion product, removed from the seal assemblies, was made after a five-day exposure to SO₂/salt spray. The electrochemical tests consisted of the corrosion potential, galvanic corrosion current and potentiodynamic polarization measurements. All electrochemical tests were performed in a 3.5% NaCl (pH2) solution. No special surface cleaning treatments were applied to the coating before testing.

RESULTS AND DISCUSSION

SHIPBOARD EXPOSURE

The 20% Zn/Sn arc-sprayed coating on the 7149-T7 Al alloy showed severe pitting and general corrosion of the substrate after a six-month exposure on the carrier, USS CONSTELLATION. Both the unexposed test specimens from the carrier were as shown in Figure 6. During the carrier's deployment in the Indian Ocean, pitting corrosion had penetrated through the coating and into the substrate. A cross section of an exposed carrier specimen, in Figure 7, shows pits in the aluminum substrate up to 12 mils deep and, the area of the panel where the Zn/Sn coating was removed.

SO₂/SALT SPRAY CHAMBER TEST

Figure 8 shows severe corrosion of the Zn/Sn coating in the EMI seal assembly after exposure for five days in 5% NaCl/SO₂ salt spray. The corrosion product analyzed indicated almost 98% leaching of zinc from the Zn/Sn coating leaving the EMI seal enriched in Sn.

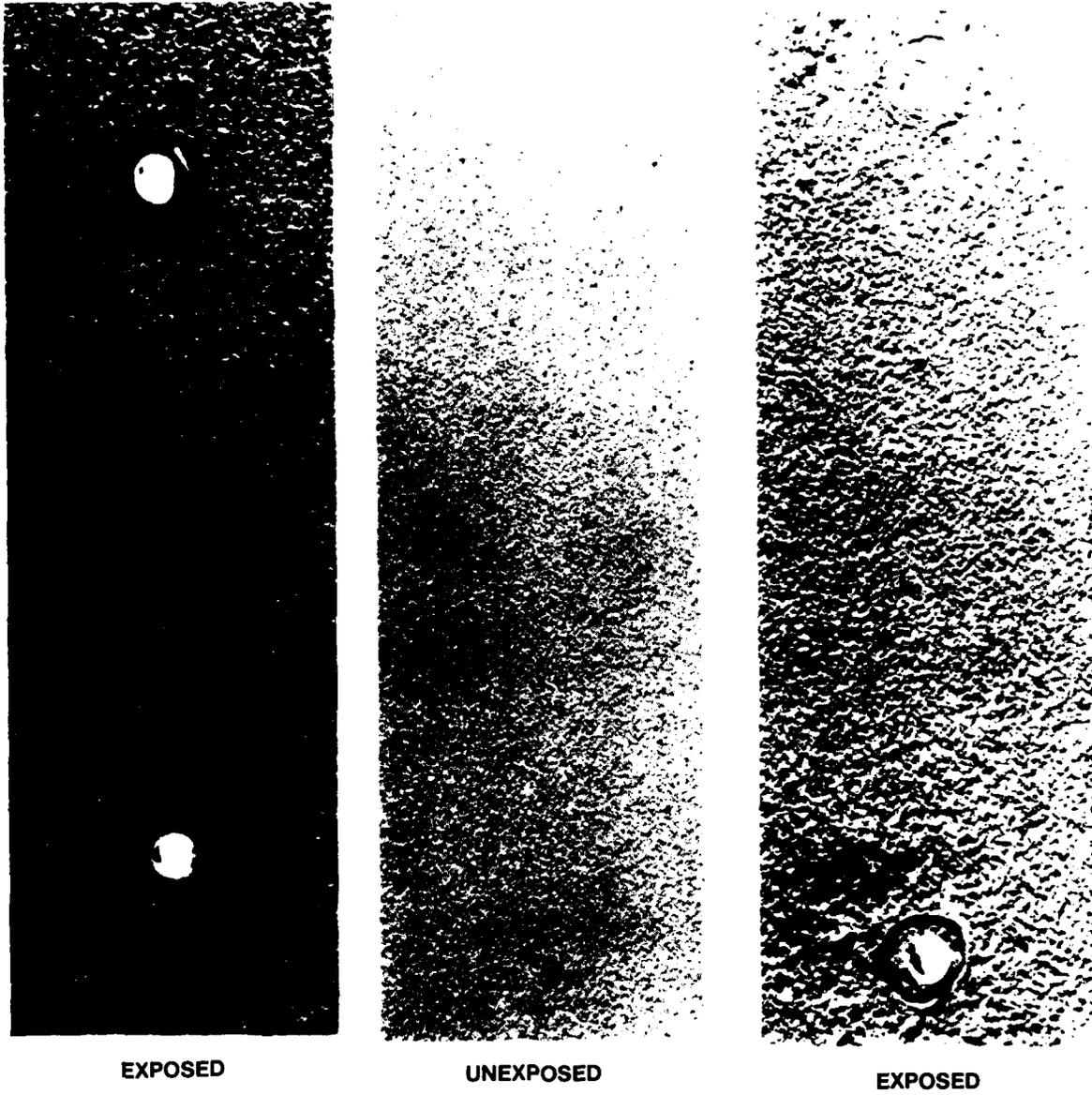
A 7149 Al panel coated with Zn/Sn, which was glass bead blasted and then coated with MIL-C-81309 and exposed to SO₂/salt spray is shown in Figure 9. Note that only half of this specimen was sprayed with MIL-C-81309. This specimen was exposed for approximately 60 hours. Specimens with only the MIL-C-81309 compound and no bead-blasting were kept 24 hours longer in the SO₂/salt spray chamber. In all cases, MIL-C-81309 compound appeared to increase the length of time before blistering occurred. As shown on the right half of Figure 9, glass bead blasting was very detrimental as it blistered the coating readily. But where the MIL-C-81309 coating was applied on the left half of specimen in Figure 9, blisters were observed to form at a much slower rate compared to the Zn/Sn coating without any pretreatment.

As mentioned earlier, extensive blistering was observed on the Zn/Sn coated Al panel test specimens. If the blisters on the test specimens were touched, for example, by a pin, they would collapse suggesting formation of gas bubbles during corrosion. The mechanism of the failure may be due to the ingress of the corrosive environment into the coating along oxide layers (cf. Figure 5) or through pores within the coating. A cross sectional view of the Zn/Sn arc-spray coating on the Al panel is shown in Figure 10. The void content in a given section of the coating varied. Also whenever incomplete mechanical bonding occurred, a void was formed (cf. Figure 10.).

ELECTROCHEMICAL

Corrosion potential versus time measurements were plotted as shown in Figure 11. Compared to 7075-T3 Al alloy, the Zn/Sn arc-spray material was highly active and closer to the open circuit potential for Zn. The high electrochemical activity of Zn leads to its high dissolution rate, hence, Zn depletion of the coating is possible. The loss of Zn from the Zn/Sn coating during the salt spray exposure tests (cf. Figure 8) confirms this result. Depletion of Zn means that the sacrificial protective properties of the coating is lost as it becomes a cathode instead, because of tin enrichment in the coating.

A potential of -0.90 volts was applied to the Zn/Sn coated 7149 panel until the anodic current (dissolution current for Zn) reached zero. At this potential Sn will not corrode as it will be a cathode and Zn will selectively dissolve away leaving the Zn/Sn coating mostly spongy (porous) and rich in Sn. Figure 12 shows a cross sectional view of such a panel after the controlled potential test.



EXPOSED TO CARRIER ENVIRONMENT FOR 6 MONTHS

Figure 6 - Corrosion of arc-sprayed Zn/Sn coating on 7149-T7 Al in a carrier environment.

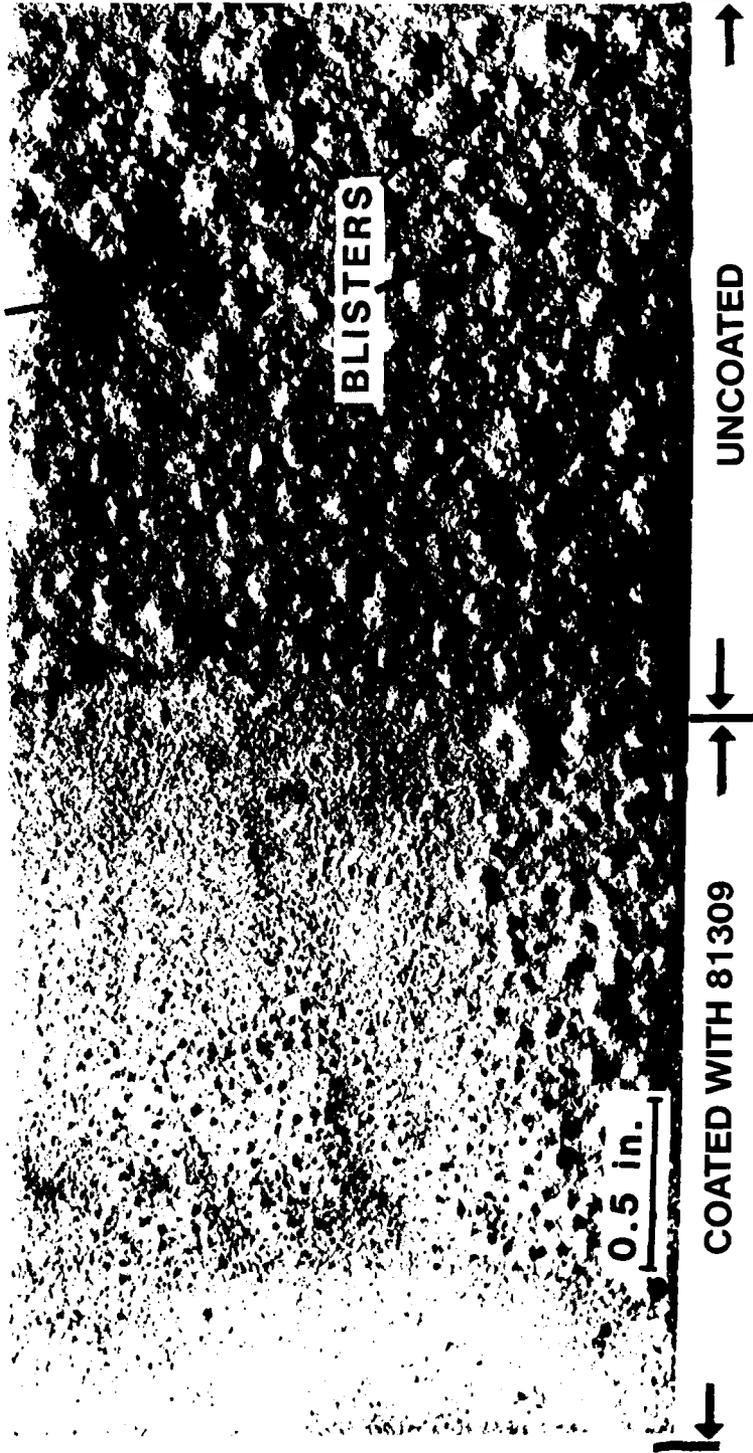


EXPOSED 6 MONTHS TO CARRIER ENVIRONMENT

Figure 7 - Cross-section view of Figure 6.

**TOP VIEW OF 20% Zn/Sn
ARC-SPRAYED COATINGS ON ALUMINUM**

**CORROSION PRODUCTS
UNDER BLISTER**



EXPOSED TO SO₂/SALT SPRAY

Figure 9 - Corrosion behavior of post-treated Zn/Sn arc-sprayed coating with Corrosion Preventative Compound and glass bead beading.

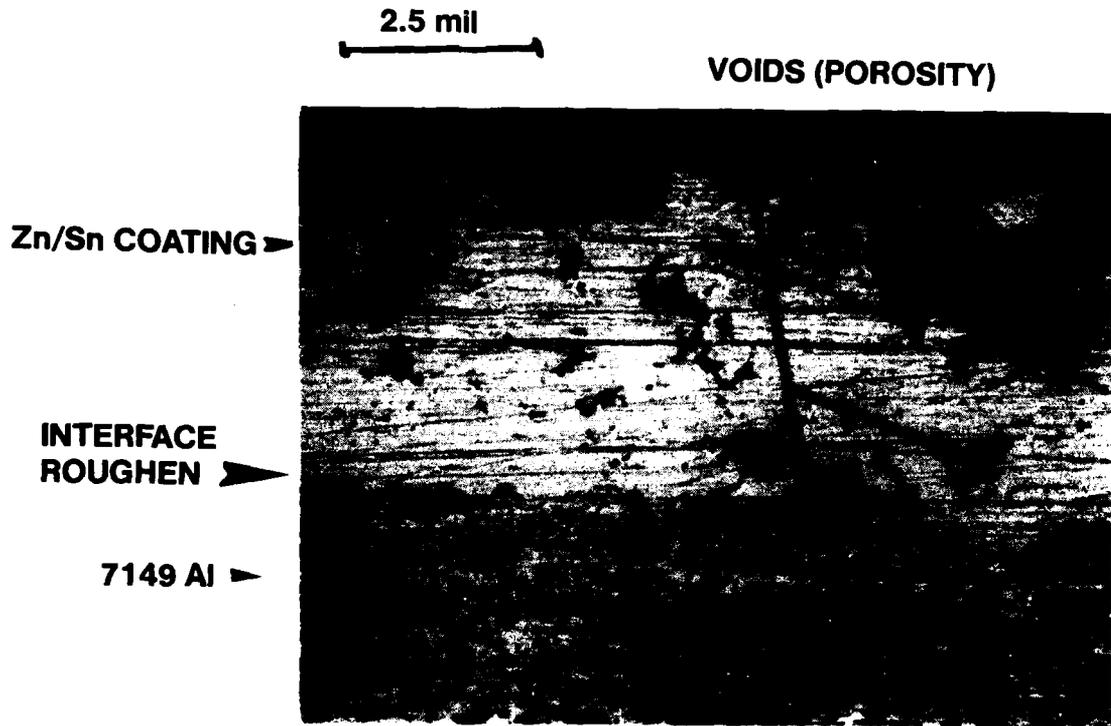


Figure 10 - Cross sectional view of the Zn/Sn coating on 7149-T7 Al panel.

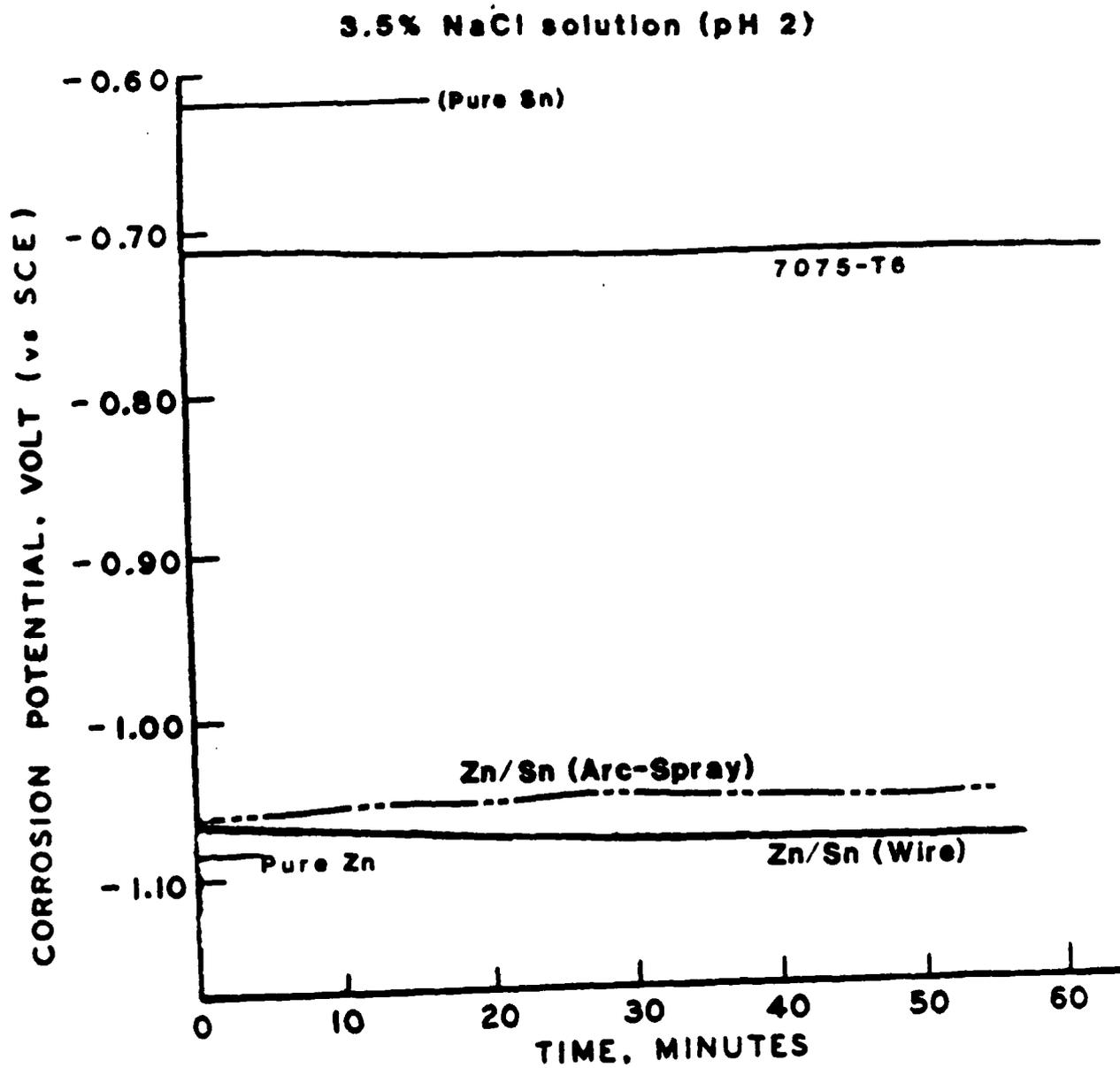


Figure 11 - Corrosion potential transients for various materials in a 3.5% NaCl solution (pH 2).

GALVANIC COUPLES

A galvanic couple between the 7075-T6 Al and Zn/Sn arc-spray coated material was made. The galvanic current between the two specimens of equal surface area was measured using a zero resistance ammeter and recorded as a function of time. It was found that high initial galvanic corrosion current (approximately 500 microamps/square centimeter) decreased to less than half of the value in about two hours of exposure. This indicates that the Zn component of the Zn/Sn arc-spray coating is sacrificed very rapidly, thus, limiting the coating's ability to protect the Al alloy substrate. However, a galvanic couple made up of 7075-T6 Al and Zn/Sn wire (material used for arc-spraying) showed a significantly initial lower corrosion current (approximately 10 microamps/square centimeter) and continued to protect the Al alloy component even after long exposures at a steady protection corrosion current of approximately 20 microamps/square centimeter. Dezincification of the Zn/Sn arc-spray coating in the former couple will result in a Sn rich coating which will act as a cathode and corrode the aluminum, instead of protecting it. Additionally, the corrosion product formed during the selective oxidation of zinc, which is in the EMI seal installation, will result in the loss of EMI protection (electrical continuity) of the structure. This agrees well with the failures observed on F/A-18 specimens (cf. Figure 8).

ELECTROCHEMICAL POLARIZATION

A potential range of -1.3 to -0.7 volts with respect to a S.C.E. reference electrode and a scan rate of 0.166 mv/sec was selected for potentiodynamic polarization measurements. Before the start of the polarization scan, the steady-state open circuit corrosion potential was determined. Potentiodynamic polarization diagrams for Zn/Sn arc-spray and wire materials were as shown in Figure 13. The anodic polarization curve for the Zn/Sn arc-spray material was at a slightly higher potential (less active) than the Zn/Sn wire indicating a lower dissolution rate for the arc-spray coating. The anodic polarization plot for the Zn/Sn arc-spray coating at potentials more positive than -950 mV showed a decrease in the current due to depletion of Zn or enrichment of Sn; this curve represented the behavior of pure Sn. If there was no depletion of Zn the extrapolated part of the anodic polarization curve for the Zn/Sn arc-spray coating would appear as shown in Figure 13. The current densities for the Zn/Sn wire material were slightly higher than for the arc-spray material. This may indicate that certain changes have occurred in the Zn/Sn material during the arc-spray process.



Figure 12 - Cross sectional view of corroded Zn/Sn coating on 7149-T7 Al after controlled potential test.

CONCLUSIONS

- A. The corrosion protection properties of the Zn/Sn arc-spray coating are very temporary in nature. From the laboratory tests, it has been estimated that the protective nature of the Zn/Sn coating may last approximately 3 to 6 months. The coating initially offers a high degree of protection but only for a short period of time. This condition changes very quickly because the coating becomes primarily rich in Sn and acts as cathode, thereby causing the substrate, Al alloy, to corrode.
- B. The carrier exposure tests have confirmed the limited protective ability of the Zn/Sn arc-spray. This is shown by general corrosion of the substrate, Al alloy panels, during long exposures.
- C. The electrochemical tests have shown that the Zn/Sn arc-spray is galvanically incompatible with Al alloys as it becomes cathodic with time (due to depletion of Zn) and may corrode through the substrate structure instead of protecting it.
- D. Corrosion product of the Zn/Sn coating produce nonconductive pathways which could be detrimental to the EMI-seal protective properties. The interfacial corrosion between the coating and the Al alloy substrate caused blistering and created corrosion pathways; porosity in the arc-spray coating was the leading cause.
- E. Glass bead blasting after the arc-spraying caused severe debonding of the Zn/Sn coating and accelerated the rate of blister formation.
- F. MIL-C-81309, Corrosion Preventative Compound, reduced the ingress of environment into the coating, therefore enhanced the time before blistering was observed.

REFERENCES

1. STRKFITRON ONE ONE THREE 040808Z May 85
2. COMCARAIRWING FOURTEEN 020508Z Jun 85
3. NAVAIRREWORKFAC 251646Z Feb 86
4. "Metallized Coatings for Corrosion Control of Naval Ship Structures and Components", National Materials Advisory Board, NMAB Report #409, (1983).
5. Shaw, B.A., "Corrosion Barrier Coatings-Investigation of Thermal Spray Coating Characteristics", Report DTNSRDC/SME-83/89.

RECOMMENDATIONS

It is recommended that the Zn/Sn arc-spray coating should not be used on the Navy's F/A-18 aircraft for the EMI-seal. For the aircraft containing the Zn/Sn coating a maximum of a 42-day corrosion inspection and maintenance interval should be instituted. Seal systems which will provide long term EMI and corrosion protection should be investigated. In the interim, Corrosion Preventative Compound, MIL-C-81309 should be applied on the Zn/Sn coating whenever possible. Glass bead blasting of the Zn/Sn coating should not be attempted as it forms blisters in the coating.

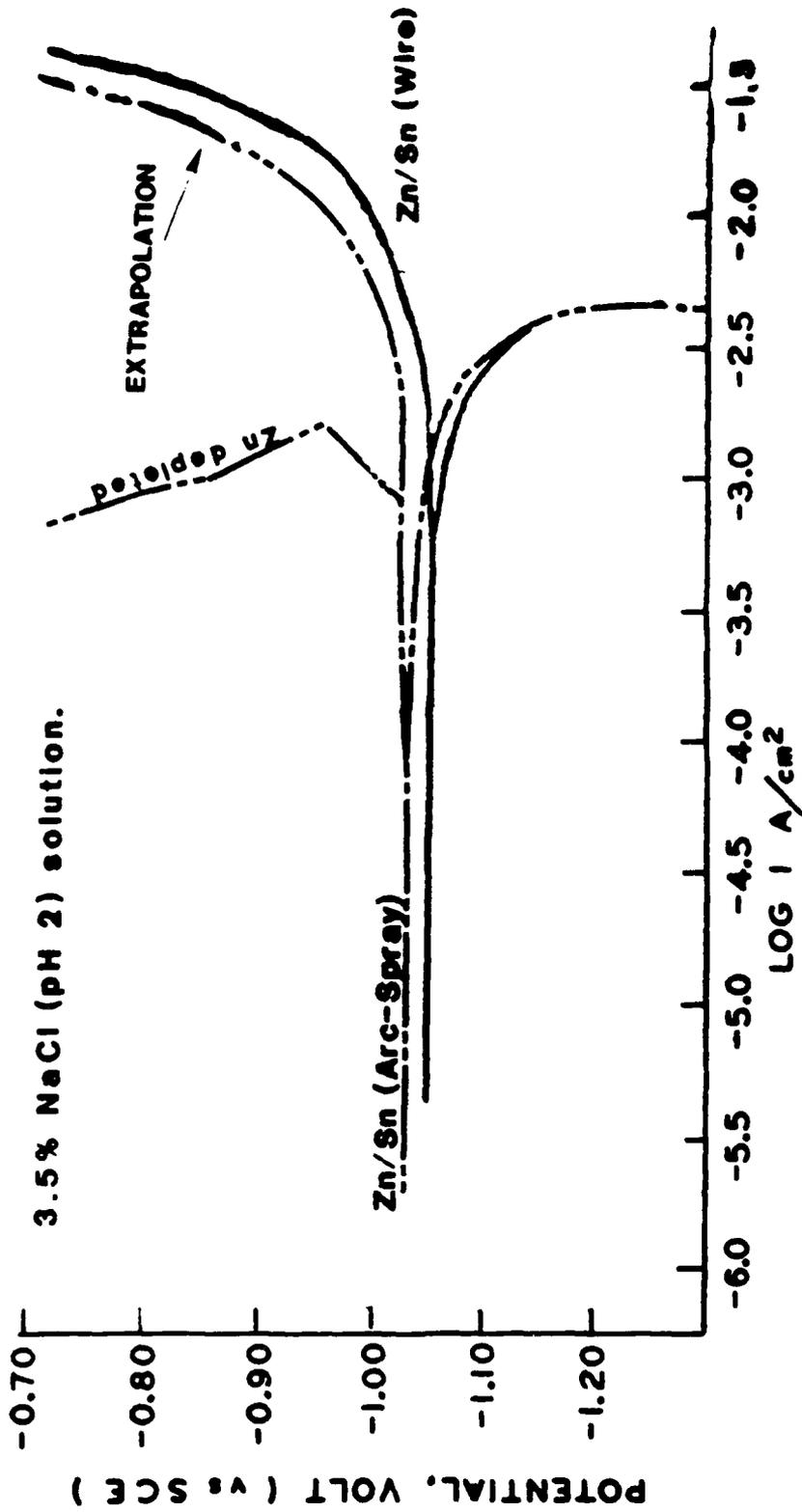


Figure 13 - Polarization diagrams for Zn/Sn material in a 3.5% solution (pH 2).

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