

Cadmium Alternative Coating Corrosion Performance on 4340 Steel

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ABSTRACT

Cadmium has been used widely for coating steel structural components and threaded assemblies principally to provide protection from corrosion and in-service hydrogen embrittlement. However, Cd is highly toxic, and the environmental and health problems resulting from its use have become a serious concern. In order to find viable replacements for the Navy, this study was conducted as part of a leveraged effort with the Joint Cadmium Alternatives Team (JCAT). In this study, Cd, Zn-6Ni and Zn-13Ni were electrocoated on 4340 steel specimens. In addition, Al coatings were applied by both ion vapor deposition (IVD) and electroplating. The relative ability of each coating to protect the substrate steel from corrosion fatigue and stress corrosion cracking was evaluated. The induced residual stresses in the coating and substrate were measured as-deposited. Then, the specimens were subjected to tests of fatigue in air and 3.5% NaCl solution and stress corrosion cracking (SCC) in 3.5% NaCl solution. As a reference, bare 4340 steel specimens were subjected to the identical tests.

The residual stress in the substrate was determined to be tensile for the bare specimen and compressive for the coated specimens. Among the employed coatings, the electroplated Al resulted in the greatest magnitude and depth of peak compressive residual stress and thickest layer of compression. All coatings were found to shorten the fatigue life in air but protect the substrate against corrosion fatigue in 3.5% NaCl solution. The electroplated Al, Zn-6Ni and Zn-13Ni, and IVD Al coatings were not as effective as the Cd coating for substrate protection. Among the Cd replacement candidates, the electroplated Al coating provided the best protection of 4340 steel against fatigue and SCC in 3.5% NaCl solution, while IVD Al was the next best.

INTRODUCTION

Cd coating has been widely used to protect iron and steel components against corrosion. Since Cd is anodic to Fe, the underlying ferrous metal is protected at the expense of the Cd coating, even if it is

scratched or nicked, exposing the substrate. In addition, Cd has other useful engineering properties, including natural lubricity. When corrosion products are formed on Cd electrocoated parts, they are not voluminous, so there is minimal change in dimension. Cd has excellent electrical conductivity and low contact resistance. Cd coated steel can be formed and shaped because of the good ductility of the Cd. Malleable iron, cast iron, powdered metals, and other hard-to-plate surfaces can be coated with Cd. These properties are responsible for the wide usage of Cd coating on structural components and threaded assemblies.

However, the environmental and health problems associated with Cd continue to be a serious concern. Exposure to respirable particles/fumes of Cd and its compounds represents the most significant risk factor. Cd and its compounds are not readily absorbed through the skin, but they can be ingested. Inhaling Cd or its compounds is linked with increased incidence of cancer, and allows the toxic metal to enter the blood stream. Once in the blood, Cd readily accumulates in the kidney, degrading its function. Thus, a viable Cd replacement must be found. Potential replacements include electroplated Al and Zn-based alloys, and IVD Al.

Electroplated Al is highly corrosion resistant and non-toxic, and does not require post-coating heat treatment for hydrogen embrittlement relief. The Al electroplating process is performed in a closed system in toluene solvent and hazardous organometallic electrolyte. The resulting pure Al deposit is fully dense and pore-free, providing a corrosion resistant barrier. The tenacious, non-degenerating oxide surface acts as a barrier layer, and the metallic high-purity Al layer serves as a sacrificial anode to nearly any metal substrate. In a recent study, electroplated Al surpassed the corrosion resistance of IVD Al, Cd, Zn-Ni and Sn-Zn coatings¹.

IVD is a vacuum deposition process developed by McDonnell Aircraft Company^{2,3}. Al is deposited in a vacuum chamber by evaporation under weak plasma bombardment of the substrate. The IVD Al coating and process are environmentally clean and produce no hazardous waste. Al can be used at temperatures up to 950°F, whereas Cd is limited to 450°F^{2,3}. The IVD Al coating process does not induce hydrogen embrittlement in high strength steel. However, the resulting coating is not fully dense, leading to potential corrosion attack on the substrate. The coating can be densified (or burnished) by peening to provide sufficient corrosion resistance²⁻⁴.

Interest in Zn alloy coatings has primarily been directed to improving the corrosion resistance of the deposit relative to pure Zn. The use of Zn alloys provides some advantages. First, these alloys are less hazardous and less of an environment and health risk. Second, they can be designed to maintain anodic protection to steel, but remain less electrochemically active than pure Zn. Therefore, Zn alloy coatings can still be sacrificial to steel components, but corrode more slowly and protect longer than Zn when exposed to a corrosive environment. Among the known candidate alloys, Zn-Ni, Zn-Fe, Zn-Co and Zn-Sn, Zn-Ni alloys have received more attention than the others. However, the Zn-Ni plating process induces hydrogen embrittlement in high strength steel, and so the coated components must receive subsequent hydrogen embrittlement relief. Zn-Ni alloys, containing from 5 to 15% Ni, provide good corrosion resistance⁵⁻⁹.

The effectiveness of these potential replacement coatings for protecting the substrate steel from corrosion fatigue and stress corrosion cracking has not been fully understood. A study was conducted to clarify the effectiveness, and the results are reported in this paper.

EXPERIMENTAL PROCEDURE

1. Substrate Material and Specimen

As the substrate material, a 4340 steel plate of 3.8 x 15 x 30 cm was chosen. Its chemical composition is shown in Table 1. From the plate, round rod specimens were prepared in a lathe and square bar specimens by means of electric discharge machining (EDM). Surfaces were manually polished with 120 grit emery cloth after machining. Specimen dimensions were: round tension test specimens of diameter 6.4 mm and gage length 25.4 mm in longitudinal (L-) orientation; round hourglass fatigue test specimens of minimum diameter 6.4 mm and gage length 49.3 mm in L-orientation; and square bar stress corrosion cracking test specimens of 10 x 10 x 50.8 mm with a central v-notch of angle 60°, tip radius 0.15 mm and depth 5 mm in L-T orientation.

TABLE 1 – Chemical Composition of 4340 Steel

Element	Weight %	Element	Weight %	Element	Weight %
C	0.42	Cu	0.17	N	0.065
Mn	0.75	Ni	1.67	Cb	0.002
P	0.13	Cr	0.83	Sn	0.009
S	0.006	Al	0.03	Mo	0.21
Si	0.22	V	0.005	Fe	Balance

2. Coating

The machined and polished specimens were electroplated with Al, Cd, Zn-6Ni and Zn-13Ni, and also vacuum coated with IVD Al. A summary of each process is provided below.

Electroplated Al: High purity Al was electrocoated on the specimens per MIL-DTL-83488 Class 2, Type 2. Specimens were subjected to chromate treatment per MIL-DTL-5541, Type 1, Class 1A. Specimens were coated by AlumiPlate Inc.

IVD Al: Al was ion vapor deposited on the specimens per MIL-DTL-83488 Class 2, Type 2. Specimens were subjected to chromate treatment per MIL-DTL-5541, Type 1, Class 1A. Specimens were coated by the Navy's Fleet Readiness Center Southwest (FRC-SW, North Island).

Cd: Cd was electrocoated on the specimens per MIL-STD-870. Specimens were subjected to the standard hydrogen embrittlement relief, and subsequent chromate treatment per MIL-DTL-5541, Type 1, Class 1A. Specimens were coated by FRC-SW.

Zn-6Ni: Zn-6Ni alloy was electrocoated on the specimens per AMS 2417G, Type 2, alkaline Zn-Ni Plating (IZ-260 product) for 30 minutes at room temperature. Then the specimens were baked at 375°F for 23 hours and chromate conversion coated. Specimens were coated by Dipsol of America.

Zn-13Ni: Zn-13Ni alloy was electrocoated on the specimen per IZ-C17 Alkaline Zn-Ni Plating Process (3 A/dm² at room temperature for 45 min). Specimens were subjected to the standard hydrogen embrittlement relief, and subsequent chromate treatment per manufacturer recommendation. Specimens were coated by Dipsol of America.

Coated specimens were examined to verify that coatings covered the specimens fully, including the notch. The coating thickness was measured from the backscattered electron image of specimen cross-sections. Chemical composition was determined using electron microprobe with wavelength dispersive X-ray spectrometer, under conditions of 15 keV, 30 nA, 1 μ m spot size and 20 second counting time. In addition, the residual stresses in the coating and substrate were measured with the aid of X-ray diffraction. For reference, the residual stress profile in a bare specimen was also determined.

3. Tension and Fatigue Tests

A closed-loop servohydraulic mechanical test machine, Interlaken, of 90 KN (20 kip) loading capacity, was employed for the tension and fatigue tests. The tension test was conducted in air using the round tension specimen, following ASTM E 8, Standard Test Methods for Tension Testing of Metallic Materials¹⁰. The tensile loading rate was 0.076 mm/min (0.003 in/min). The fatigue test was carried out with the hourglass specimen under stress control in cyclic tension-tension at stress ratio 0.1 and frequency 10 Hz in air as well as aqueous 3.5% NaCl solution (pH 7.3). This test followed ASTM E 466, Standard Practice for Conducting Force Controlled Constant Amplitude Axial Fatigue Tests of Metallic Materials¹¹.

4. Open Circuit Potential Measurement

Open circuit potential (OCP) is an electrochemical parameter of corrosion resistance which is measurable in a corrosion cell, consisting of a specimen electrode and a reference electrode [saturated calomel electrode (SCE)] in an electrolyte. In this investigation, the specimen electrode was a rectangular flat sheet, 38 x 7 x 1 mm, bare or coated. The specimen surface was coated with Stop-Off Lacquer, except for a 5 x 7 mm area on one face. This area became the working electrode in the electrolyte, aqueous 3.5% NaCl solution of pH 7.3. The specimen and reference electrodes were connected to the ground terminals of an electrometer, and the change of electrode potential with time was recorded in reference to the SCE. The electrode potential, stabilized after 24 hours, was taken as the OCP.

5. SCC Test

Since the cantilever bend and double cantilever beam SCC tests are long duration tests, an accelerated SCC test¹² was conducted in a RSL 1000 SI-Multi-Mode Test System. This System included a bending frame, a tensile loading frame, and an electrolyte reservoir with a pump for circulation, an SCE reference electrode, a platinum counter-electrode, a computer and a printer. The as-machined, as-coated (un-precracked) and precracked specimens were step-loaded until the load dropped in four-point bending under constant displacement control, while held at a given potential in aqueous 3.5% NaCl solution of pH 7.3. The load drop corresponded to the threshold stress intensity for SCC, K_{OSCC} for the as-machined and as-coated (un-precracked) specimens and K_{ISCC} for the precracked specimens. The K_{OSCC} and K_{ISCC} were calculated as a function of applied bending moment and notch depth or crack length, using the following equation.

$$K_{OSCC} \text{ or } K_{ISCC} = \sigma \sqrt{\pi a} * F(a/W)$$

where

σ : gross stress = $6M/bW^2$

M: bending moment = Px

P: applied load

x: moment arm length

b: specimen thickness

W: specimen width

a: notch depth or crack length

$$F(a/W) = 1.122 - 1.40(a/W) + 7.33(a/W)^2 - 12.08(a/W)^3 + 14.0(a/W)^4$$

The K_{OSCC} and K_{ISCC} values, determined at the open circuit potential, are the measure of SCC resistance of as-machined or as-coated (un-precracked) and precracked specimens, respectively, under free corrosion condition. In this investigation, K_{OSCC} was defined especially for the coated specimens, which should not be precracked.

RESULTS

1. Microstructure

The microstructure of the substrate is a mixture of tempered martensite and carbides, typical of 4340 steel, hardened and tempered, Figure 1.



FIGURE 1 - Microstructure of 4340 Steel

2. Coating Thickness and Composition

The measured coating thickness and chemical composition are shown in Tables 2 and 3, respectively.

TABLE 2 – Thickness of Coating

Coating	Thickness, μm (mil)
Electroplate Al	55 (2.2)
IVD Al	13 (0.5)
Cd	9 (0.35)
Zn-6Ni	16 (0.63)
Zn-13Ni	12 (0.5)

TABLE 3 – Chemical Composition of Coating (wt%)

Coating	Al	Cr	Fe	Ni	Zn	Cd	Total
Electroplated Al	99.83	0.00	0.16	0.00	0.00	0.01	100.00
IVD Al	99.21	0.04	0.66	0.02	0.07	0.00	100.00
Cd	0.00	0.02	0.52	0.00	0.04	99.43	100.00
Zn-6Ni	0.02	0.03	1.30	6.42	92.23	0.00	100.00
Zn-13Ni	0.01	0.00	1.12	12.61	86.24	0.03	100.00

The electroplated Al coating thickness is largest among the coatings employed in this study at 55 μm (2.2 mil), while the Cd coating is least thick at 9 μm (0.35 mil), Table 2. Each coating contains a certain amount of impurity as may be seen in the chemical compositions, Table 3.

3. Residual Stress

The residual stress measured from the coating surface is compressive for the Cd, IVD Al and Zn-13Ni, whereas it is tensile for the electroplated Al and Zn-6Ni, as shown in Table 4.

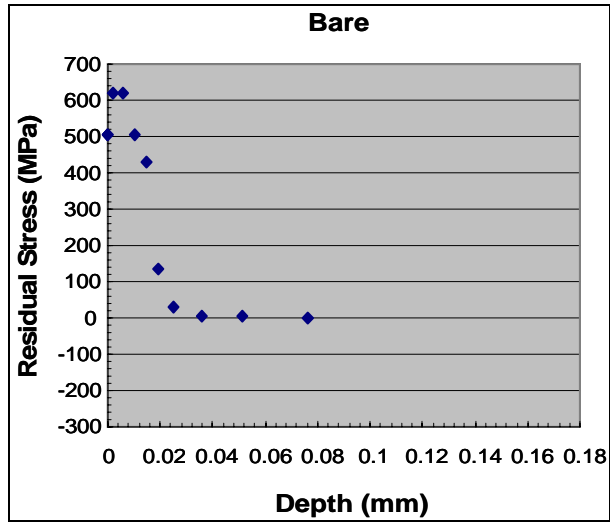
TABLE 4 – Residual Stress in Coating

Coating	Residual Stress [MPa (ksi)]
Electroplated Al	+ 21 (+ 3.0)
IVD Al	- 61 (- 8.8)
Cd	- 22 (- 3.2)
Zn-6Ni	+ 319 (+ 46.3)
Zn-13Ni	-25 (- 3.6)

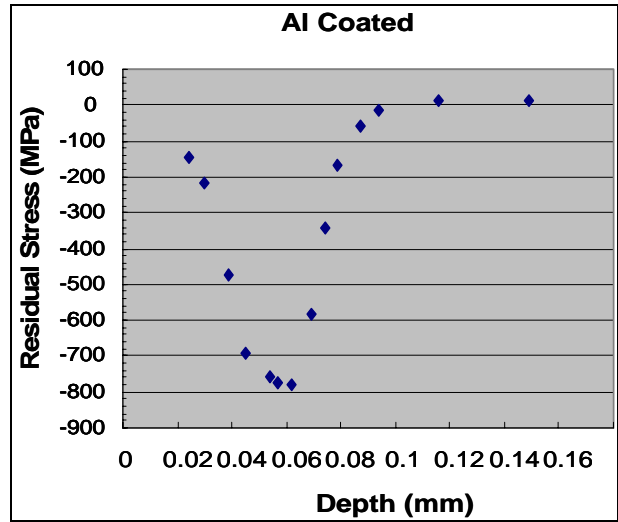
The residual stress in the bare specimen is tensile. The residual stress in the substrate of the coated specimens is compressive, and changes with depth, increasing to a peak and diminishing to zero. Among the coated specimens, the electroplated Al specimen has the greatest magnitude and depth of the peak compressive residual stress and thickest layer of compression. The peak residual stress, tensile or compressive, is located at a certain depth beneath the surface in the bare and electrocoated specimens, and on the surface in the IVD Al specimen. The magnitude and depth of its peak and the thickness of residual stress layer in Table 5, and the profile of residual stress in the substrate is shown in Figure 2.

TABLE 5 – Residual Stress in Substrate

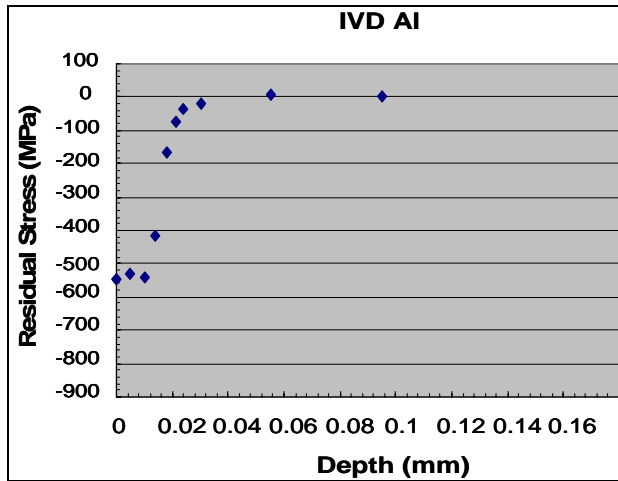
Peak Residual Stress		Residual Stress Layer	
Coating	Magnitude [MPa (ksi)]	Depth [mm (mil)]	Thickness [mm (mil)]
Bare	+ 621 (+ 90.0)	0.006 (0.24)	0.076 (2.99)
Electroplated Al	- 781 (- 113.2)	0.062 (2.44)	0.116 (4.57)
IVD Al	- 549 (- 79.6)	0 (0)	0.055 (2.17)
Cd	- 674 (- 97.7)	0.016 (0.063)	0.058 (2.28)
Zn-6Ni	- 617 (- 89.5)	0.049 (1.93)	0.097 (3.82)
Zn-13Ni	- 385 (- 55.8)	0.023 (0.91)	0.036 (1.42)



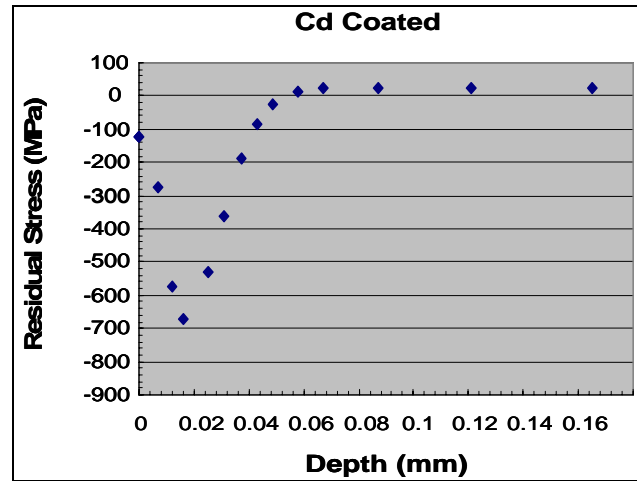
(a)



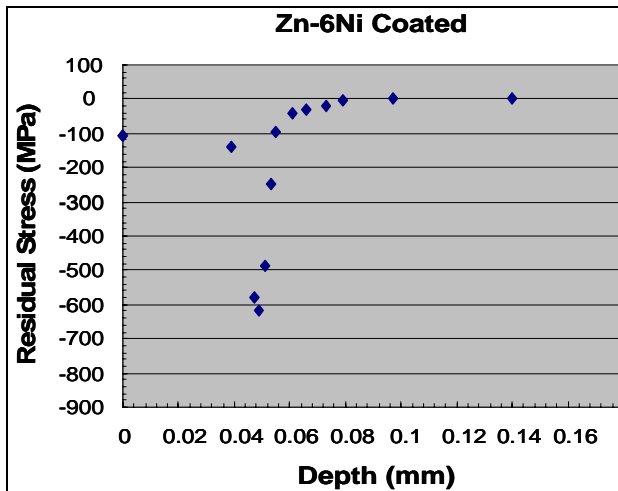
(b)



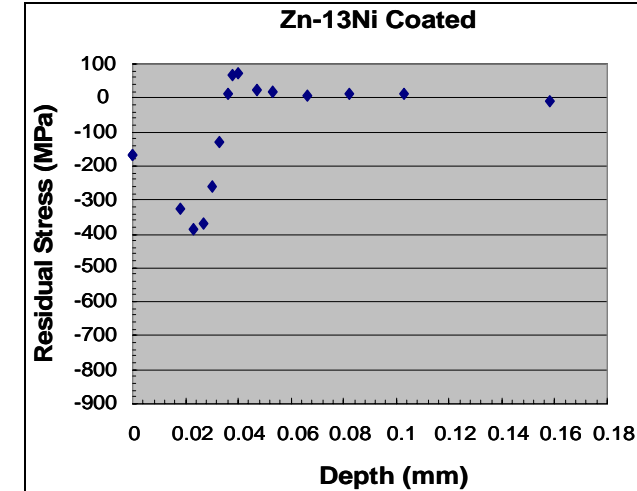
(c)



(d)



(e)



(f)

FIGURE 2 – Residual Stress in (a) Bare, (b) Al Coated, (c) IVD Al, (d) Cd Coated, (e) Zn-6Ni Coated, and (f) Zn-13Ni Coated Substrates

4. Tensile Properties of Bare Specimen

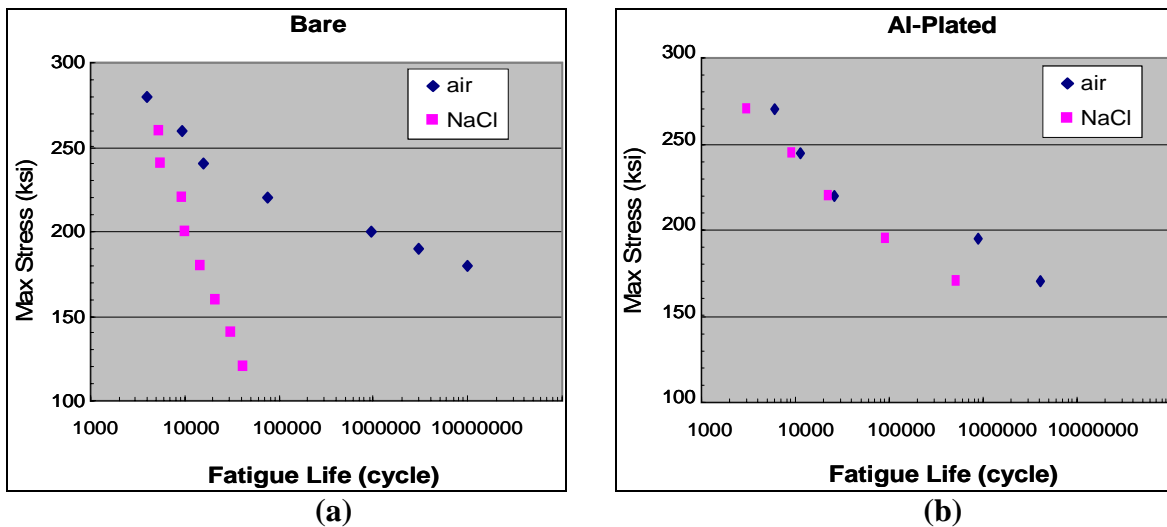
The tensile properties of the bare substrate material, 4340 steel, are determined to be: 0.2% yield strength 1,582 MPa (230 ksi), ultimate tensile strength 1,964 MPa (285 ksi) and elongation 21%.

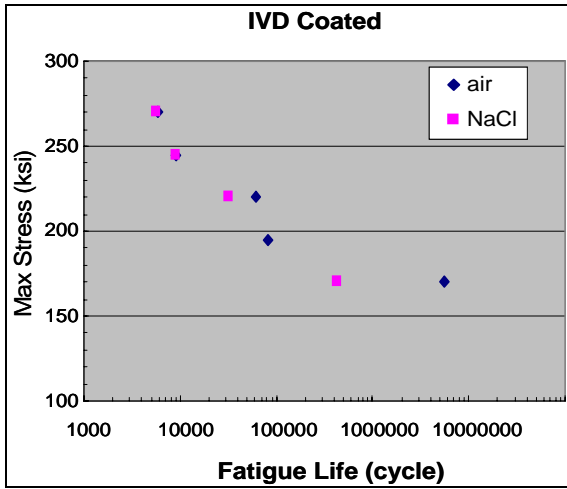
5. Fatigue Behavior

The stress-life (S-N) curves for the bare and coated specimens, tested in air and 3.5% NaCl solution, are shown in Figure 3. The fatigue life of the bare specimen is much shorter in 3.5% NaCl solution than in air, especially at lower applied stresses. On the other hand, the fatigue life of the coated specimens is slightly reduced in 3.5% NaCl solution. The fatigue lives of the bare and coated specimens are compared in air and 3.5% NaCl solution, respectively, in Figure 4(a) and (b). In air, the fatigue life of the coated specimens is generally shorter than that of the bare specimen, Figure 4(a). In 3.5% NaCl solution, the fatigue life of the coated specimens is longer than those of the bare specimen, Figure 4(b). This observation evidences that coating generally improves the fatigue life or protects the substrate against corrosion fatigue in 3.5% NaCl solution.

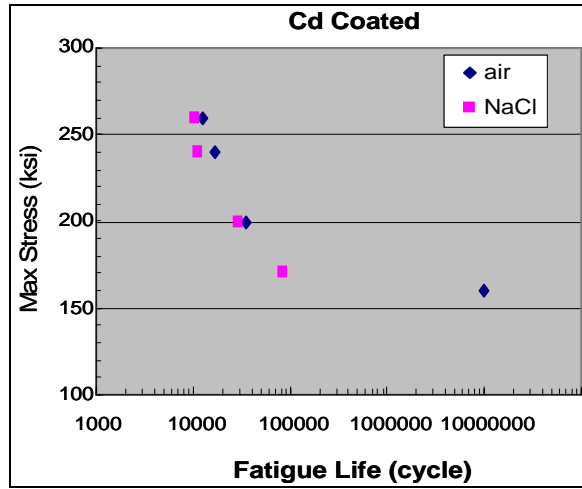
6. Open Circuit Potential

During its measurement, the specimen electrode potential was initially fluctuating and unstable, but eventually stabilized with time. The final stabilized potential at 24 hours was taken as the OCP of the specimen. The OCP values of the bare and coated specimens are included in Table 6.

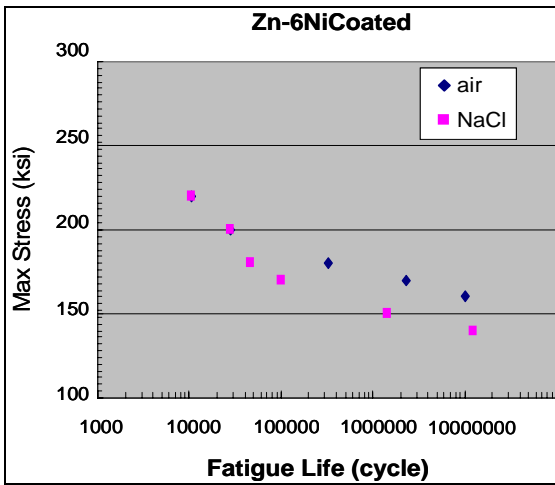




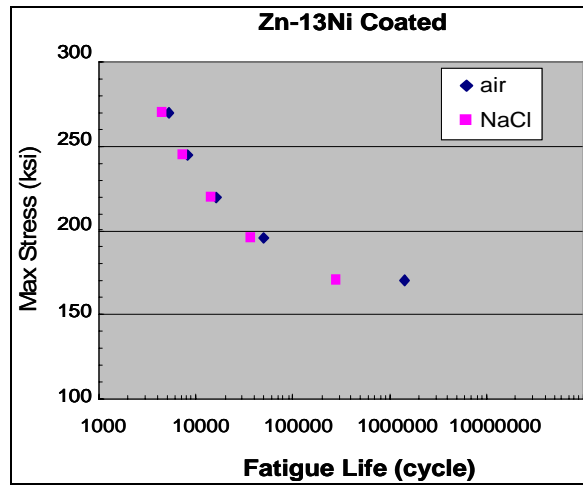
(c)



(d)

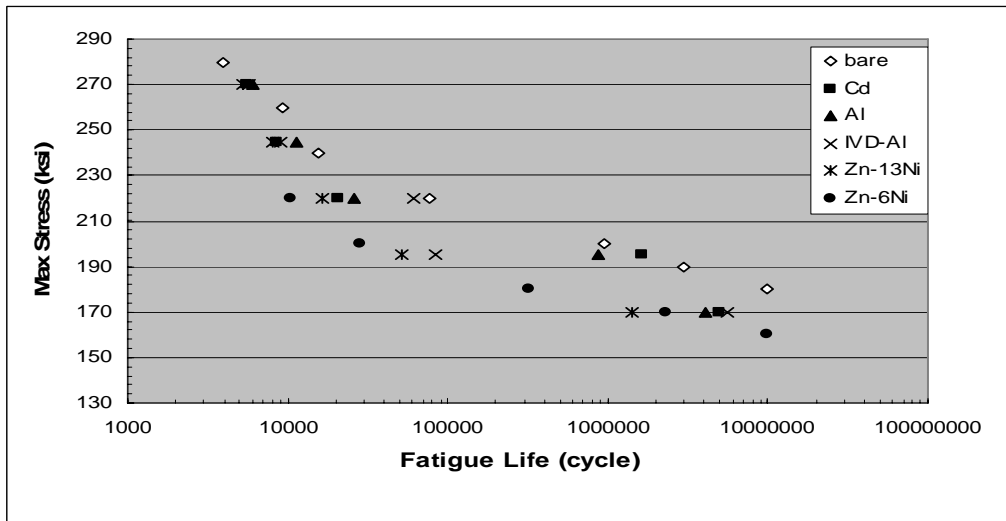


(e)

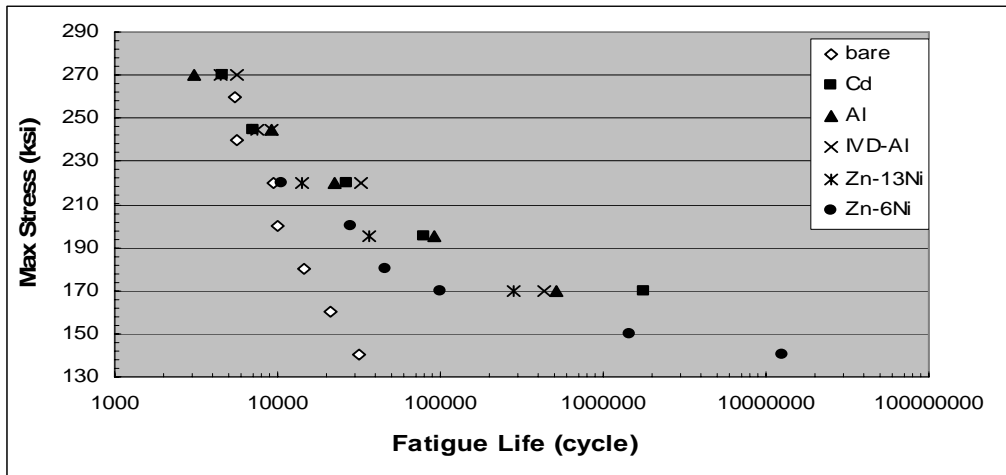


(f)

Figure 3 – Stress Life Curves of (a) Bare, (b) Al Coated, (c) IVD Al, (d) Cd Coated, (e) Zn-6Ni, and (f) Zn-13Ni in Air and 3.5% NaCl Solution



(a) Air



(b) 3.5% NaCl

Figure 4 – Comparison of Fatigue Lives of Bare and Plated Specimens in (a) Air and (b) 3.5% NaCl Solution

7. SCC Resistance

Bare Specimen: The variations of K_{OSCC} and K_{ISCC} with applied electric potential V_{SCE} are shown for the bare specimen in Figure 5. With increasing V_{SCE} , K_{OSCC} increases steadily, but K_{ISCC} peaks at $V_{SCE} = -1$ volt and decreases. Their values at the OCP -0.64 volt are $K_{OSCC} = 98.5 \text{ MPa}\sqrt{\text{m}}$ (89.6 $\text{ksi}\sqrt{\text{in}}$) and $K_{ISCC} = 11.5 \text{ MPa}\sqrt{\text{m}}$ (10.5 $\text{ksi}\sqrt{\text{in}}$), respectively. This observation confirms that the un-precracked specimen has a greater resistance to SCC than the precracked specimen.

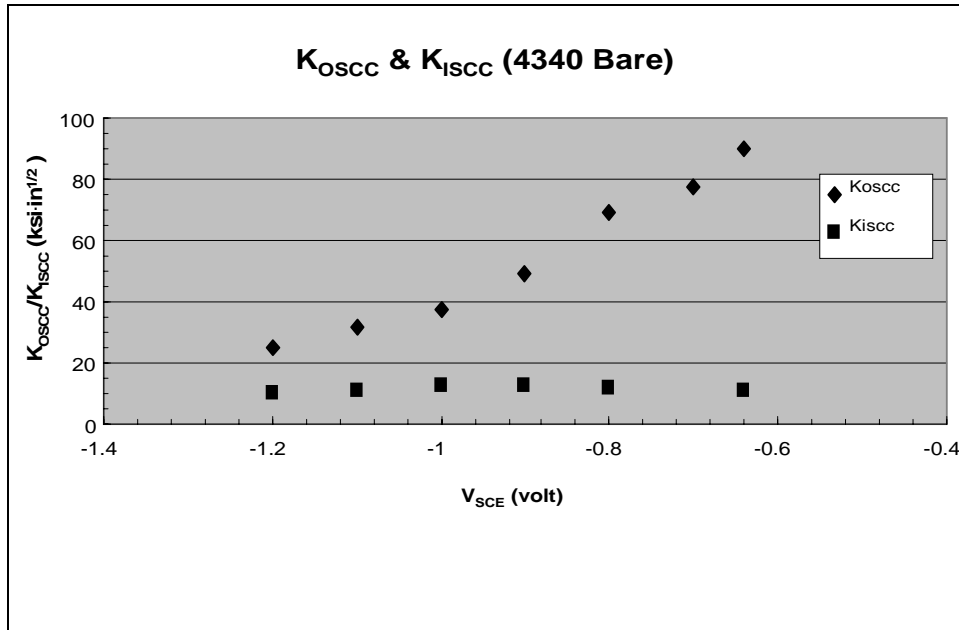


FIGURE 5 – Variation of Threshold Stress Intensity for Stress Corrosion Cracking in As-Machined (Un-Pre-cracked) and Pre-cracked Bare Specimens, K_{OSCC} and K_{ISCC} with Applied Electric Potential V_{SCE}

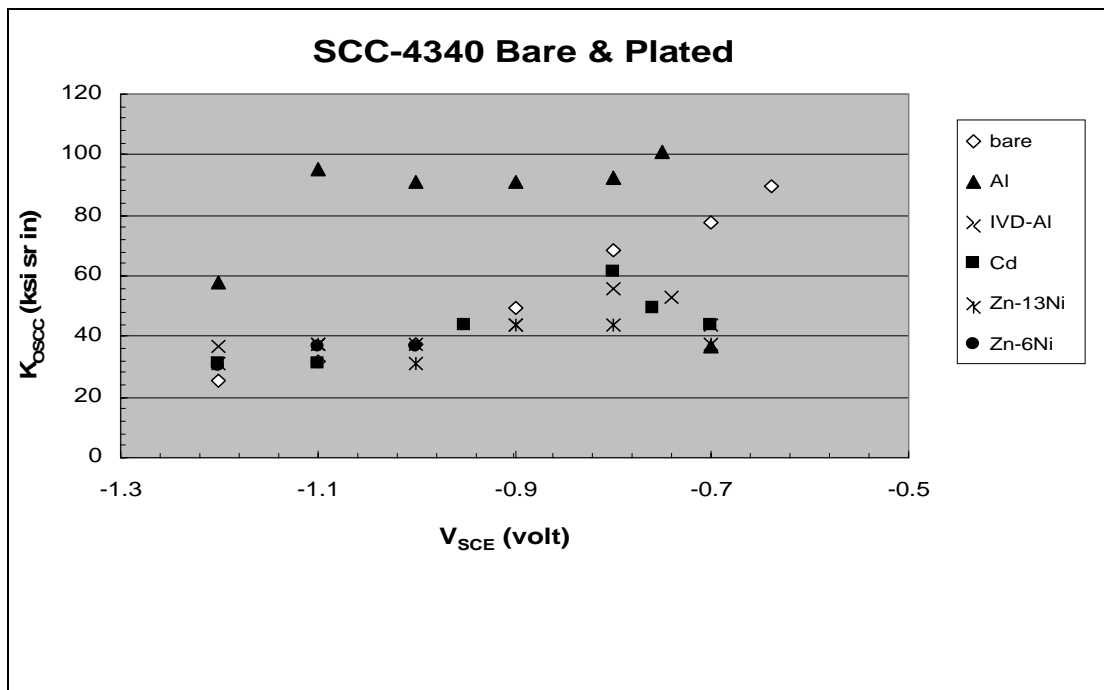


FIGURE 6 – Variation of K_{OSCC} with V_{SCE} for Bare and Coated Specimens

Coated Specimens: The variation of K_{OSCC} with V_{SCE} for the bare and coated specimens is shown in Figure 6. Within the region of V_{SCE} taken, the K_{OSCC} is greatest for the electroplated Al coating compared to the other coatings, indicating the greatest SCC resistance in 3.5% NaCl solution. The values of OCP and the corresponding K_{OSCC} are listed for the bare and coated specimens in Table 6.

TABLE 6 – Open Circuit Potentials OCP and Threshold Stress Intensities for Stress Corrosion Cracking of Un-Precracked Specimen K_{OSCC} of Bare and Plated Specimens

Coating	OCP [volt]	K_{OSCC} [MPa \sqrt{m} (ksi \sqrt{in})]
Bare	-0.64	98.5 (89.6)
Electroplated Al	-0.75	111.0 (101.0)
IVD-Al	-0.74	57.9 (52.7)
Cd	-0.76	54.4 (49.5)
Zn-6Ni	-1.00	40.4 (36.8)
Zn-13Ni	-0.75	61.8 (56.2)

DISCUSSION

1. Residual Stress

Metallic coating has been known to contain residual stress within itself as well as inducing stress into the substrate. The residual stress may be either tensile or compressive. It can be divided into two categories: (a) that resulting from distortion due to lattice misfit at the interface between the coating and substrate, and (b) the intrinsic residual stress which arises as a result of particular coating conditions and bath composition¹³. Lattice misfit is likely to occur when a metal is deposited onto a dissimilar substrate. The extent to which the misfit is perpetuated depends on the surface characteristics and the deposition condition.

The residual stress in the bare square bar specimen was determined to be tensile, Figure 2 and Table 5. The specimen was machined using EDM and subsequently hand polished with emery cloth. The tensile residual stress must have been induced by the EDM process, involving electric sparking, thin layer melting, cooling, solidification and shrinkage. Since the hand-polishing presumably induces some compressive residual stress, the tensile residual stress by EDM must have overwhelmed the compressive stress induced by the hand-polishing.

The lattice parameters of the coating materials are greater than that of the substrate 4340 steel, resulting in lattice misfit, Table 7. When Al, Cd, Zn-6Ni and Zn-13Ni are deposited on substrate 4340 steel of martensitic crystal structure, in order to conform to the larger coating lattices, the substrate must be in tension and a tensile stress arises at the interface, if there is no intervention by other phenomena. The measured residual stress in the substrate is tensile before coating, and the post-coating stress is compressive, Figure 2. Therefore, it is likely that some compressive residual stress was induced by the coating process¹³ and overcome the tensile residual stresses induced by EDM and lattice misfit between the coating and substrate. The peak of residual stress is located at a certain depth beneath the surface in the electrocoated specimens. The difference in the location and magnitude of the peak residual stress appears to be due to the different coating processes.

TABLE 7 – Lattice Parameters of Coating and Substrate Materials

Element	Crystal Structure	Lattice Parameter (Angstrom)
Al ¹³	fcc	a = 4.0491
Cd ¹³	hcp	a = 2.9787, c = 5.6173
Zn ¹³	hcp	a = 2.6649, c = 4.9470
Fe-C: Martensite ¹⁵	bct	a = 2.8530, c = 2.9060 (0.4% C)

The compressive residual stress in substrate was also reported previously¹⁶. The residual stress in AerMet 100 steel, which was shot-peened and High Velocity Oxygen Fuel (HVOF) thermal spray coated or Cr plated, was measured to be compressive¹⁶. The compressive residual stress increased to the peak and then diminished with increasing depth. Compared to the Cr plating, the HVOF coating had a lower peak but a deeper layer of compressive residual stress in the substrate.

The residual stress in the coating is compressive for IVD Al, Cd and Zn-13Ni and tensile for Al and Zn-6Ni, Table 4. The difference is attributable to the difference in material, alloy composition and coating process. The reported electrodeposited metals with residual stress include Al (0.06 kg/mm²), Cd (-0.35 to -2.1 kg/mm²), Cu (-4.2 to 5.5 kg/mm²), Au (-0.6 to 1.1 kg/mm²), and Zn (-0.7 to 9 kg/mm²)¹⁷. A small compressive stress of 0.35 kg/mm² was reported for Zn alloy deposits containing 6.5 to 9.5% Ni². Stress became tensile and reached a level of 3.5 kg/mm² when the Ni content was raised to 15%³. Cr deposit had a large tensile residual stress¹⁸⁻²², which caused the deposit to crack and relieve the stress.

Residual stress arising from fabrication and surface or heat treatments, when superimposed with the applied fatigue stress, alters the mean level of the fatigue cycle and the material behavior in the same way as a static mechanical stress superimposes on a cyclic stress amplitude. Therefore, the residual stress state is favorable if compressive, detrimental if tensile; and this is especially true for high strength materials²³.

2. SCC Resistance

The K_{OSCC} value at the open circuit potential, a measure of SCC resistance, is smaller for the coated specimens than for the bare specimen except for the electroplated Al coating, Table 6. This indicates that the SCC resistance of 4340 steel is reduced by all the coatings in this study except electroplated Al. Based on the K_{OSCC} values, electroplated Al may improve the SCC resistance of 4340 steel. This is associated with the thicker, denser coating, and the higher peak and thicker layer of compressive residual stress in the substrate, Tables 2, 5 and 6. The coating-induced reduction of SCC resistance in 3.5% NaCl solution was also reported for the AerMet 100 steel, shot-peened and Cr plated or HVOF coated¹⁶. Compared to the electroplated Al specimen, the IVD Al specimen has lower SCC resistance as indicated by the lower K_{OSCC} at the OCP, Table 6 and Figure 6. This lower SCC resistance is presumably associated with the greater porosity²⁻⁴, which diminishes corrosion resistance, and the lower coating thickness of IVD Al compared to electroplated Al, Table 2. The substrate of IVD Al was found to be corroded more in marine atmosphere for a thinner coating²⁴.

3. Fatigue Resistance in Air

Compared to the bare specimen, the coated specimens generally had similar or shorter fatigue life in air, Figure 4(a). In other words, the fatigue life of 4340 steel in air is shortened by coatings. Other

investigators also reported changes in fatigue resistance due to coatings applied by electrodeposition or thermal spray. The use of a Ni electrocoat was shown to be responsible for a loss in fatigue strength of coated steel parts, as much as 50% in some cases²⁵. This effect was greatest when the thickness ratio of Ni to substrate was highest. The internal tensile stress in the Ni deposit had a linear relationship with the change in fatigue strength and was regarded as a major cause of the reduction in fatigue resistance²⁶. Cr deposits, stressed in tension, reduced fatigue strength at least 22% or as much as 73 %, depending on the strength of the substrate material¹⁶. Cr and HVOF coatings on 4340 steel^{27,28}, E35NCD16 (a French ultrahigh strength steel)²⁹ and AerMet 100 steel¹⁶ were found to lead to lower fatigue resistance, compared to the bare substrate steels. Cd coating reduced the fatigue strength of substrate steel by approximately 10%, compared to the bare substrate²⁵.

If only the compressive residual stress in the substrate is considered, Figure 2, the fatigue resistance of the coated specimen should be greater than that of the bare specimen. However, the reverse was observed. There must be other causes for the reduced fatigue resistance of the coated specimens. Since the IVD and electroplated Al specimens also showed a reduction of fatigue life, hydrogen embrittlement can not be considered as a cause.

The fatigue limit of a material is known to be proportional to its UTS³⁰. The magnitudes of the UTS, and so the fatigue limit, of the coating materials employed in this study are much smaller than those of the bare substrate 4340 steel, Table 8. The coatings crack at lower stress levels than the substrate steel because of the coatings' lower intrinsic fatigue strength and possible tensile residual stress. The stress on the substrate at the base of the crack is enhanced because of the notch effect. As the result, the crack can propagate into the substrate of a coated specimen before a crack can be initiated in a bare specimen, and the fatigue life of the coated specimen must be shortened. In other words, the coating becomes the site for crack initiation under applied stress, lowering the fatigue strength of the system. As the result, the fatigue life of the coated specimen becomes shorter than that of the bare substrate material in air.

TABLE 8 – Ultimate Tensile Strength of Coating and Substrate Materials

Material	UTS [MPa (ksi)]
Al ¹³	45 – 70 (6.5 – 10.2)
Cd ³²	69 – 83 (10.0 – 12.0)
Zn ³³	283 – 324 (41.0 – 47.0)
Ni ³⁴	317 (46.0)
4340	1964 (284.8)

4. Fatigue Resistance in 3.5% NaCl Solution

The fatigue life of the bare specimen is greatly reduced in 3.5% NaCl solution as compared to air, Figure 3. This evidences that the bare 4340 steel is highly susceptible to corrosion fatigue in 3.5% NaCl solution. On the other hand, the fatigue lives of the coated specimens are similar or very close in air and 3.5% NaCl solution, Figure 3. In addition, compared to the bare specimen, the coated specimens have longer fatigue lives in 3.5% NaCl solution, Figure 4(b). From these observations, it is clear that the coatings in this study can protect the 4340 steel against corrosion fatigue in 3.5% NaCl solution, though there is some difference in the extent of protection.

At lower applied stress, the fatigue life appears to be longer for the Cd coated specimen than for the other coated specimens in 3.5% NaCl solution, Figure 4(b). This indicates that Cd coating can provide better protection against corrosion fatigue than the alternatives in 3.5% NaCl solution. At higher stress the Cd and both Al coatings performed similarly. The lowest performing coatings in this study were the zinc-nickel alloys, with the Zn-13Ni slightly outperforming the Zn-6Ni coating in corrosion fatigue resistance. It was reported that the fatigue strength of bare steel was reduced by 78% when tested in 3% NaCl, whereas Cd coating reduced the loss in fatigue strength to only 67%¹¹. Cd, like Zn, is electronegative or anodic to iron, steel, copper and brass, and protects exposed areas of the substrate by sacrificing itself. The protective value of Cd is reportedly proportional to its thickness. Similarly, it was reported that Cr and HVOF coatings protected the substrate AerMet 100 steel against corrosion fatigue in 3.5% NaCl solution, more obvious at lower applied stress levels¹⁶.

CONCLUSIONS

1. The residual stress in substrate is tensile prior to coating, but it becomes compressive as a result of the coating process, overcoming the tensile residual stresses induced by EDM and lattice misfit.
2. The residual stress in coating is either compressive or tensile, attributable to the difference in material, alloy composition and coating process.
3. Coatings shorten the fatigue life of 4340 steel in air, due to their lower UTS and fatigue limit values. A crack can be initiated and grown in the coating and then propagated into the substrate at an applied fatigue stress, lower than the fatigue limit of the bare substrate material.
4. Bare 4340 steel is highly susceptible to corrosion fatigue in 3.5% NaCl solution. On the other hand, the coated 4340 steel is quite resistant to corrosion fatigue and the fatigue life is largely preserved in 3.5% NaCl solution.
5. The electroplated Al, IVD-Al, Zn-6Ni and Zn-13Ni provide similar to slightly less protection against corrosion fatigue than Cd on 4340 steel in 3.5% NaCl solution. However, the effectiveness of electroplated Al and IVD-Al for protection against corrosion fatigue is mostly similar to that of Cd. At low stress the effect is more pronounced.
6. Among the electroplated Al, IVD Al, Zn-6Ni and Zn-13Ni coatings, the electroplated Al coating is the best protector of the 4340 steel against SCC in 3.5% NaCl solution, while both Al coatings performed similarly in corrosion fatigue resistance.
7. The greater SCC resistance of electroplated Al specimen is attributable to the coating density and thickness, as well as compressive residual stress of greater peak and thicker layer in the substrate.
8. The Zn-13Ni coating performed better than the Zn-6Ni coating in corrosion fatigue resistance, whereas both of the coatings exhibited similar fatigue debits in air.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Jim Green for his support and helpful discussions and the 0817 Program for funding this project.

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