

Cadmium Alternative Coating Corrosion Performance on Steel; Non-Cr⁺⁶ Primer Considerations

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AIR 4.3.4

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Patuxent River, MD 20670

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Outline

- **NAVAIR Test Result Summary / HSS JTP Sec. 4**
 - **Acidified Salt Fog, ASTM G 85.A4**
 - **Bare Inorganic Coatings w/Cr⁺⁶ post**
 - **Primed/Painted (MIL-PRF-23377 Class C2 and N; MIL-PRF-85582-N (non-chromate inhibitors); Topcoat: MIL-PRF-85285 polyurethane**
 - **Fatigue (Air & 3.5% NaCl), SCC, Residual Stress**
 - **NACE Dec. 07 (E. Lee, et. al.)**
- **Cd Alts Comparisons / Conclusions**
- **Non-Cr Primer Demonstration Status**

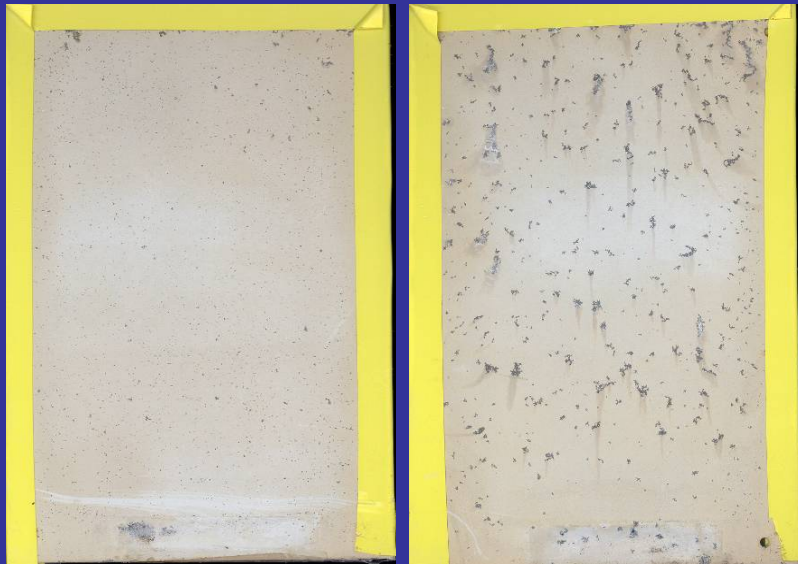
Sulfur Dioxide (SO₂) Acidified Corrosion Test Results, ASTM G 85, Annex 4

Tested panel images, duration:

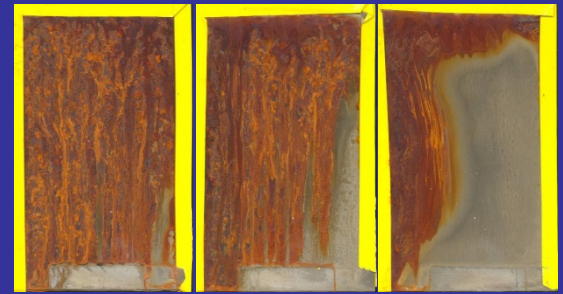
- 168 h (1 week)
- 500 h (3 weeks)
- 1000 h (6 weeks) - Painted

Corrosion Ratings: ASTM D 1654

Alumiplate, Unscribed – 500 hrs



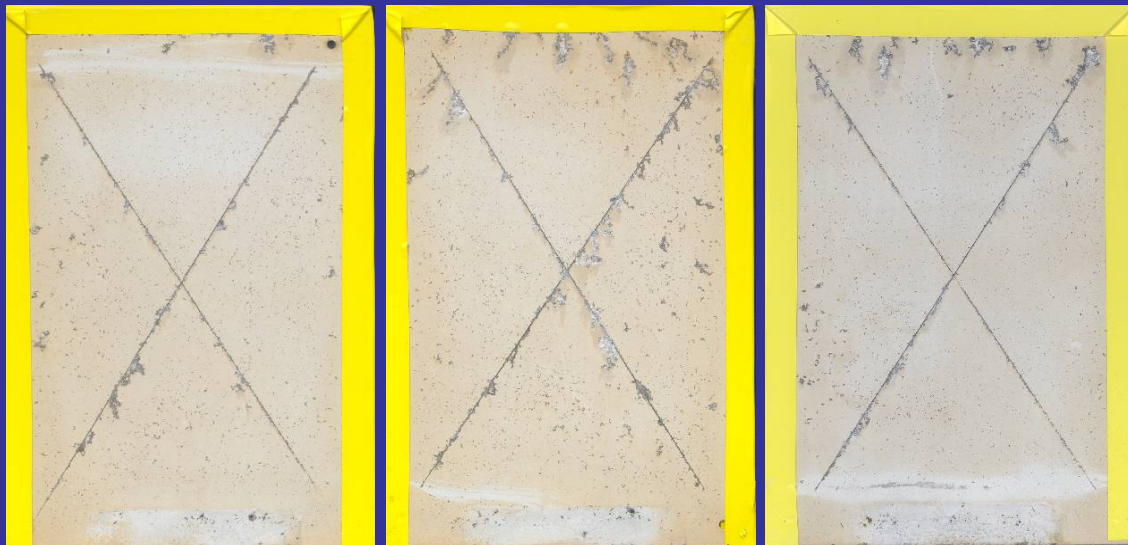
Cadmium,
Unscribed
168 hrs



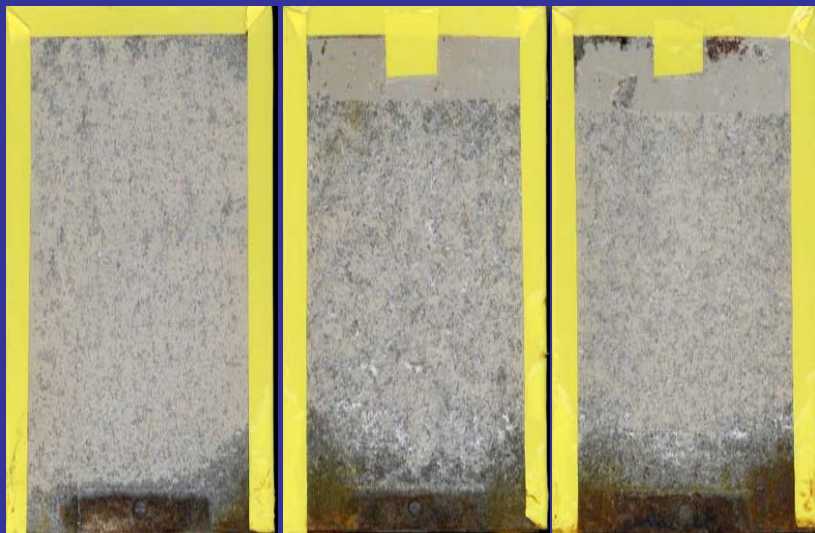
LHE Zn-Ni,
Scribed
– 168 hrs



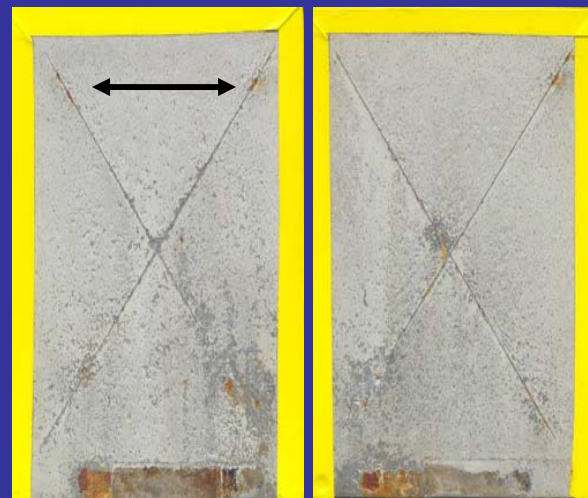
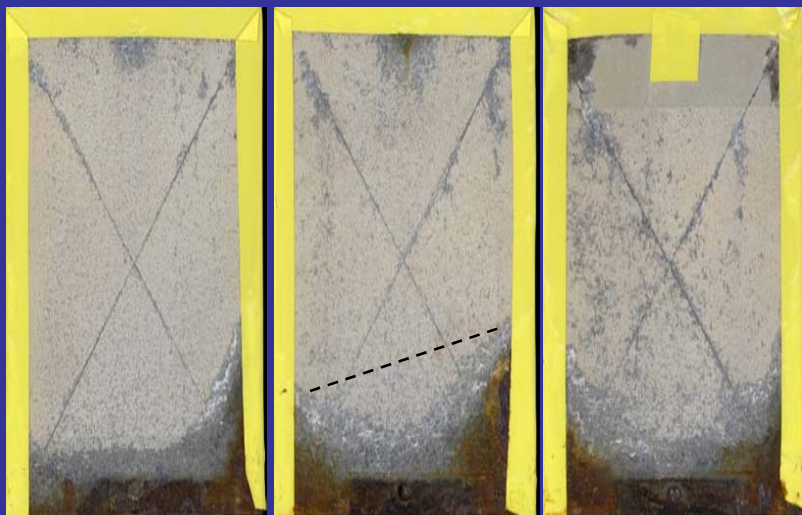
Alumiplate,
Scribed – 500 hrs



Sputtered Al, Unscribed – 500 h



IVD-Al, Unscribed – 500 h

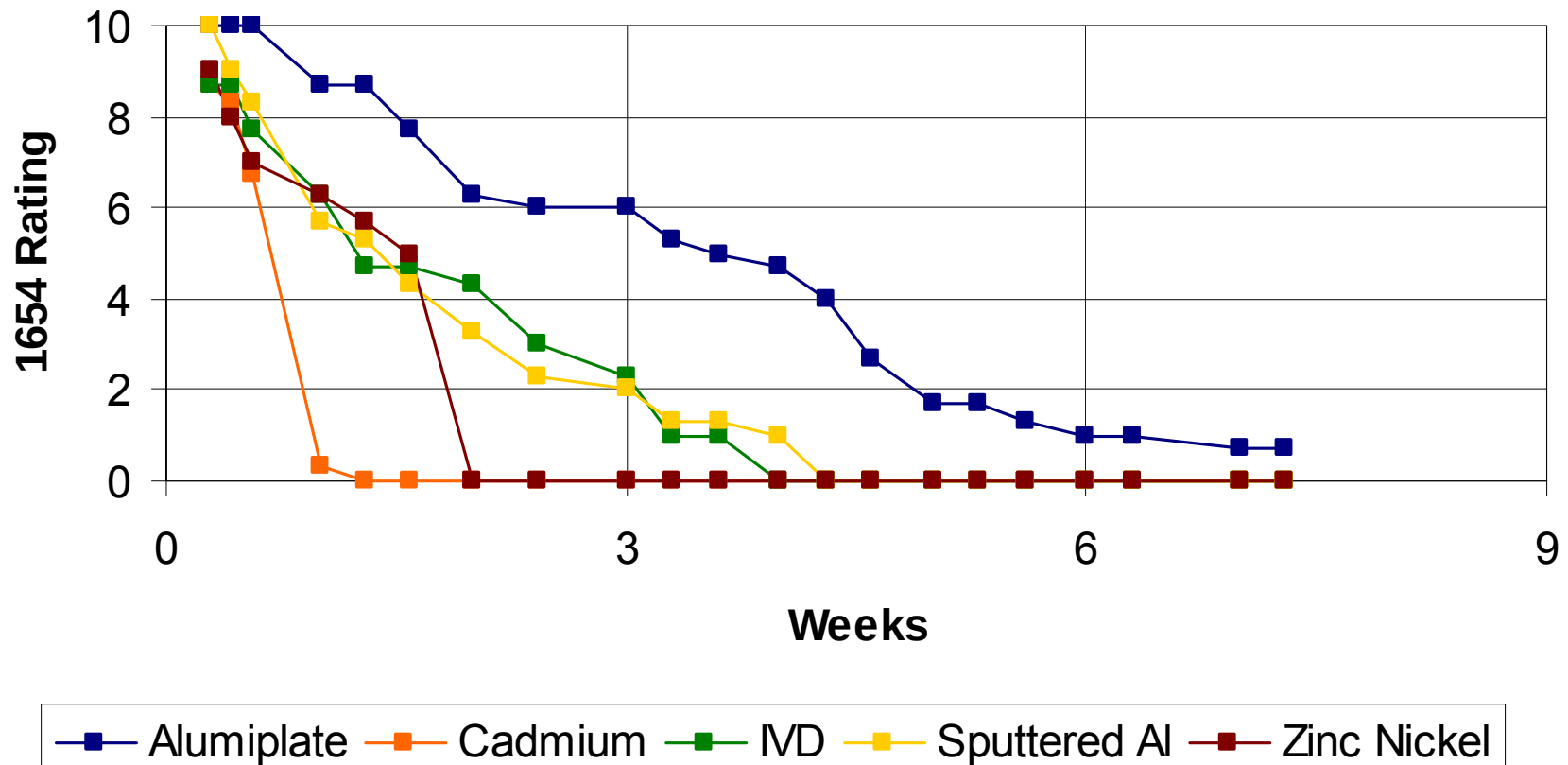


Sputtered Al, Scribed – 500 h

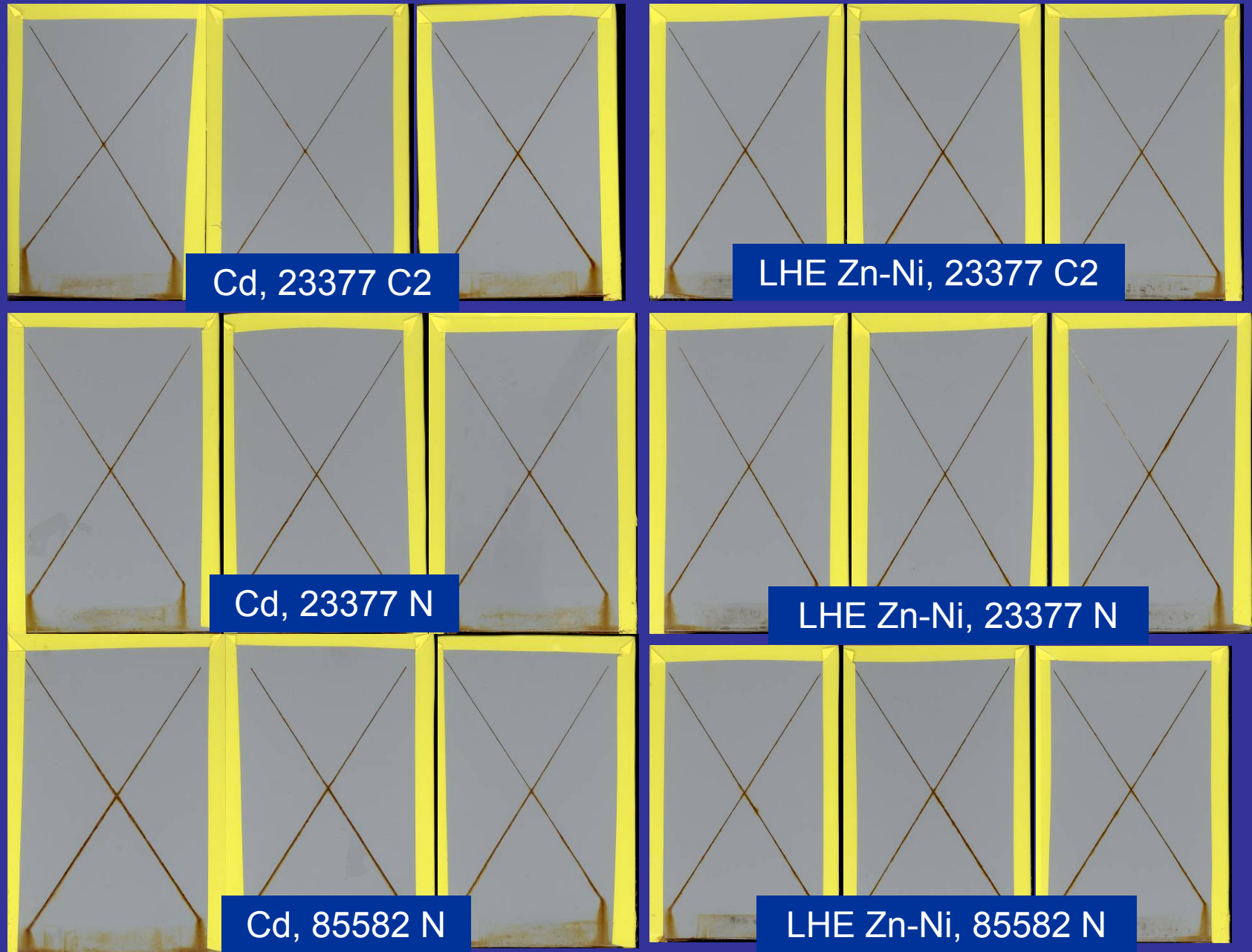
IVD-Al, Scribed – 500 h

Graphical Representation of Bare, Unscribed Test Panel Ratings

SO2 Ratings - Unscribed & Unpainted



Primed & Painted SO₂ Salt Fog, 1000 h

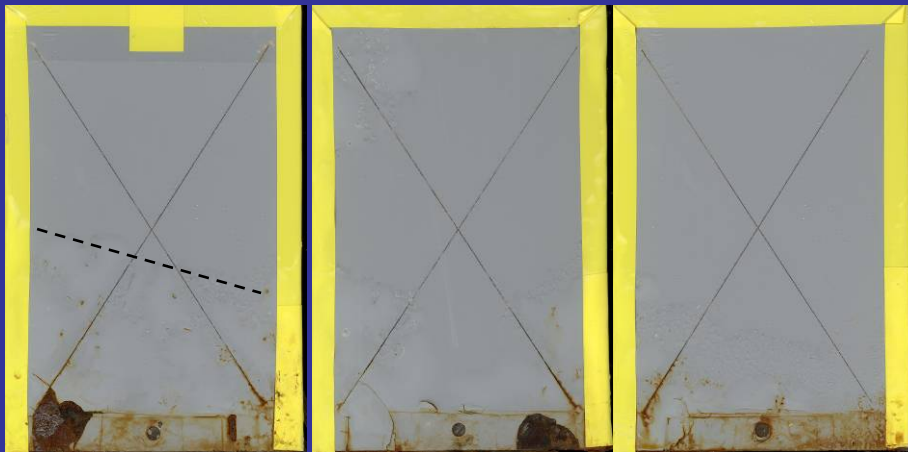


Alumiplate - 1000 h

23377 C2

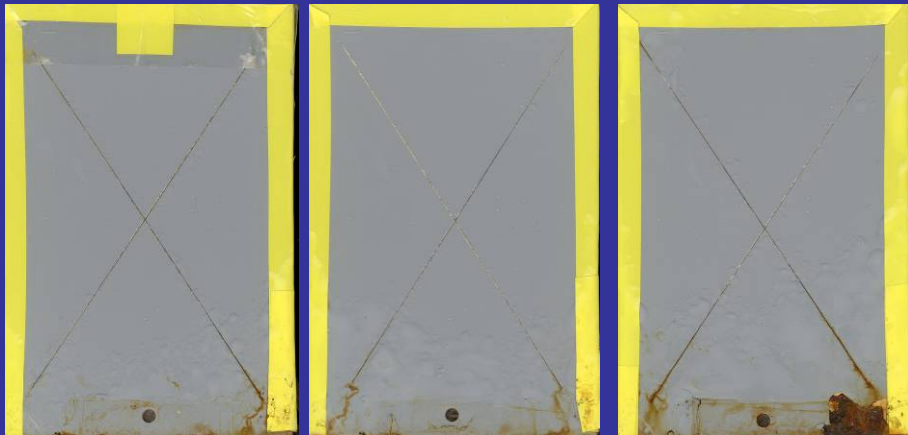
23377 N

85582 N

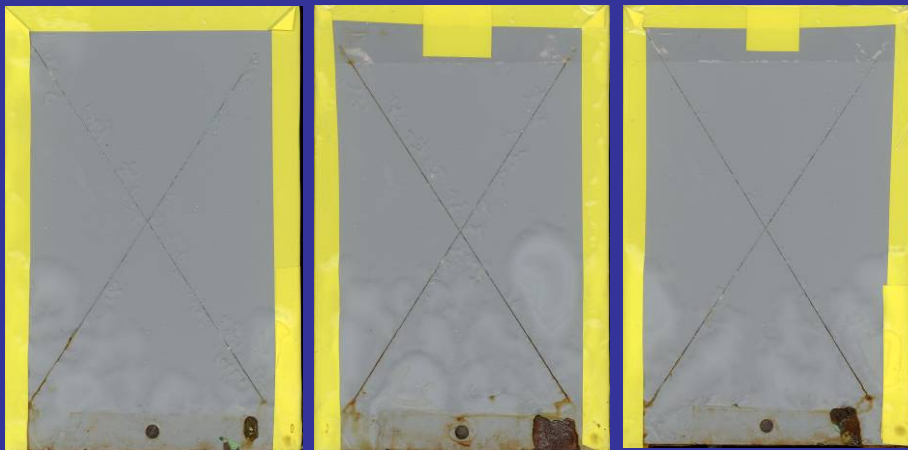


Sputtered Al –
840 h

23377 C2



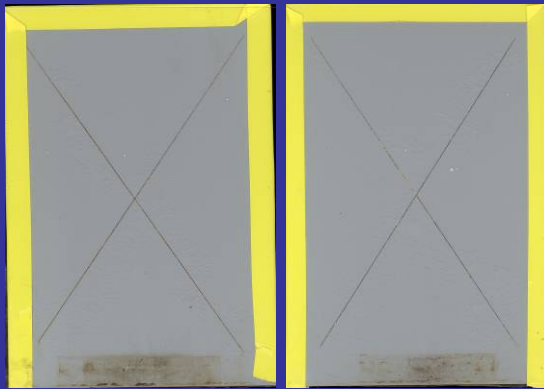
23377 N



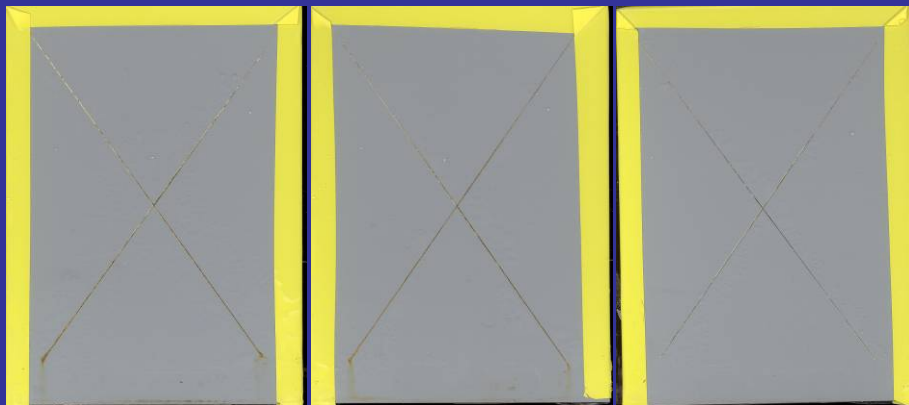
85582 N

IVD-AI – 500+ h

23377 C2

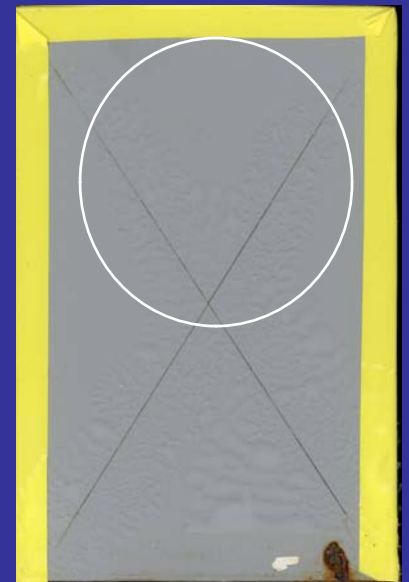
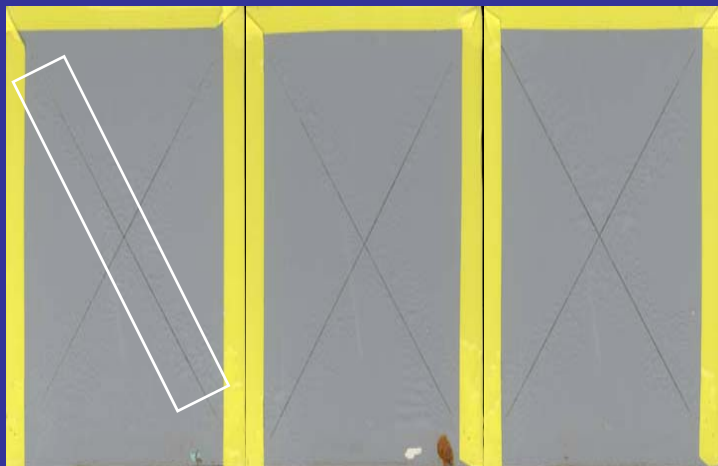


23377 N



85582 N, 840 hrs;

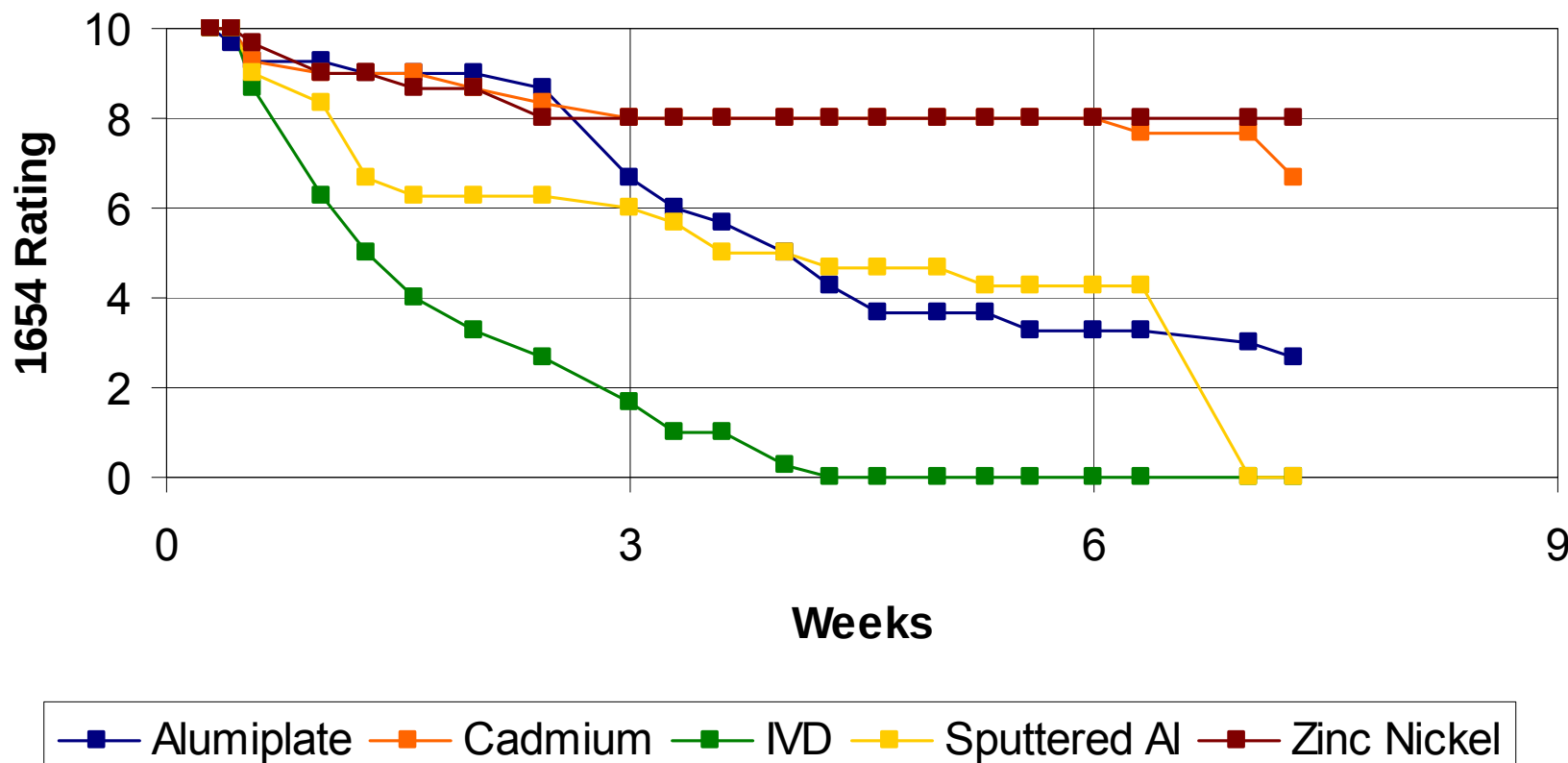
1000 h



- Graphical Representation of Results, weekly through test (ASTM G 85.A4)

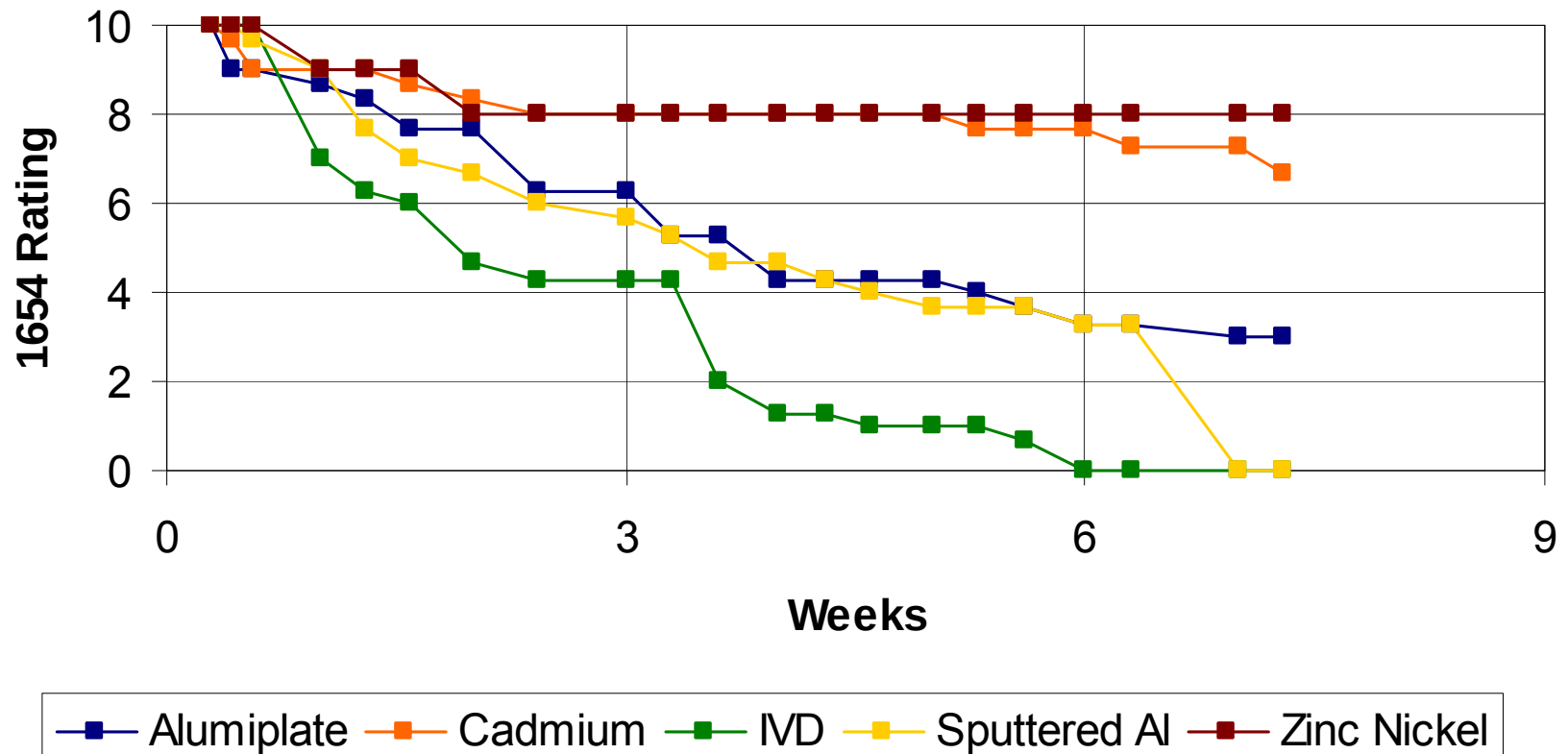
23377 Class N

SO2 Ratings - Scribed & 23377N

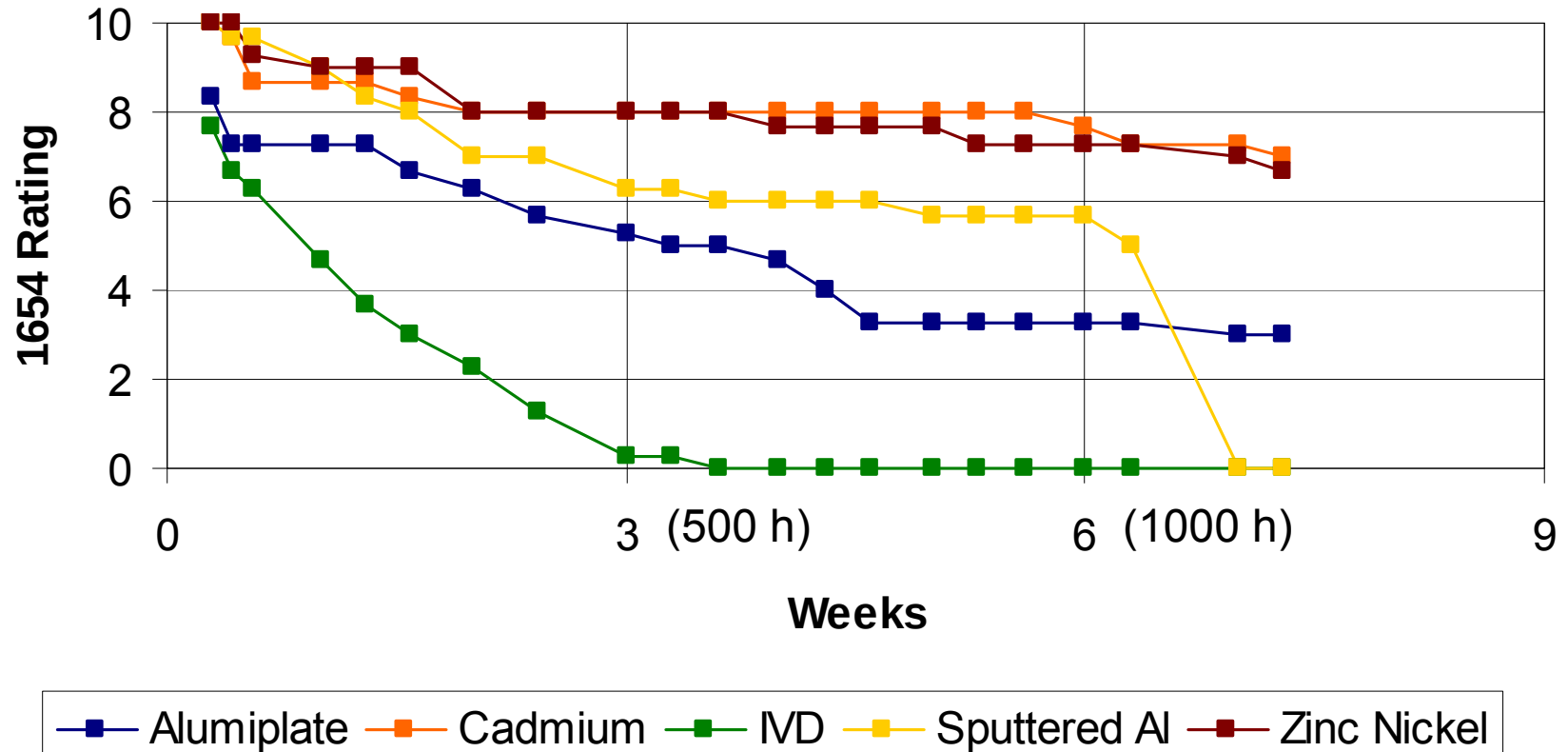


1. Cadmium and LHE Zn-Ni were approximately equivalent in scribe ratings with all three tested primers (red rust contained to scribe);

SO2 Ratings - Scribed & 85582N



SO2 Ratings - Scribed & 23377C2



- Overview of Cd Alternatives Test Performance
 - Residual Stress (Coating)
 - Residual Stress / layer thickness (Substrate)
 - Air Fatigue
 - Corrosion Fatigue
 - SCC
 - Acidic Salt Fog

Cd Alternative Coating Corrosion Performance Overview (4340 Steel)*

Coating	Thickness (mil), on SCC bars	Residual Stress (ksi) COATING	Residual Stress (ksi) Substrate	R.S. Layer Thickness (mil) Substrate	Open Circuit Potential (V)
Electroplated Al	2.20	+3.0	-113.2	4.57	-0.75
IVD-Al	0.50	-8.8	-79.6	2.17	-0.74
Cd	0.35	-3.2	-97.7	2.28	-0.76
LHE Zn-Ni	0.50	-3.6	-55.8	3.82	-0.75
Zn-6Ni	0.63	+46.3	-89.5	1.42	-1.00
	B.E.I.	X.R.D.			

* Source: NACE Tri-Service, Dec. '07, P1792.

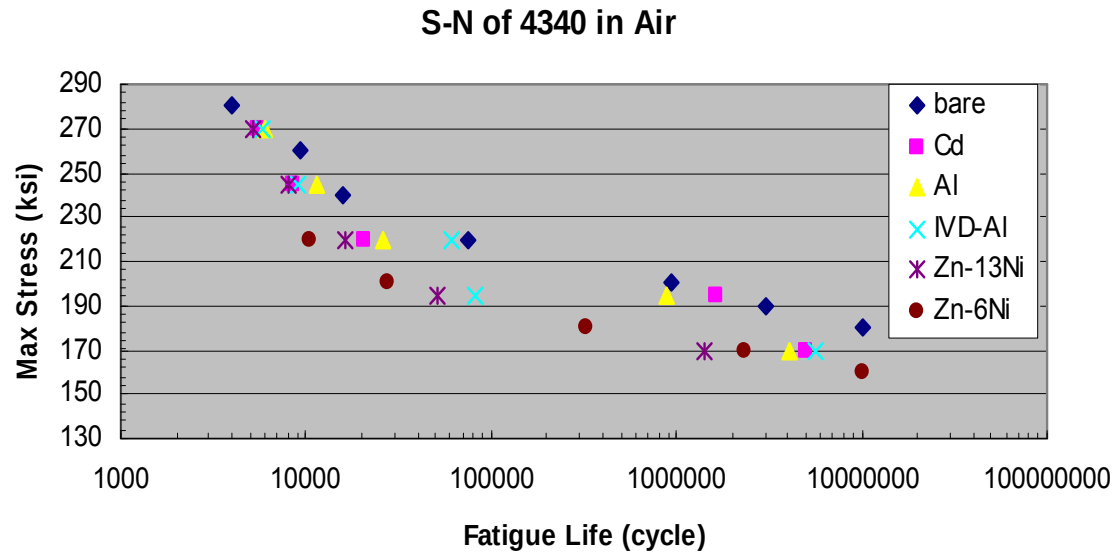
Cd Alternative Coating Corrosion Performance on 4340 Steel*

Coating	Stress Corrosion Cracking (Koscc)	SCC Ranking	Air Fatigue Ranking	Corrosion Fatigue Ranking	Acid SO2 Salt Fog, ASTM G85.A4
Sputtered Al	Not Tested	---	---	---	≥IVD
Electroplated Al	101.0	Best	Best	Best	Best (bare)
IVD-Al	52.7	Comparable to Cd	Best	Best	Least among Al coatings
Cd	49.5	CONTROL	CONTROL	CONTROL	CONTROL
LHE Zn-Ni	56.2	> Cd	Debit	Debit	> Cd (bare); Comparable (painted)
Zn-6Ni	36.8	OK (less data)	Debit	Debit	---
Method→	RSL Method		ASTM E 466; R=0.1; f=10/s	ASTM E 466; R=0.1; f=10/s	ASTM G85.A4

* Source: NACE Dec. '07, P1792.

Air

(a)



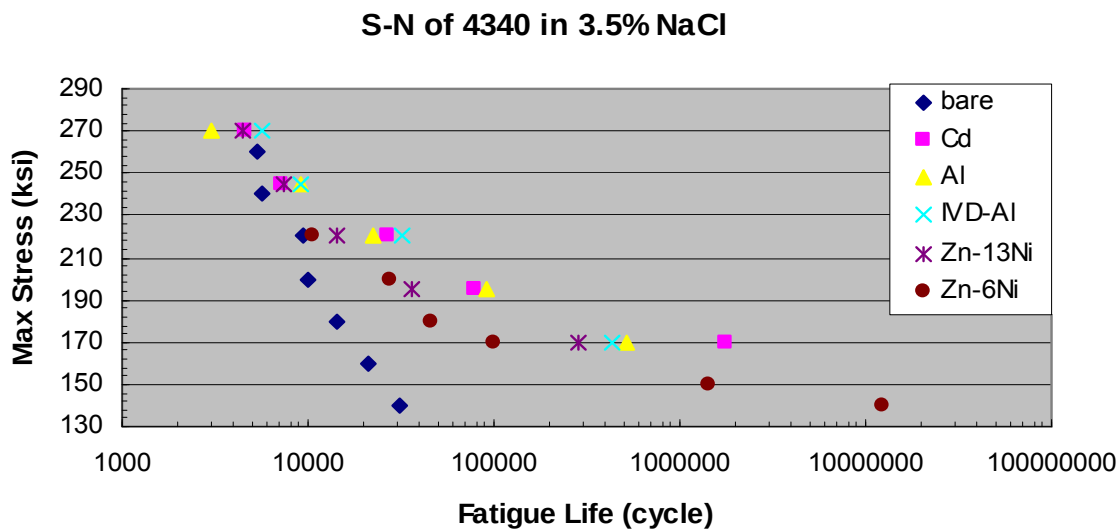
ASTM E 466
Fatigue Test
Protocol;

R = 0.1

F = 10 Hz

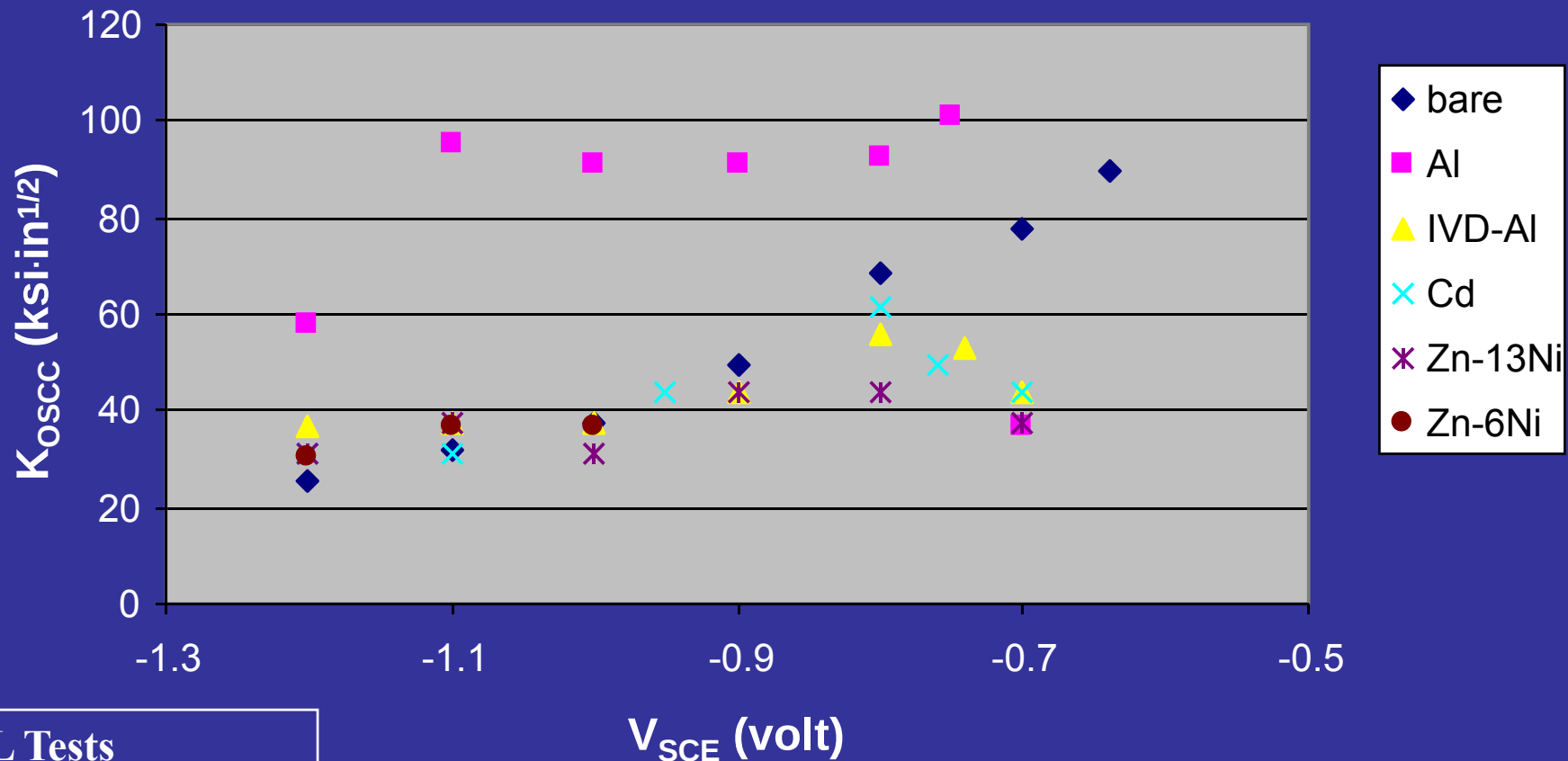
3.5%
NaCl

(b)



Comparison of Fatigue Lives of Bare and Coated Specimens in (a) Air; and
(b) 3.5% NaCl Solution

Stress Corrosion Cracking – Rising Step Load Tests (Coated vs. Bare 4340)



RSL Tests
w/notched square
bar specimens

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

Conclusions

- Coatings induced substrate compressive stress states of varying degrees
 - Zn-6Ni and Alumiplate retained tensile stress in coating
- Sacrificial coatings reduce inherent fatigue resistance of 4340 in air, but largely preserve that value in 3.5% NaCl
- Al-based coatings performed best in:
 - Air & Corrosion Fatigue, bare SO₂, SCC (Alumiplate)
 - Thickness dependence of SCC results not characterized
- LHE Zn-Ni appears to have some fatigue advantage over Zn-6Ni; SO₂ results comparable or better than Cd (painted and bare, respectively); process advantages
- A more complete comparison of these Cd Alts includes Phase II tests nearing completion at ARL: (1) GM9540; (2) B 117, Galvanic, ...

Non-Chromate Primer Demonstration

- Phase I
 - Qualification testing
 - Enhanced requirement testing (3000+h ASTM B 117, ASTM G 85, D 3359...)
- Phase II
 - Primer down-select testing; review beach exposure data
 - Vendor Reformulation Validation
- Depot Validation
- Field demonstrations



Paint hanger for North Island demonstrations.

Primer Candidates

- Primer downselection:

- Waterborne MIL-PRF-85582 primer options:

- EWDY048- Good beach results (5 yrs); Ltd. use on E-2/C-2; possible T-45 transition (2 yr demo).

- 44-GN-098

- Solvent borne MIL-PRF-23377 primer options:

- 16708TEP—Army helo demonstrations (2 yr)

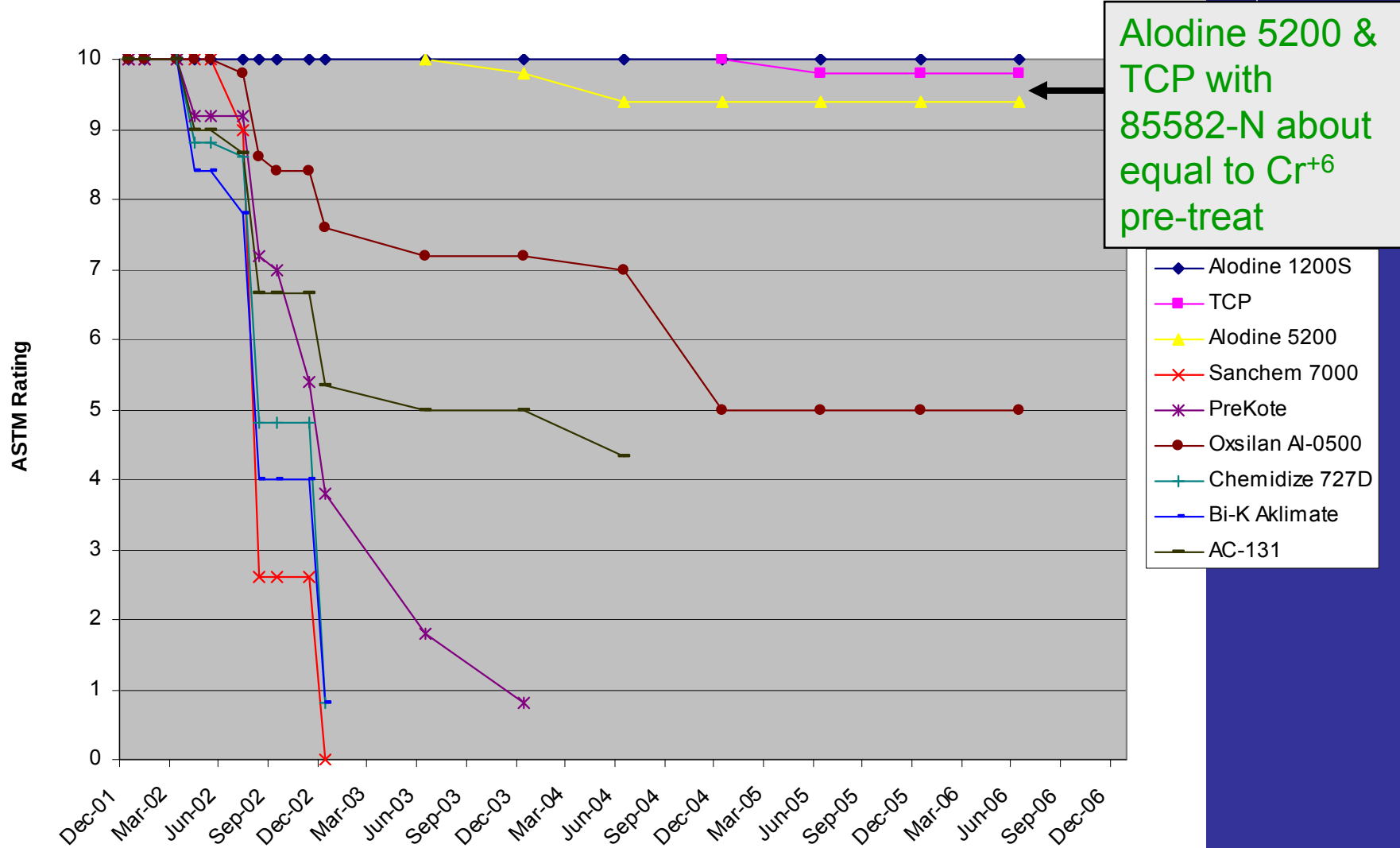
- 02-GN-083

- 02-GN-084

- Mg-rich Primer Efforts

Beachfront Corrosion

MIL-PRF-85582 Class N Primer & MIL-PRF-85285 Topcoat on 2024-T3 Aluminum



4.5 year Beach Data (NCAP Project), Matzdorf & Nickerson

Depot validation

E-2/C-2 platform
demonstration

- NAS North Island
 - 3 Primers Selected
 - PPG 85582-N (EWDY048) – Control
 - Painters to conduct sprayouts on practice a/c sections for (a) sprayability, (b) thickness control, (c) pot life... Evaluation datasheets
 - Using std hex chrome pretreatment
- FRC-SW (JAX)
 - Limited P-3 demo, several primers (wheel)



Acknowledgments

- NESDI (Naval Environmental Sustainability Development to Integration Program)
 - Fatigue, SCC, Residual Stress, G85
- ESTCP
 - Continuing support of Joint Cad Alts
- JG-PP
 - Demonstration setup (Cd Alts / LHE Zn-Ni), Cost-Benefit Analysis (through CTC); Non-Cr primer dem/val & test efforts
- FURTHER QUESTIONS ?

BACKUP SLIDES

Experimental Procedure

- **Substrate Material & Specimen**
 - **Substrate Material:** 4340 Steel Plate (3.8x15x30 cm)
 - **Specimen:** Round Tension Specimen, Round Hourglass Fatigue Specimen, Square Bar SCC Specimen with Center V-Notch of 60°
- **Coating: Polished Specimens were**
 - Electrocoated with Al, Cd, Zn-6Ni & Zn-13Ni
 - Vacuum-Coated with IVD Al
- **Coating Thickness, Chemical Composition & Residual Stress Determination**
- **Tension & Fatigue Tests**
- **Open Circuit Potential Measurement**
- **SCC Test: Accelerated SCC Test, Using Rising Step Load Test System, K_{OSCC} & K_{ISCC} Determination**

Tension & Fatigue Tests

- * Interlaken of 90 KN (20 kip) Capacity for Tension & Fatigue Tests
- * Tension Test in Air, following ASTM E8
- * Fatigue Test at $R = 0.1$ & $f = 10$ Hz in Air & 3.5% NaCl Solution of pH 7.3 under Load Control, following ASTM E466

OCP Measurement

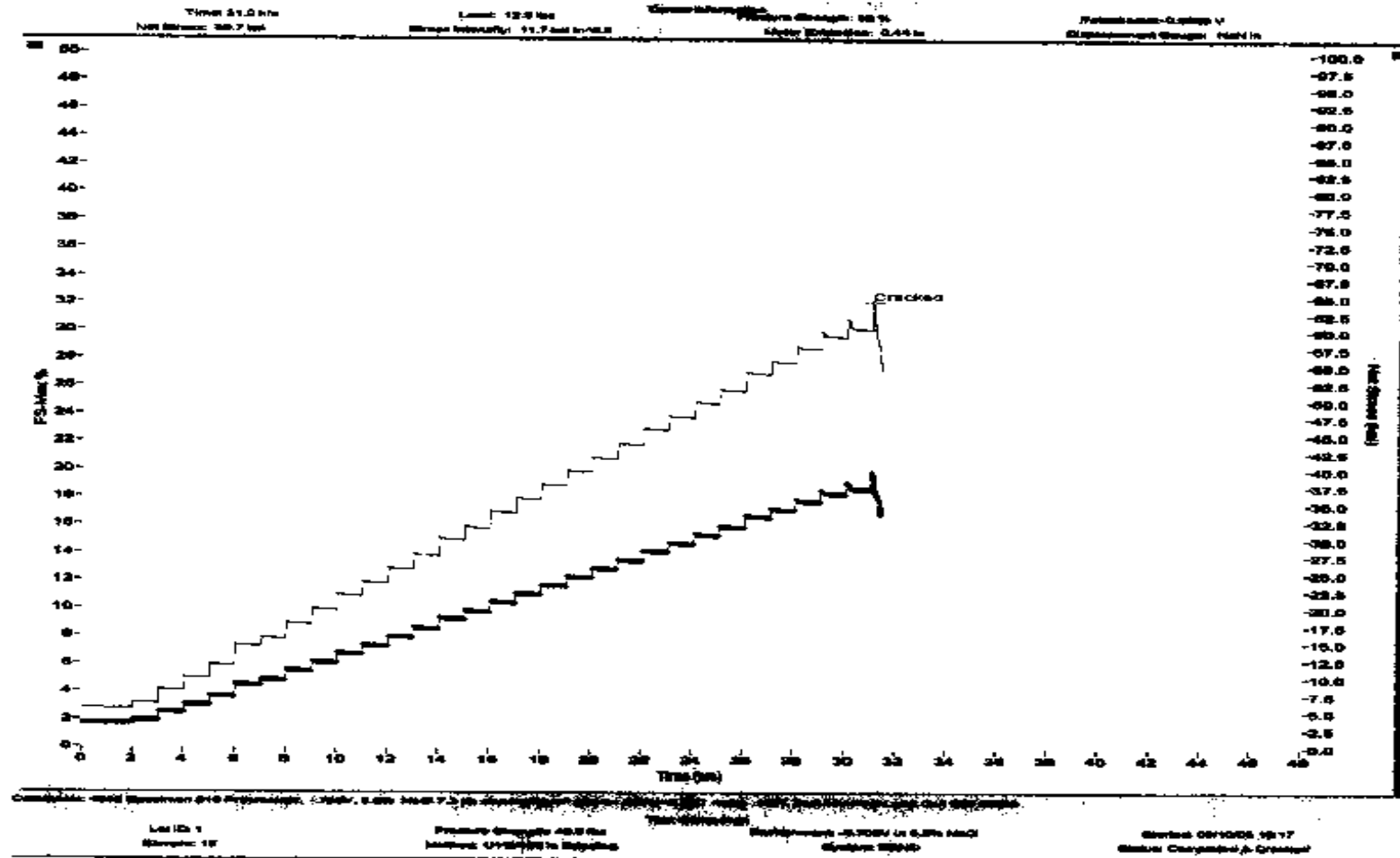
- * **Open Circuit Potential (OCP): Electrochemical Parameter of Corrosion Resistance, Measurable in Corrosion Cell**
- * **OCP Cell, consisting of Specimen Electrode & Reference Electrode (SCE) in 3.5% NaCl Solution of pH 7.3**
- * **Specimen Electrode: Flat Sheet of 38 x 7 x 1 mm, Bare & Coated**
- * **Electrode Potential, Stabilized in 24 Hours, Taken as OCP**

SCC Test

- * **Accelerated SCC Test in Rising Step Load (RSL) System**
- * **RSL System, consisting of Bending Frame, Electrolyte Reservoir, Circulation Pump, Reference Electrode (SCE), Pt Counter Electrode, Computer & Printer**
- * **Specimens: Bare (Unprecracked & Precracked) & Coated (Unprecracked)**
- * **Loading: Step Loading in Four Point Bending at a Given Potential**
- * **Load Drop: Indication of Threshold SCC, Calculation of Threshold Stress Intensity for SCC (K_{OSCC} & K_{ISCC})**



Sketch of Rising Step Loading



(* Load Drop: Threshold Stress Intensity for SCC, K_{OSCC} & K_{ISCC})

Threshold Stress Intensity for SCC

K_{OSCC} or K_{ISCC}

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

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

$F(a/W)$: correction function

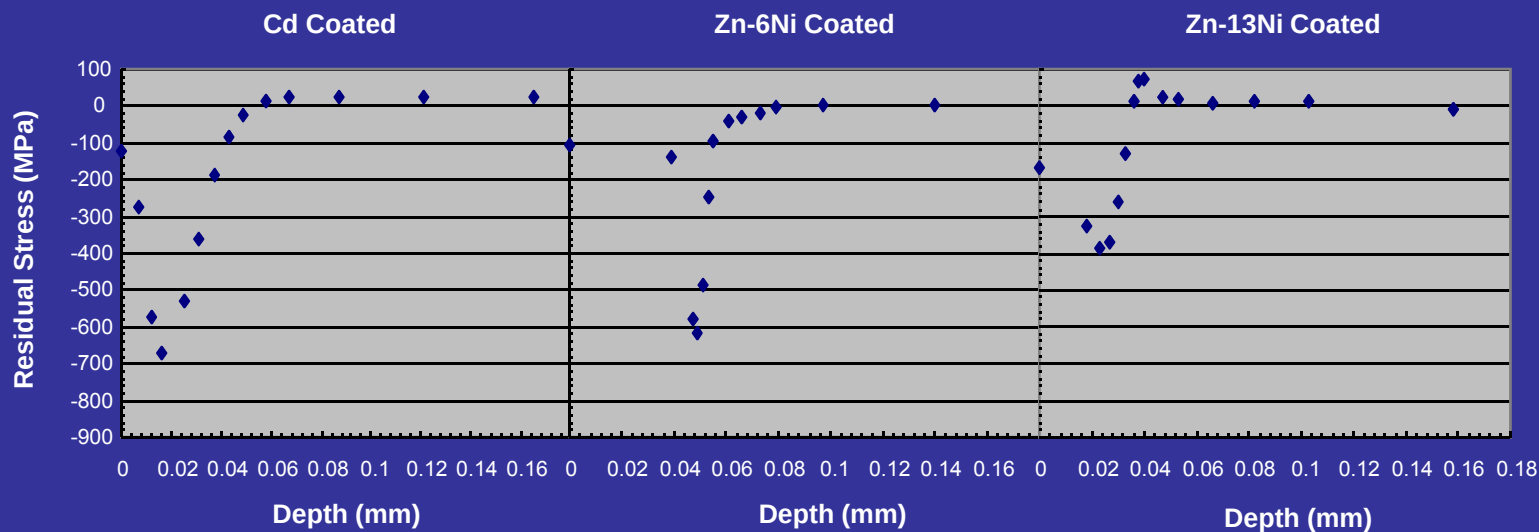
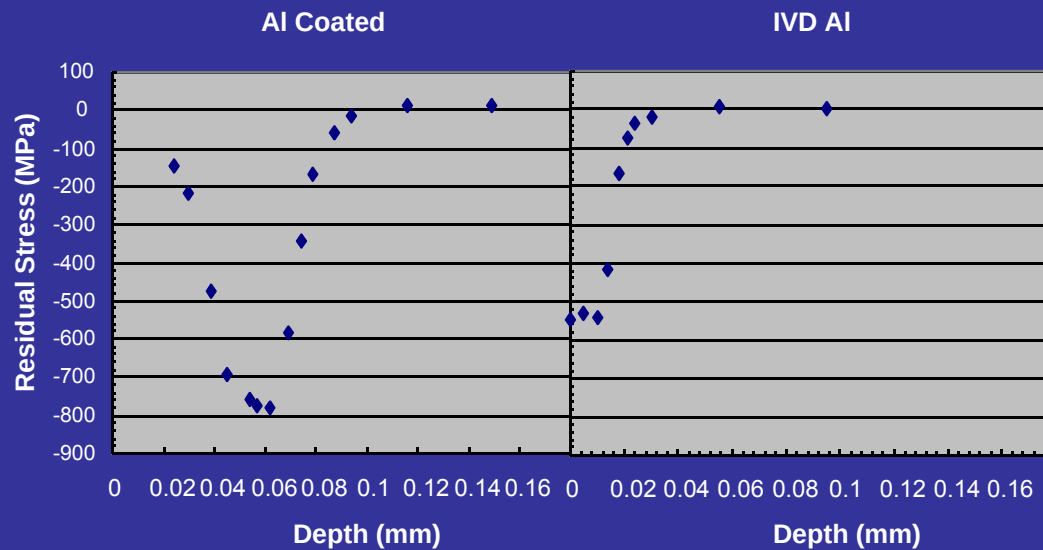
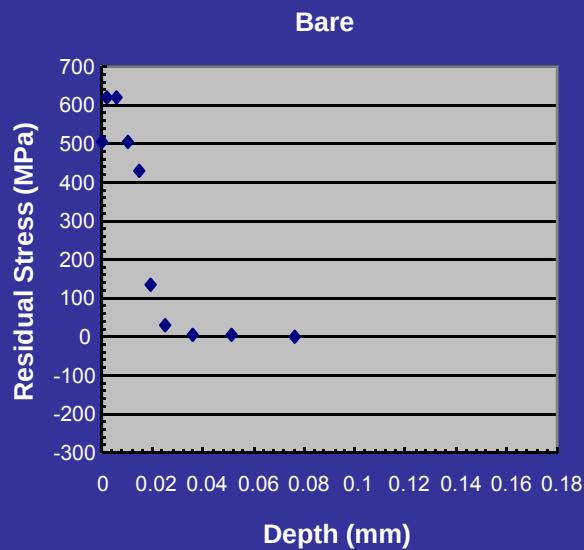
$$= 1.122 - 1.40(a/W) + 7.33(a/W)^2 - 12.08(a/W)^3 + 14.0(a/W)^4$$

Coating Composition (wt %)

<u>Coating</u>	<u>Al</u>	<u>Cr</u>	<u>Fe</u>	<u>Ni</u>	<u>Zn</u>	<u>Cd</u>	<u>Total</u>
Electrocoated 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

Residual Stress in Coating

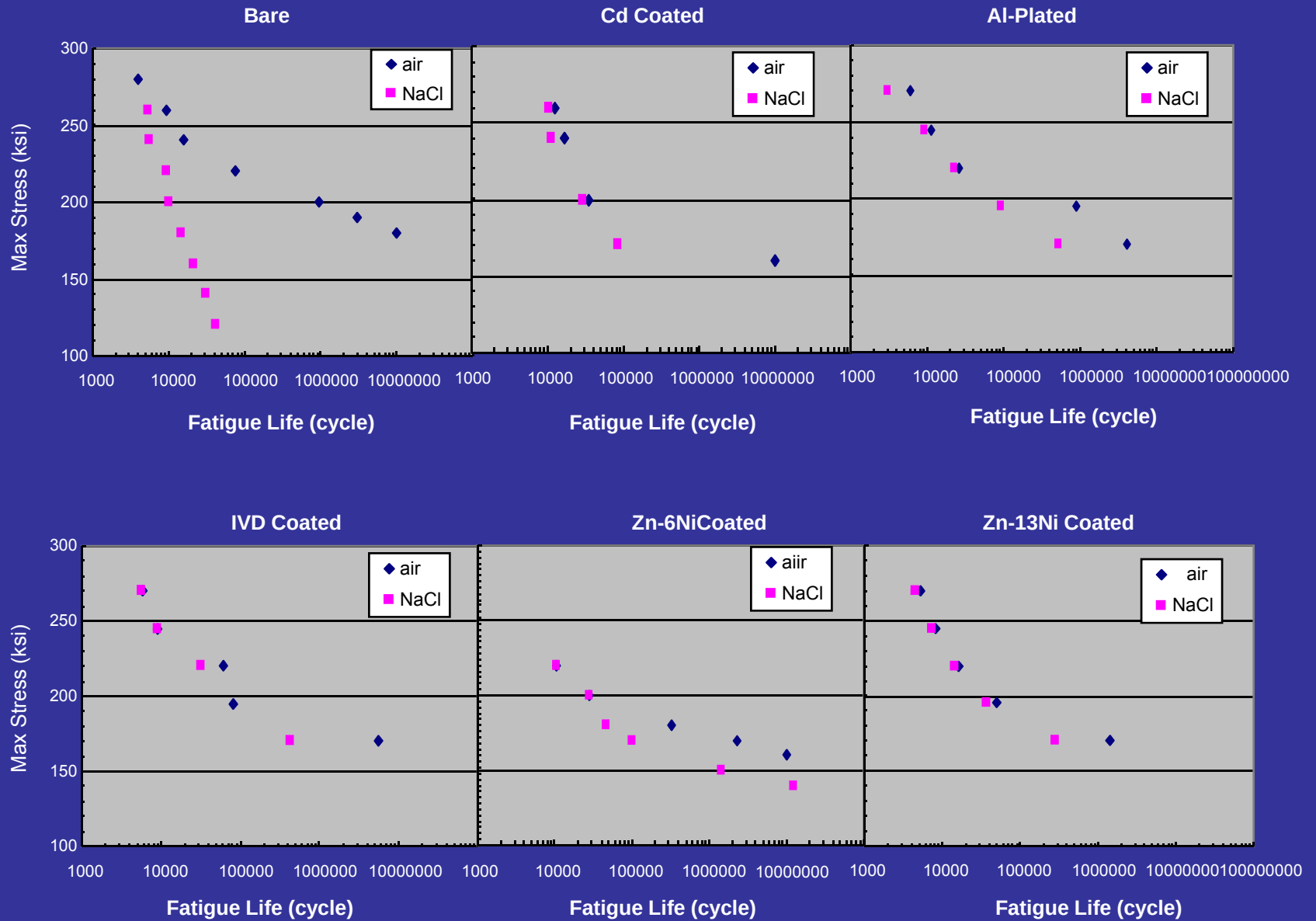
<u>Coating</u>	<u>Residual Stress, MPa (ksi)</u>	
Electrocoated Al	+ 21	(+ 3.0)
IVD Al	- 61	(- 8.8)
Cd	- 22	(- 3.2)
Zn-6Ni	+ 319	(+ 46.3)
Zn-13Ni	- 25	(-3.6)



Residual Stress in Substrate

Residual Stress in Substrate

<u>Coating</u>	Peak Residual Stress		Residual Stress Layer
	<u>Magnitude, MPa (ksi)</u>	<u>Depth, mm (mil)</u>	<u>Thickness, mm (mil)</u>
Bare	+ 621 (+ 90.0)	0.006 (0.24)	0.076 (2.99)
Electro 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 (0.63)	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)

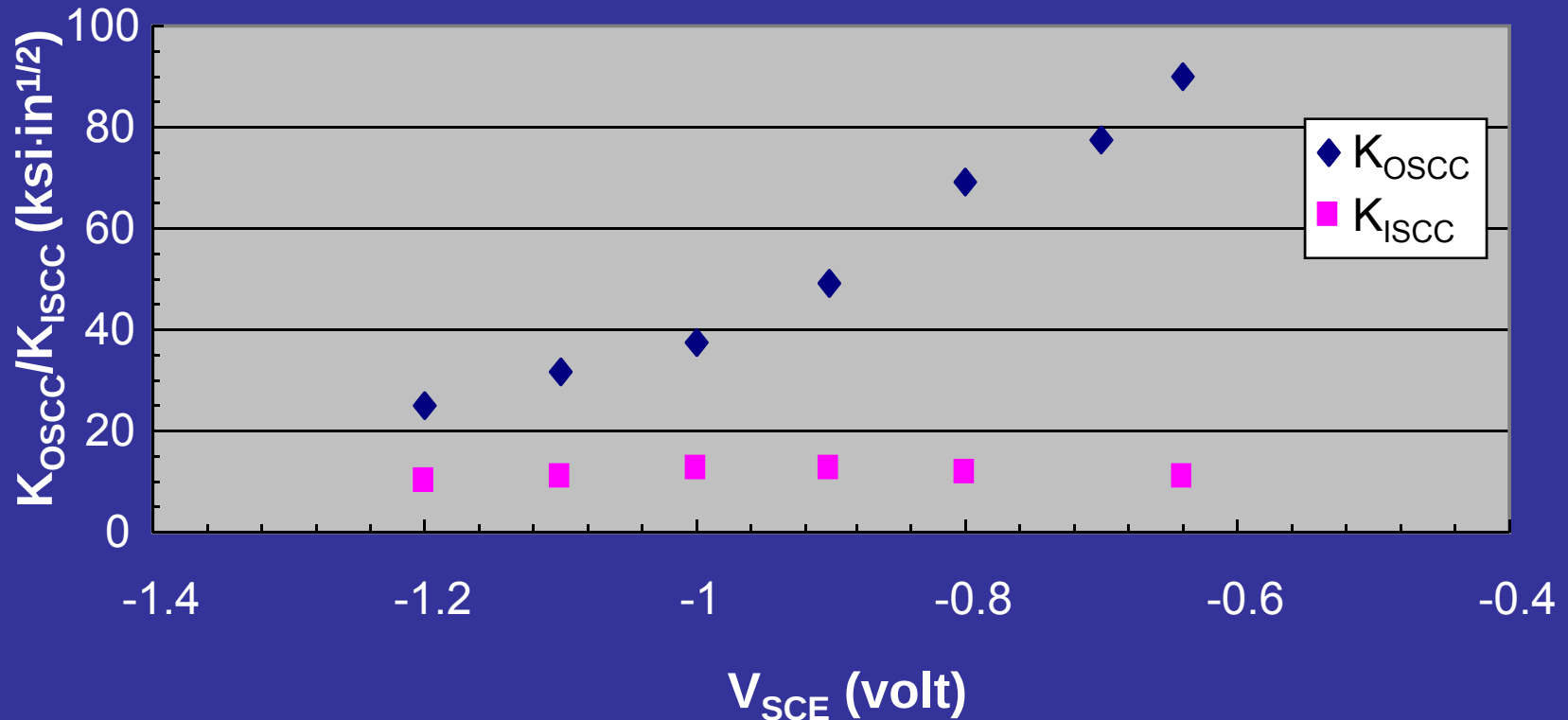


Stress-Life Curves of Bare and Coated Specimens in Air and 3.5% NaCl Solution

Open Circuit Potential OCP & Threshold Stress Intensity for SCC K_{OSCC}

<u>Coating</u>	<u>OCP (volt)</u>	<u>K_{OSCC}</u>	
		<u>MPa√m</u>	<u>ksi√in</u>
Bare	- 0.64	98.5	89.6
Electrocoated 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

K_{OSCC} & K_{ISCC} (4340 Bare)



Variation of Threshold Stress Intensity for Stress Corrosion Cracking in As-Machined (Un-precracked) and Precracked Bare Specimens, K_{OSCC} and K_{ISCC} , with Applied Electric Potential V_{SCE} {At OCP = - 0.64 volt, K_{OSCC} = 98.5 MPa√m (89.6 ksi√in) & K_{ISCC} = 11.5 MPa√m (10.5 ksi√in)}

Discussion

- **Residual Stress**
- **Fatigue**
- **SCC**

Residual Stress

- **Residual Stress in Structural Components**
 - **Beneficial, if Compressive**
 - **Detrimental, if Tensile**
- **Residual Stress in Coated Components Generated by:**
 - **Lattice Distortion due to Its Misfit at Interface between Coating & Substrate**
 - **Coating Condition & Bath Composition**

Residual Stress in Bare Specimen

- * Residual Stress Determined: Tensile**
- * Specimen Prepared by EDM and Hand Polishing with Emery Cloth**
- * EDM, involving Electric Sparking, Thin Layer Melting, Cooling, Solidification & Shrinkage, inducing Tensile Residual Stress**
- * Hand Polishing, inducing Compressive Residual Stress**
- * Residual Stress by EDM > Residual Stress by Hand Polishing**

Lattice Parameters of Coating & Substrate

<u>Element</u>	<u>Crystal Structure</u>	<u>Lattice Parameter (Angstrom)</u>
Al	fcc	$a = 4.0491$
Cd	hcp	$a = 2.9787, c = 5.6173$
Zn	hcp	$a = 2.6649, c = 4.9470$
Fe-C, Martensite (0.4% C)	bct	$a = 2.8530, c = 2.9060$

Residual Stress (RS) in Coating

- * Lattice Parameter of Cd > Lattice Parameter of Martensite, and RS: Compressive in Cd Coating
- * Lattice Parameter of Al > Lattice Parameter of Martensite, but RS: Tensile in Electro Al & Compressive in IVD Al
- * Lattice Parameter of Zn > Lattice Parameter of Martensite, but RS: Tensile in Zn-6Ni & Compressive in Zn-13Ni

UTS of Coating & Substrate

<u>Material</u>	<u>UTS, MPa (ksi)</u>
Al	40 – 70 (6.5 – 10.2)
Cd	69 – 83 (10.0 – 12.0)
Zn	283 – 324 (41.0 – 47.0)
Ni	317 (46.0)
4340	1,964 (284.8)

[* UTS proportional to Fatigue Strength]

Open Circuit Potential OCP & Threshold Stress Intensity for SCC K_{OSCC}

<u>Coating</u>	<u>OCP (volt)</u>	<u>K_{OSCC}</u>	
		<u>MPa√m</u>	<u>ksi√in</u>
Bare	- 0.64	98.5	89.6
Electrocoated 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