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Linking Global Technologies with Markets

Cadmium replacement options

Keith Legg
Rowan Technology Group
JSF ESOH Working Group
klegg@rowantechnology.com

10/2003 JSF European Trip

Definition

- Cd used on almost all exposed steel, usually chromated, primed, painted
- Specs
  - QQ-P-416
    - Class 1 0.0005”; Type I as-deposited
    - Class 2 0.0003”; Type II chromated
    - Class 3 0.0002”; Type III phosphated
  - BAC 5701
  - AMS 2400

Usage

Steel Components

- The “cure-all” corrosion coating
- Good salt spray and scribed corrosion protection
- No hydrogen embrittlement or stress corrosion cracking
- ODs and IDs
- Plate steel to protect Al

Fasteners

- Correct lubricity (avoid changes to torque-tension specs)
- No hydrogen embrittlement
- Retain thread profile

Connectors

- For electrical equipment
- Low contact resistance
- Non-insulating corrosion products
- Solderable a plus

klegg@rowantechnology.com

Cd – a life-cycle issue

- Deposition – Cd and CN solution
- Scuff-sanding for repaint
  - Personnel exposure
- Wash-down of engines
  - Environmental contamination
- Strict new European Cd rules
  - End-of-life vehicles

klegg@rowantechnology.com

Requirements

- Cd is a sacrificial material
  - Meets B117 and SO_2 salt fog tests
  - If scratched it still protects
  - Compatible with Al so a Cd-plated bolt or rivet does not corrode an Al aircraft skin
  - Ni and other barrier coatings are not replacements
- For threaded fasteners need right lubricity
  - Consistent break-away torque and torque-tension
    - Otherwise have to redo all the manuals
- Need to be able to repair during manufacture
- Need to be able to prime and paint

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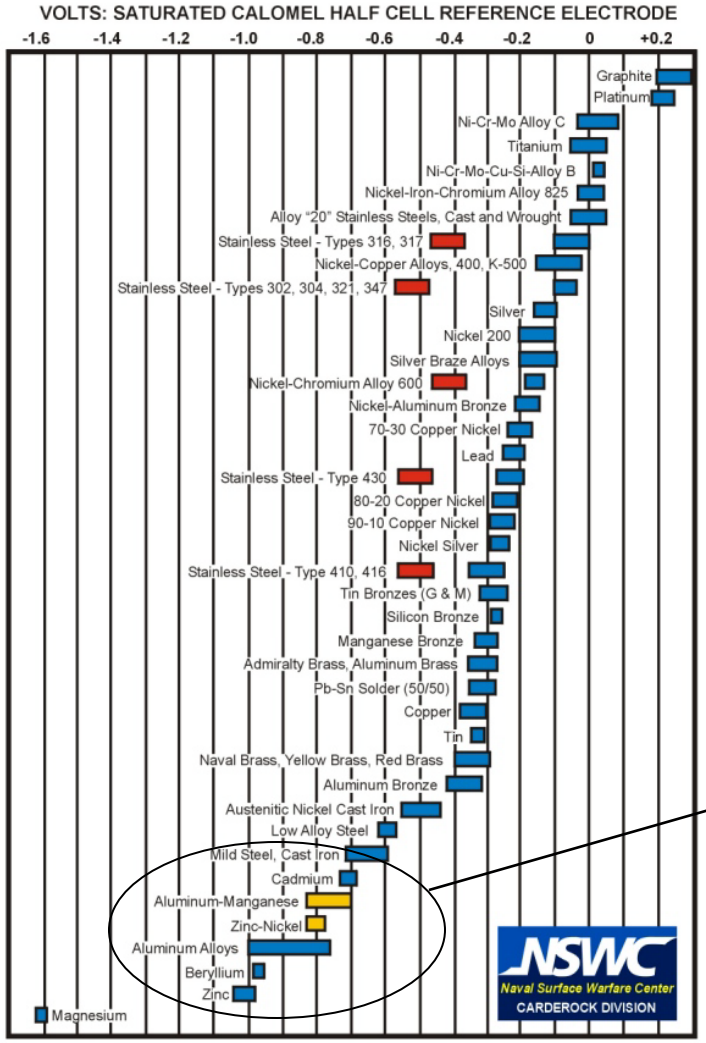
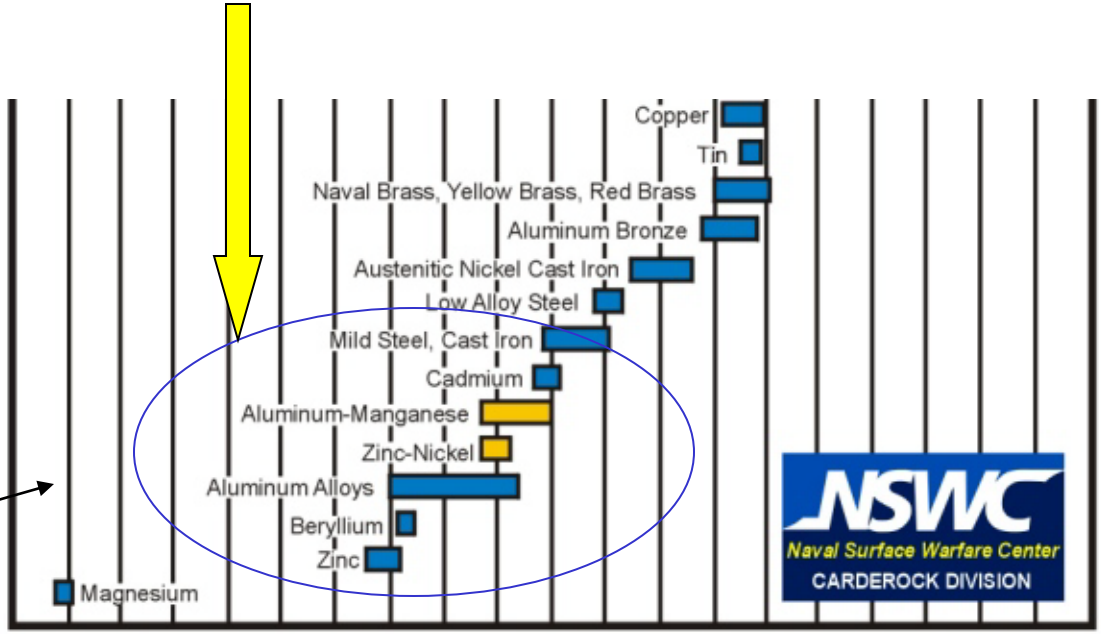
Galvanic series



- **Al and Al alloys**
- **Zn-Ni**
- **Al-Mn**
- **Zn**
- **Be!!**

Mother Nature left us short on options!



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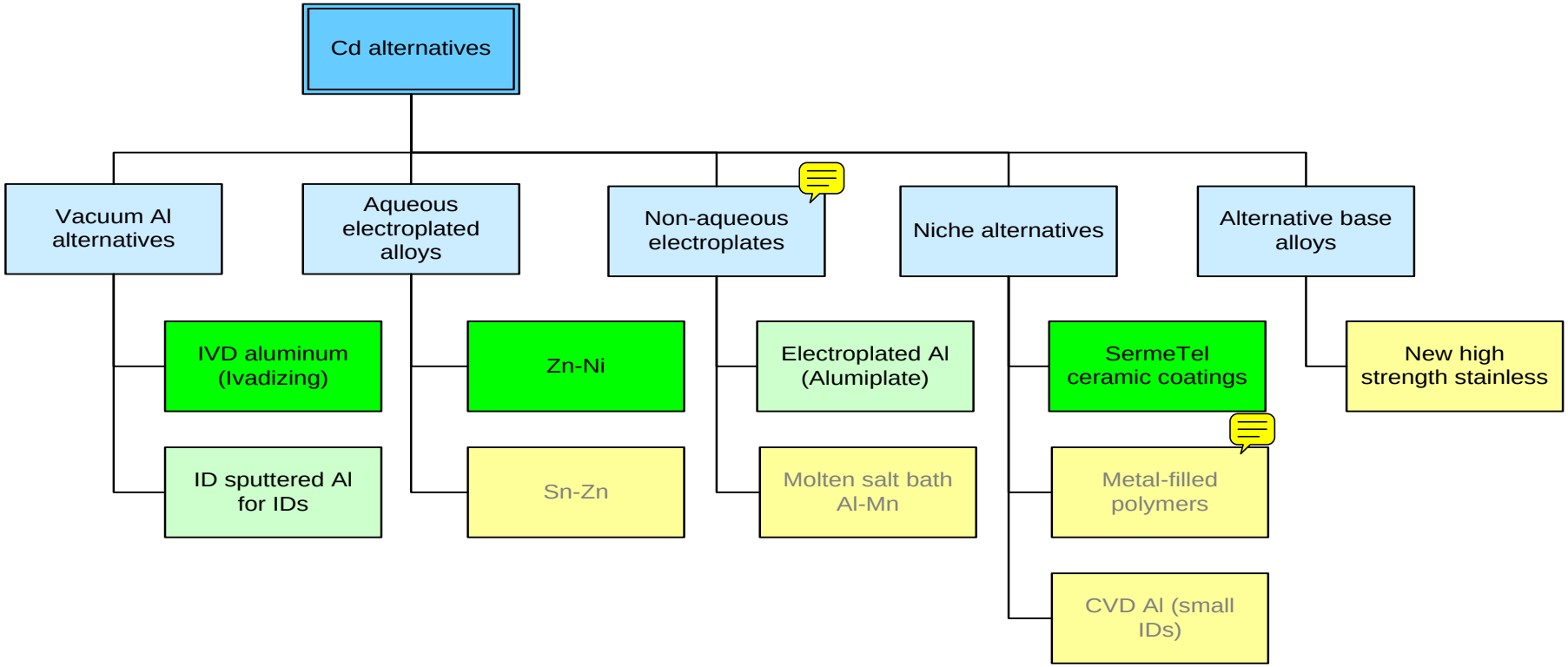
Summary of Cd alternative options



Al is the only "global" replacement
Almost everything needs chromate conversion

In use | In test | In development

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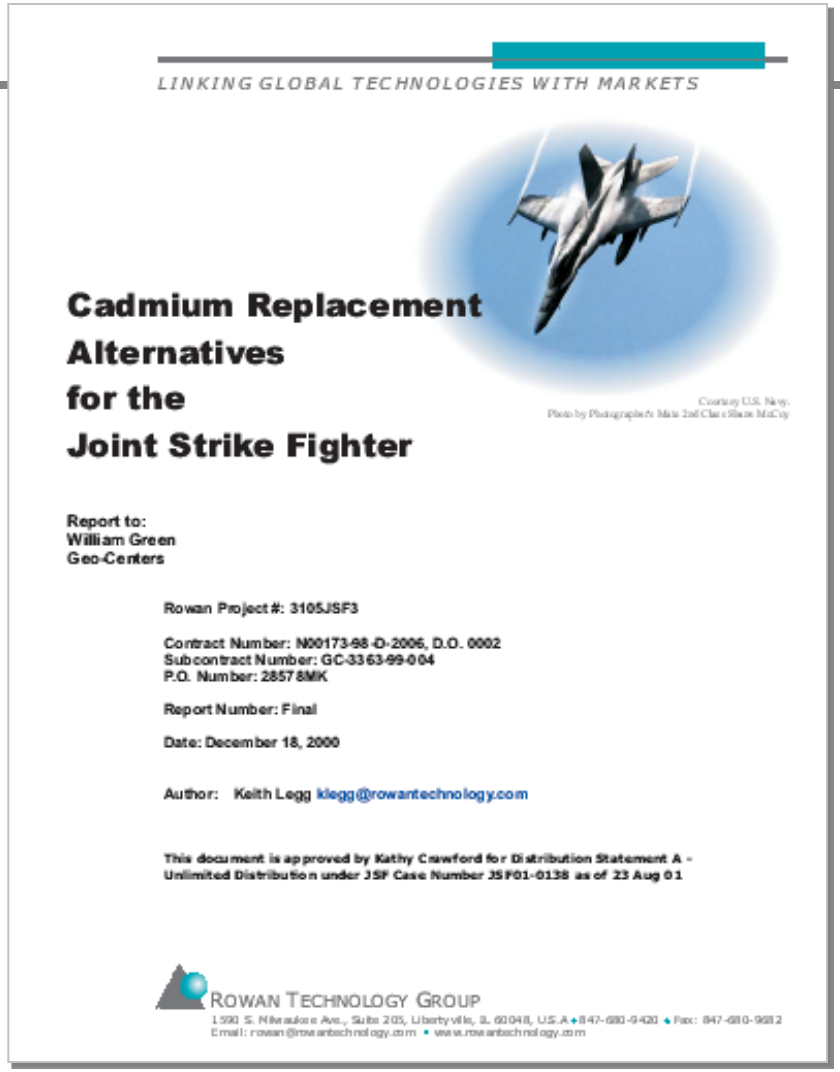
JSF Cd Alternatives Report

- Requirements
- Alternatives
  - Zn-Ni, Sn-Zn electroplates
  - Alumiplate
  - Al-Mn molten salt bath
  - IVD and CVD Al
  - Sputtered Al
  - Thermal spray
  - SermeTels
  - Filled polymers
  - High strength stainless steel



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Cadmium Replacement Alternatives for the Joint Strike Fighter

Report to:
William Green
Geo-Centers

Rowan Project #: 3105JSF3

Contract Number: N00173-98-D-2006, D.O. 0002
Subcontract Number: GC-3363-99-004
P.O. Number: 28578MK

Report Number: Final

Date: December 18, 2000

Author: Keith Legg klegg@rowantechnology.com

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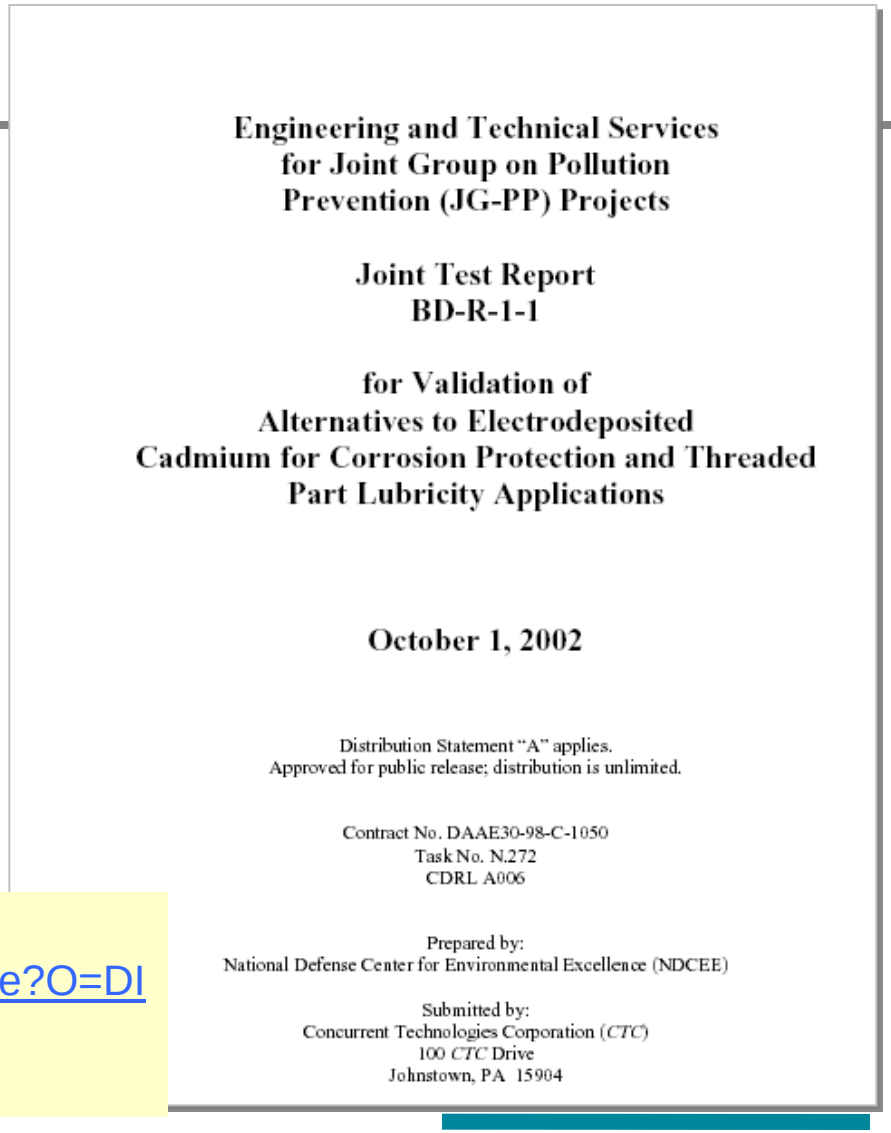
ROWAN TECHNOLOGY GROUP
1590 S. Milwaukee Ave., Suite 205, Libertyville, IL 60048, U.S.A. • 847-680-9420 • Fax: 847-680-9882
Email: rowan@rowantechnology.com • www.rowantechnology.com

klegg@rowantechnology.com

Joint Test Report

- Cd alternatives report for low strength steels (<220 ksi)
  - Boeing, JGPP
  - Sn-Zn
  - Acid Zn-Ni (Boeing)
  - Alkaline Zn-Ni
  - IVD Al



Engineering and Technical Services
for Joint Group on Pollution
Prevention (JG-PP) Projects

Joint Test Report
BD-R-1-1

for Validation of
Alternatives to Electrodeposited
Cadmium for Corrosion Protection and Threaded
Part Lubricity Applications

October 1, 2002

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Prepared by:
National Defense Center for Environmental Excellence (NDCEE)

Submitted by:
Concurrent Technologies Corporation (*CTC*)
100 *CTC* Drive
Johnstown, PA 15904

http://www.jgpp.com/projects/cadmium/jtr.html
http://www.materialoptions.com/w2g/cgi/kmcgi.exe?O=DIR000000I6D&V=0

klegg@rowantechnology.com

IVD Al

Vacuum PVD process

Fully qualified and quite widely used by OEMs and depots

Spec MIL-C-83488 for Al coating does not define deposition method

Keith Legg 847-680-9420
www.rowantechnology.com

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IVD Aluminum (Ivadizing)

Vacuum evaporation of Al
Bead blasting to densify
Chromate conversion

Abar Ipsen
Depots

Pros:
Long history of successful use
Clean process (except chromating)
High volume chamber (up to 5'x1.5'x15' load)

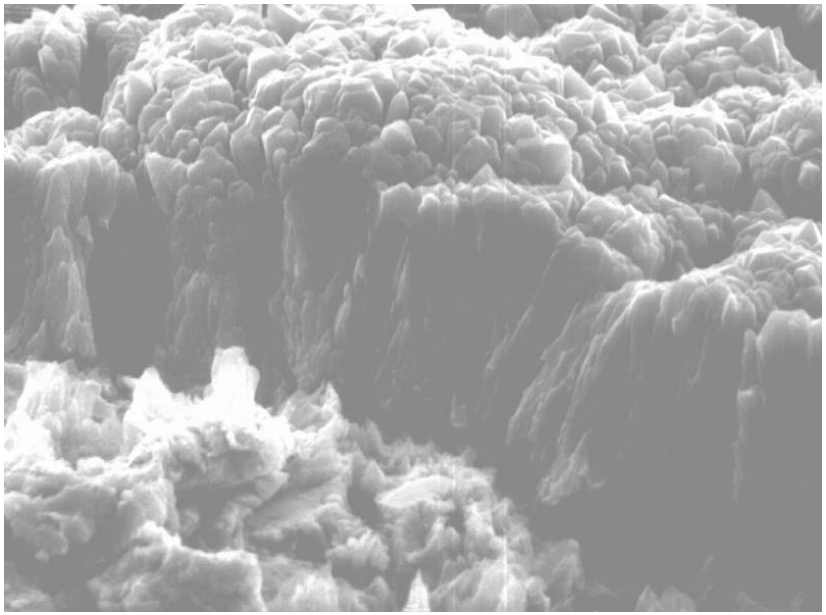
Cons:
Vacuum process - expensive
Requires shot blasting and chromate conversion
Poor throwing power (especially in holes)
Solid lubricant for torque-tension
Limited data on fasteners, electrical connectors

Stage of development:
Commercial
Available at many depots

klegg@rowantechnology.com

Description

- Deposition
  - Al evaporated from bottom of chamber
  - Substrates hang on frame, biased for weak plasma
  - Gives coating poorly adhered and porous
- Consolidation
  - Glass bead peen
- Convert
  - Chromate convert
    - Iridite 14-2
- Dry lube (threads)
  - MoS_2 in resin binder



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Applications

- Military
  - F-4
  - F-14
  - F-15
  - F-16
  - F-18
  - AV-8B
  - A-12
  - V-22
  - Apache
- Commercial
  - Boeing 737, 747, 757, 767
  - McDonnell-Douglas DC9, 10, MD-80, 90, 11
  - Bombardier Dash 7, 8
  - Airbus A300, A310

Specification – MIL C-83488

		B117 Salt Fog (hours)	
Class	Thickness (min)	Type I	Type II
1	0.001”	504	672
2	0.0005”	336	504
3	0.0003”	168	336

Type I – Deposit + glass bead peened
Type II – Deposit + peen + chromate convert

klegg@rowantechnology.com

Advantages and limitations

Advantages

- Qualified commercial process
  - Commercial coating shops
  - IVD-coated fasteners available commercially
- Clean and safe
- Good performance
- No H embrittlement

Limitations

- Vacuum process
  - Expensive
  - Awkward
- Poor quality coating as-deposited
  - Peen and chromate
- Poor throwing power
- Soft and easily damaged
  - Cannot easily be repaired
- Dissolves in alkaline cleaners
  - MRO users may have to change cleaning process

klegg@rowantechnology.com

Data available

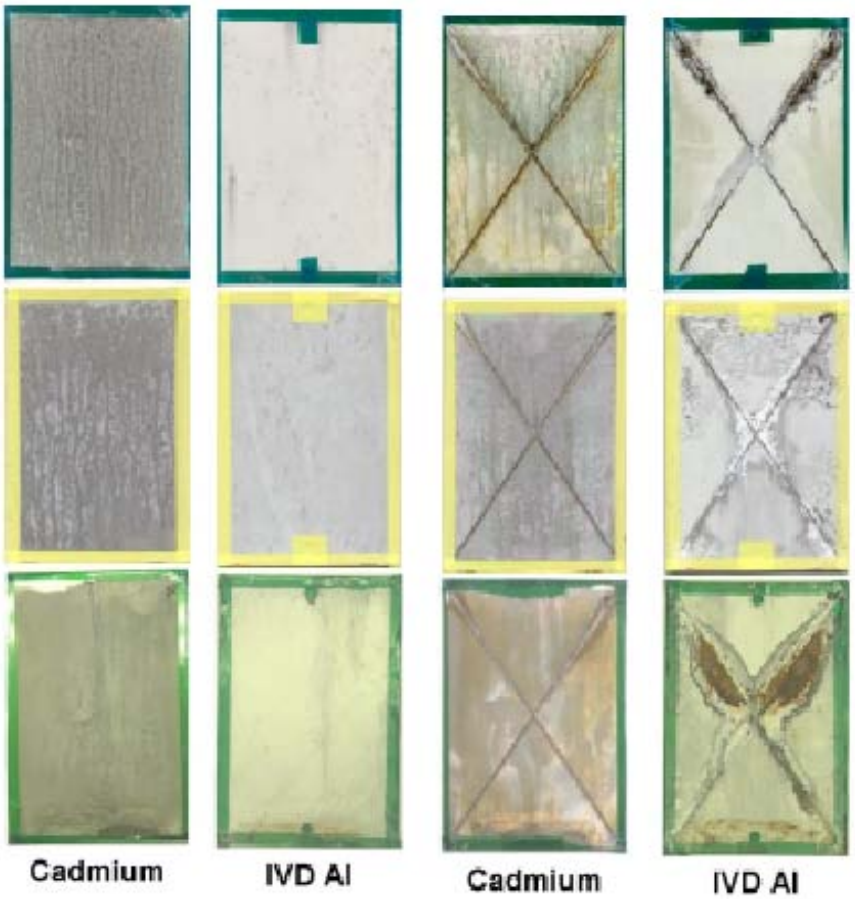
Keith Legg 847-680-9420
www.rowantechnology.com

Boeing/JGPP low strength steel report

- Boeing/JGPP report on Cd alternatives for low strength steels
  - http://www.jgpp.com/projects/cadmium/jtr.html
  - Also on HCAT site for convenience
  - Covers 4 alternatives:
    - Sn-Zn
    - Neutral Zn-Ni (Boeing process)
    - Alkaline Zn-Ni
    - IVD Al
- IVD and neutral Zn-Ni best
  - Scribed B117 inconsistent
  - Lubricity on fasteners acceptable with

Corrosion

- Data from B117 testing at 3 locations
  - Unscribed excellent
  - Scribed – variable corrosion from scribe



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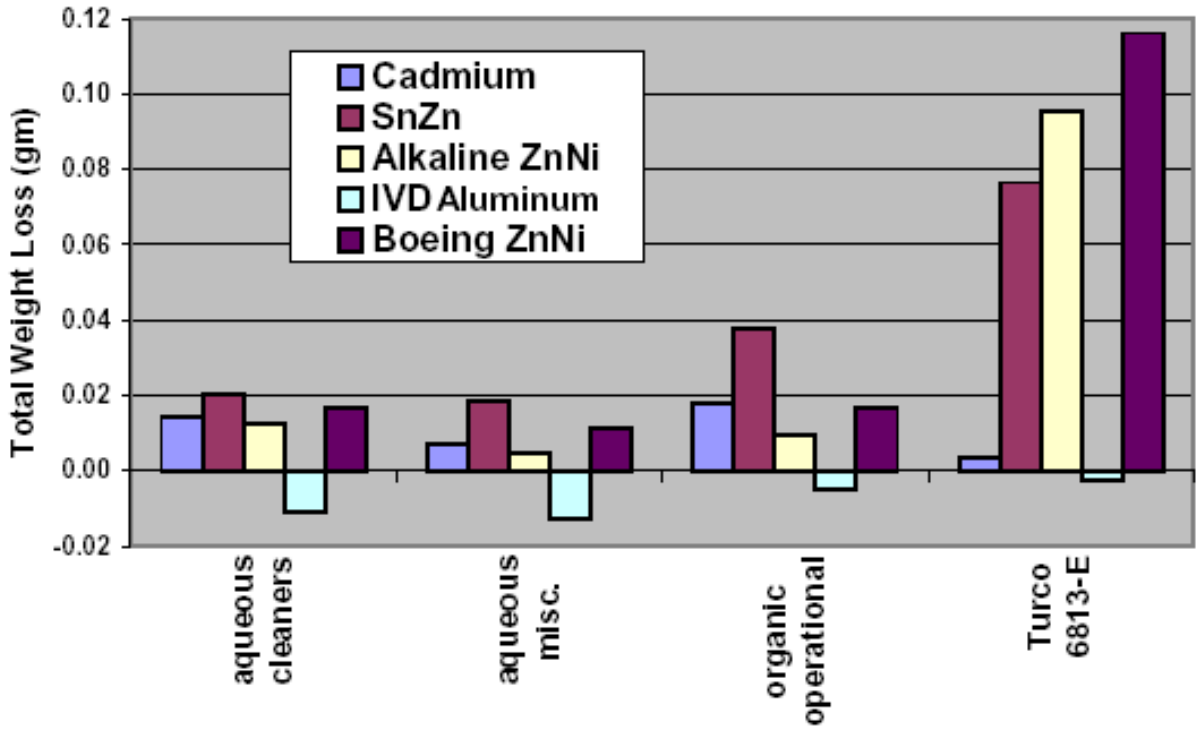
Fluid compatibility

- Weight loss after immersion, scrubbing
- In most cases IVD gains weight
  - Ascribed to adherent oxide
  - Could be absorption in porosity



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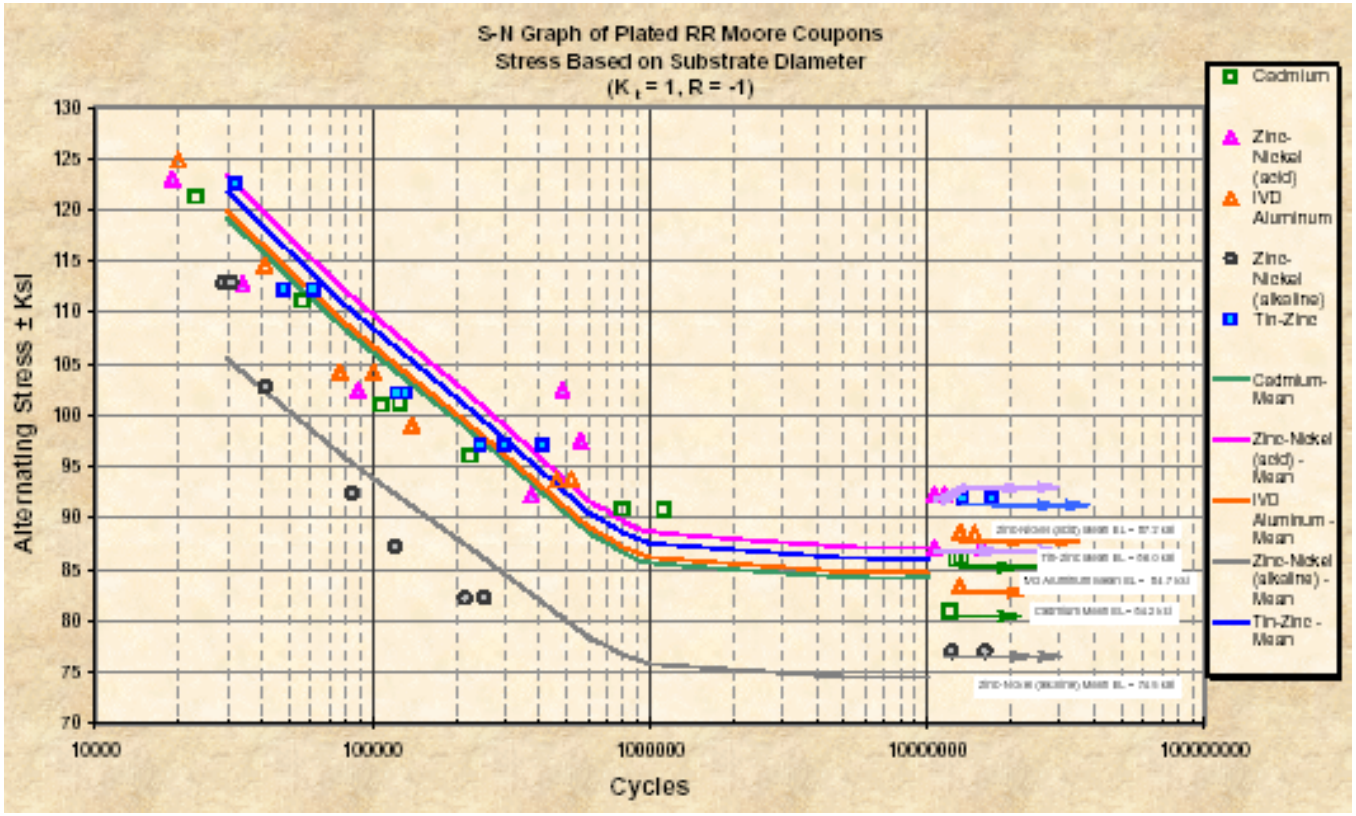
Fatigue



- No difference between uncoated and soft Cd alternatives
- Fatigue debit with harder alkaline Zn-Ni

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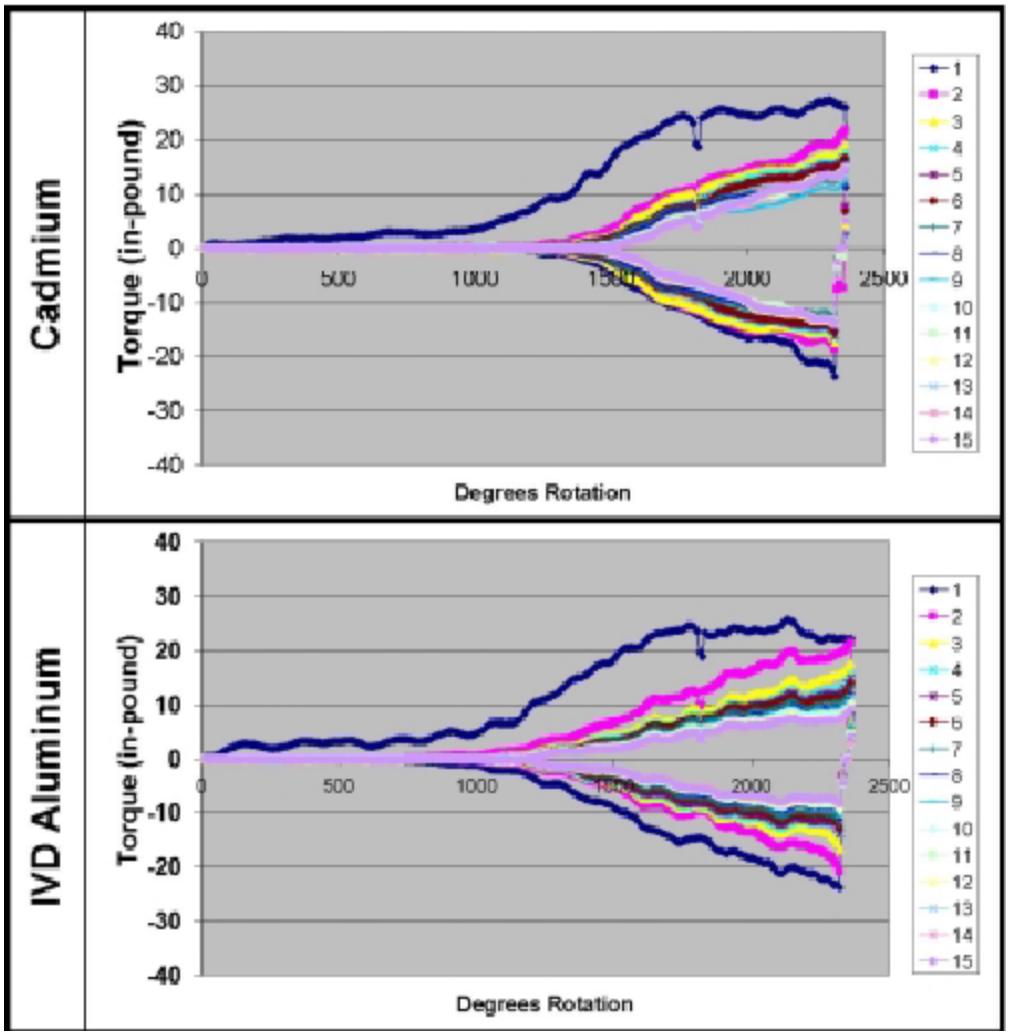
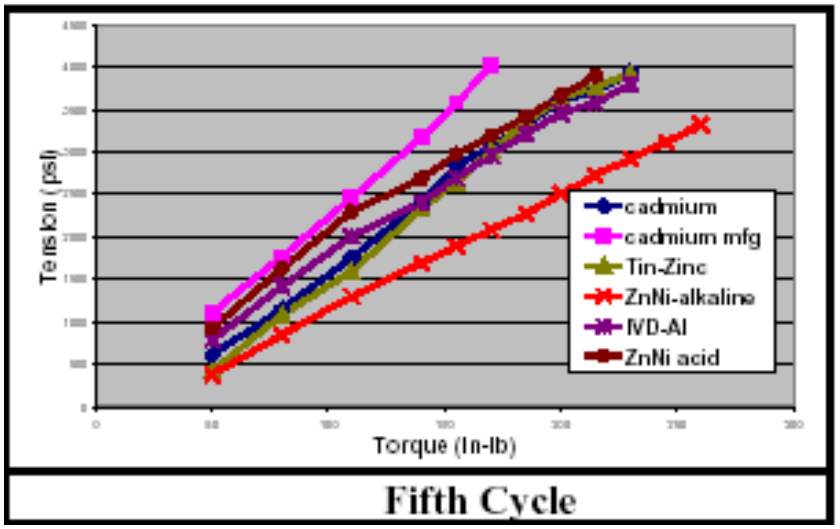
Breakaway torque and torque-tension



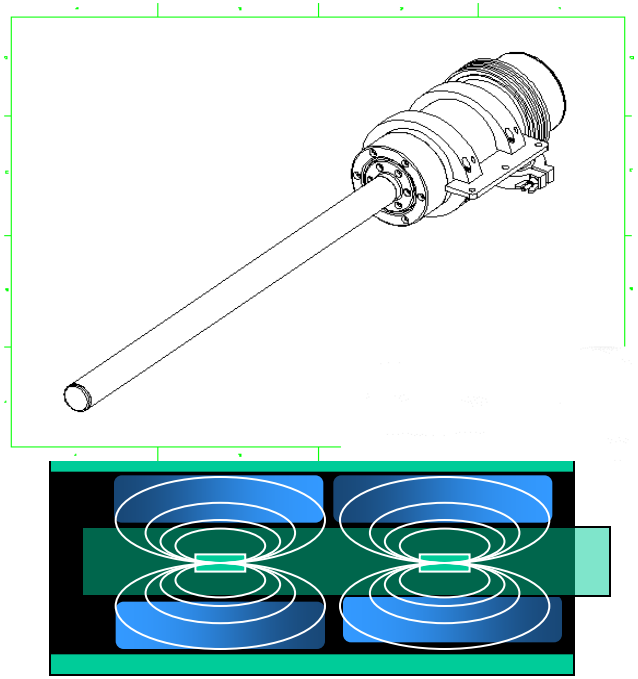


- MoS_2 lubricated IVD passes testing

klegg@rowantechnology.com

PVD Al for IDs – sputtered Al

- Marshall Labs Plug and Coat
  - Works inside IVD chamber
- Makes it possible to coat OD and ID simultaneously Plug & Coat
  - Add-on to existing IVD chamber
- Status
  - Being installed at Hill AFB
  - Commercially available
  - Meets MIL Spec.
- Note: All Al coatings require use of proper aqueous cleaners (avoid alkaline cleaners)



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ID sputtering data

- Report # BOEING-STL-01P0041
  - Meets MIL-83488
  - Better coating quality than IVD
  - Higher plasma density
  - Lower porosity
    - no need for glass bead peening
    - may be able to get away without chromating
  - Only uncertainty is environmental embrittlement
    - testing issues
    - not part of MIL spec
    - Avoid alkaline cleaners

klegg@rowantechnology.com

Developments needed

- Some additional environmental embrittlement data needed
- Plug and Coat miniaturization needed for smaller IDs
  - Under way at Marshall Labs
- Porosity and need for peening always an issue
  - Various approaches for better coating quality
    - Higher plasma density
    - Sputtering instead of IVD
    - Pulse biasing

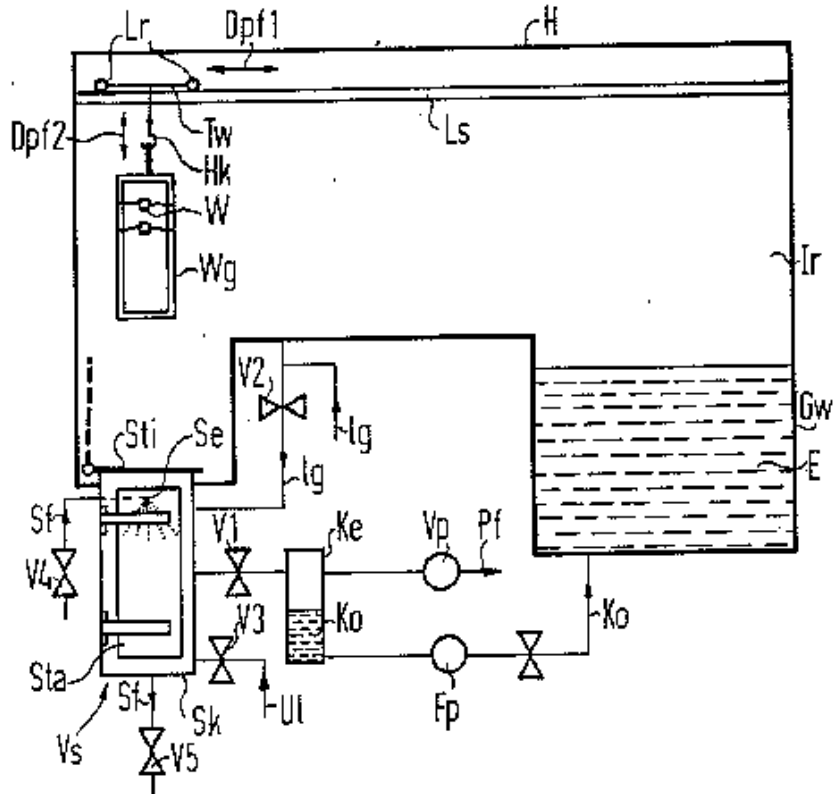
Electroplated Al (Alumiplate™)

Alumiplate, Minneapolis

Deposited from organic solution

Keith Legg 847-680-9420
www.rowantechnology.com

Alumiplate



Electroplating using organic Al salt in a toluene bath

Pros:
- Excellent corrosion resistance
- No H embrittlement
- Looks good for components, fasteners, connectors

Cons:
- Potentially hazardous bath - toluene-based
- Requires enclosed tank
- Sole production source, but willing to license

Stage of development:
- Under extensive DoD evaluation
- No aerospace qualification yet
- Probable part numbers shortly for Alumiplated composite connectors
- Being evaluated for landing gear

Alumiplate, Inc
Minneapolis

klegg@rowantechnology.com

Alumiplate description

- Organic electroplate
  - Requires enclosed tank and plating line in inert environment
    - Similar to vacuum processing but less
  - Al salts in toluene solution
  - Reasonable throwing power
    - Needs conformal or secondary electrodes for complex shapes, IDs
  - Frequently uses Ni strike for adhesion
  - Recent development uses grit blasting and activation with no Ni strike
    - Equivalent adhesion
  - Metallic strike needed for insulators such as composites
  - Coating thickness 0.0001 – 0.001”
    - Usually 0.0003 – 0.0005”
  - Conversion coat (traditionally chromate) for best corrosion performance (as with all other Cd alternative)

klegg@rowantechnology.com

Applications and specifications

- Applications
  - Hydraulic hose fittings
  - Various others in production
  - No current aerospace
    - Has successfully passed all testing for electrical connectors
    - Alumiplated connectors from Amphenol will probably be assigned part numbers shortly
    - Under testing for landing gear (Goodrich)
- Specifications
  - Meets MIL-C-83488
  - No AMS or other specs at this point

Advantages and limitations

Advantages

- "Drop-in" replacement
- Able to coat complex shapes
- Higher quality coating than as-deposited IVD AL
- Suitable for components, connectors, fasteners (with dry lube)
- Directly compatible with Al skins
- Can be anodized for better wear and abrasion

Limitations

- Size limited
  - Landing gear about 3' long
  - Limited by current bath size
  - Appears scalable
- Requires dry lube for threads to prevent galling
- Sole source is Alumiplate, Minneapolis
  - Willing to license, but no current licensees
  - Not yet available in Europe
- High capital cost
- Toluene bath not suitable for DoD depot use
- Cannot brush plate Al repair
  - Can brush plate Sn-Zn to repair Al

Data available

A great deal of data becoming available as a result of ongoing JSF and Army testing. Rowan is currently putting together a report on the technology – available by year's end

Keith Legg 847-680-9420
www.rowantechnology.com

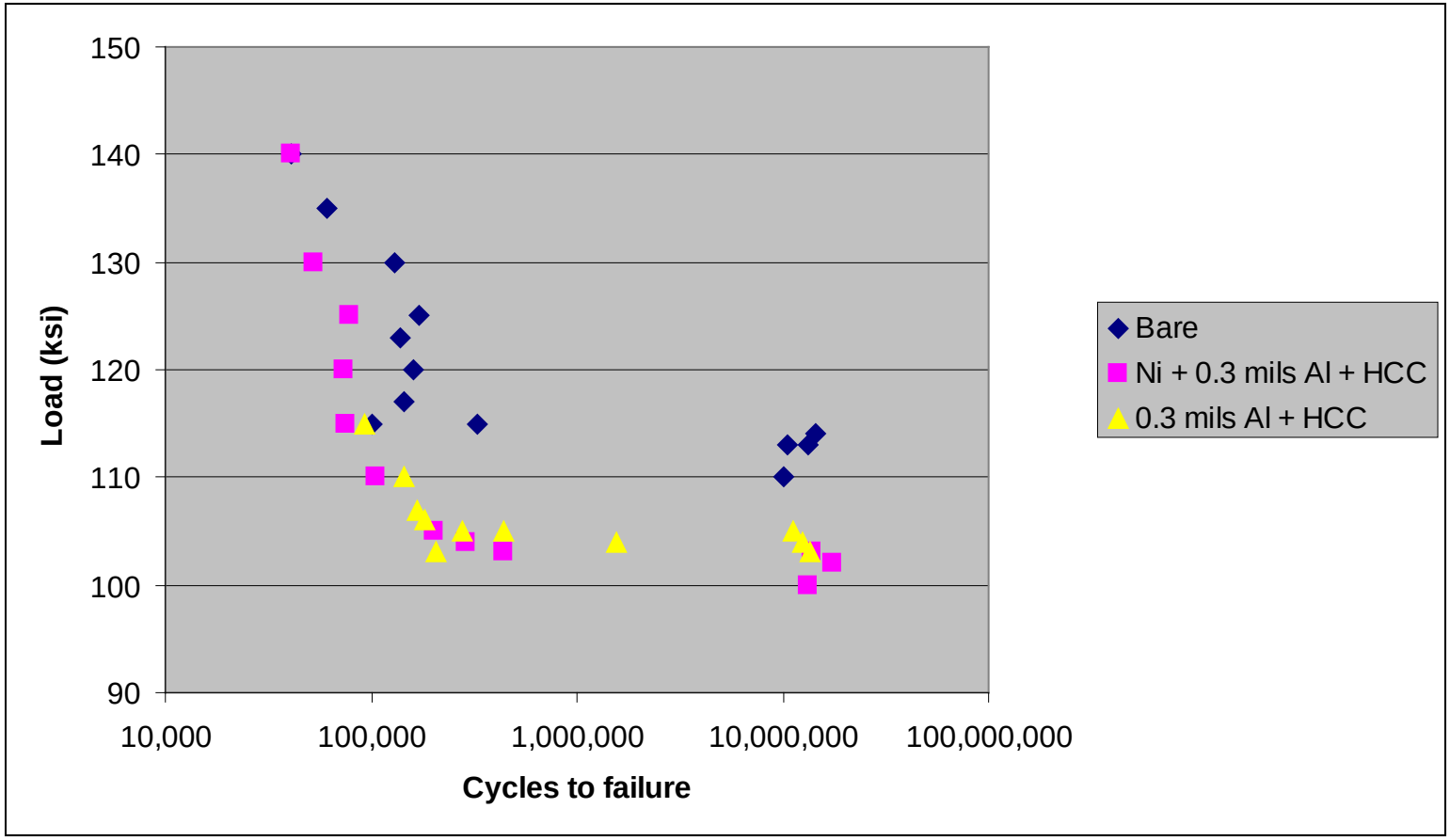
General corrosion data

- With chromate conversion passes 5,000 hr B117 salt fog and >336 hr SO_2 salt fog
- 0.0007” Al lasts for 1,000hr to red rust with no Ni strike or chromate conversion
  - Ni strike helps a bit
  - Chromate conversion is major contributor (as with most Cd and alternative coatings)
- Tests on connector shells show excellent corrosion resistance with Ni strike and chromate conversion
  - Better than Cd

Hydrogen embrittlement

- Does not appear to cause hydrogen embrittlement
  - Passed F-519 and RSL tests conducted by NAVAIR
  - Embrittlement seen in CTC tests, but tests not reliable
    - specimens stripped and replated several times
    - standard plating process not used
- Note: Cd causes major embrittlement
  - Hence need for LE Cd

Fatigue



Small fatigue debit with and without Ni strike

klegg@rowantechnology.com

Electrical connectors

- Meets all tests for qualification on connector shells (MIL-DTL-38999K testing)
  - Al and C-fiber/PEEK composite
  - Corrosion, conductivity stability in salt fog
  - Mate/unmate testing (wear, torque, conductivity)
  - No insulating corrosion products
- Amphenol expected shortly to offer process with part numbers

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Threads and lubricity

- Requires thread lubricant (as with IVD)
- MoS_2 in thin polymer binder looks good
  - Acceptable torque-tension and breakaway torque
  - Long term stability looks good (many cycles)
  - No change during salt fog testing
- Passes tests for connectors
- Will probably work for threaded fasteners

klegg@rowantechnology.com

Other issues

- Repairability
  - Al can be repaired by brush plating Sn-Zn after suitable activation (Boeing)
  - Can also be repaired with brush-on SermaTel
- Anodizing
  - Can be anodized, leaving Al layer beneath anodize layer
  - Will improve wear and abrasion, but hard coating on soft underlay not a good high load wear surface
- Any form of Al avoids Cd embrittlement
  - Very bad form of embrittlement
  - Can occur when aborted takeoff heats brake discs and nearby landing gear components

Developments needed

- Non-toluene solution needed for depot use
  - Present chemistry cannot be used in depots
- Additional sources for plating service
- Additional embrittlement testing
- Well-defined brush plate or other repair
  - Both for OEM and MRO use

klegg@rowantechnology.com

Other ways to deposit Al

- Arc or flame spray
  - Used on some Bombardier aircraft
  - Thick coating (0.001 – 0.003”)
  - Rough
  - Al-Zn arc spray used on support equipment, radar towers, bombs
- CVD
  - Generally high temperature
  - Used for cooling passages in hot section blades
- Slurry Al – developed by Liburdi Engineering
  - High temperature heat treat
  - For hot section turbine blades (oxidation resistance)

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SermeTel®

Metal-filled ceramics from SermaTech

Keith Legg 847-680-9420
www.rowantechnology.com

SermeTel

- Al flakes in ceramic matrix
- Brush or spray on
- Older formulations contain Cr^{6+}
- Heat treat 375-700°F
  - Hard, glassy coating
- Grit blast to uncover Al

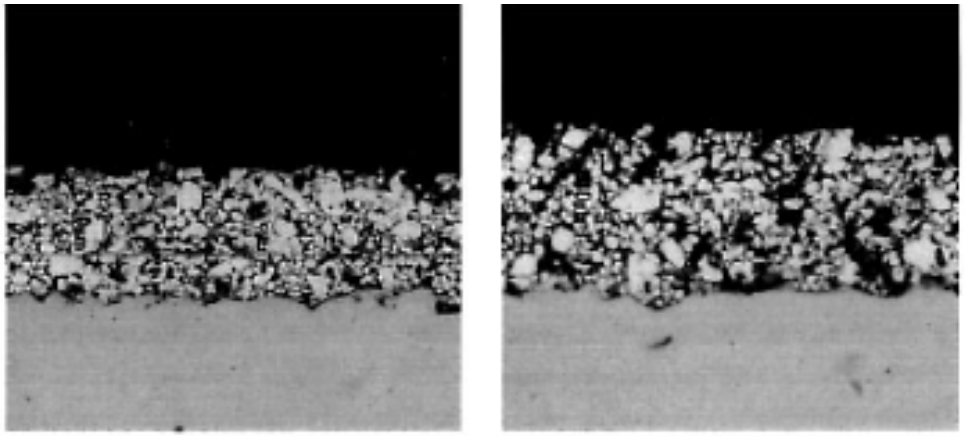


Figure 17. SermeTel aluminum-ceramic coating cross sections 500x. Left chromate-containing coating; right chromium-free coating.

klegg@rowantechnology.com

Applications

- Used in turbine engines
  - Cases and discs
- Landing gear in some older aircraft (commercial)
- F-22
  - Extensive use of SermeTel coatings on landing gear and other systems
  - See Baltimore meeting on Materials Substitution for P2 in Advanced Aircraft (2002)

Specifications

- Specs from SermaTech

klegg@rowantechnology.com

Advantages and limitations

Advantages

- Simple spray or paint
  - Can be used for repair
- Hard coating
  - Abrasion resistant

Note: There are now some other similar coatings on the market

Limitations

- Sole source
  - Licensing to major users only (e.g. Goodrich)
  - Others (inc. depots) must send to SermaTech
  - Very high cost
- Requires heat treat
  - Can be low enough T for HSS
- Embrittlement from acids in formulation
  - When using 984/985 HE on A100 for F-22
  - New formulation, not yet tested or approved
- Contains chromates
  - New non-chromate formulations now available

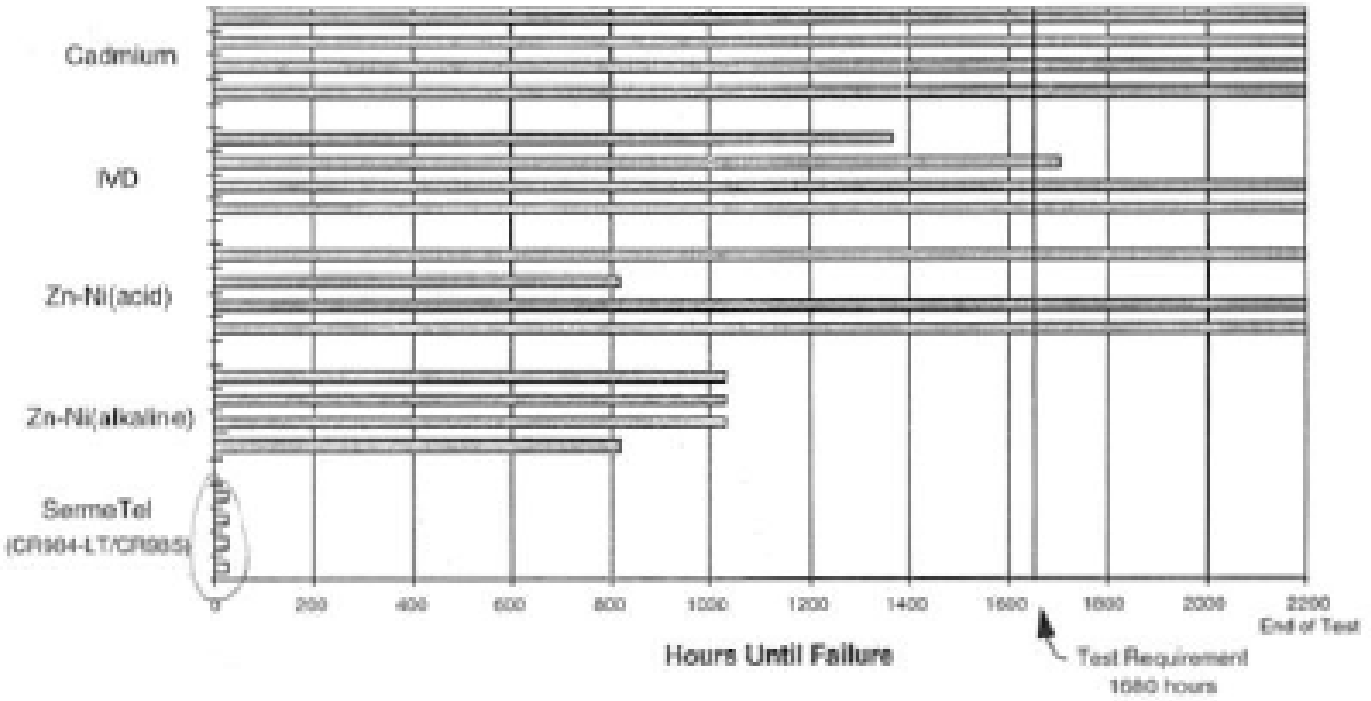
Data available

Little publicly available data

Keith Legg 847-680-9420
www.rowantechnology.com

Data

- Little publicly available data
  - Boeing test data showed poor B117 performance
  - Successful performance in commercial aircraft



klegg@rowantechnology.com

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Zn-Ni electroplate

Keith Legg 847-680-9420
www.rowantechnology.com

Zn-Ni

- Aqueous electroplate
- **Acid zinc-nickel developed and used**
  - **Boeing patented process**
  - **BAC 5637 Class 2 Type II (SAE AMS2417E)**
  - **E-Chrome 864 chromate conversion coating**
- **Alkaline zinc-nickel under development**
  - **AMS 2417 – Dipsol Gumm Ventures DGV Zinic IZ-260**
  - **DGV Zinic IZ-268S chromate conversion coating**

klegg@rowantechnology.com

Description

- Alloy electroplate
  - 5-15% Ni
  - Aqueous solution – mixture of chlorides
  - No CN
  - Coating chemistry depends on bath chemistry, current density, process parameters
- Can also be brush plated for repair

Applications

- Boeing uses acid Zn-Ni
  - Restricted to UTS<220 ksi because of embrittlement issues
- Oklahoma City ALC
  - Replaced Cd and TiCd with brush Cd, Zn-Ni and IVD in 1991

Specifications

- **Acid Zn-Ni**
  - **BAC 5637**
- **Alkaline zinc-nickel**
  - **AMS 2417**

klegg@rowantechnology.com

Advantages and limitations

Advantages

- Aqueous electroplate
  - Easier application in open tanks
- Qualified process
- Tank and brush plate

Limitations

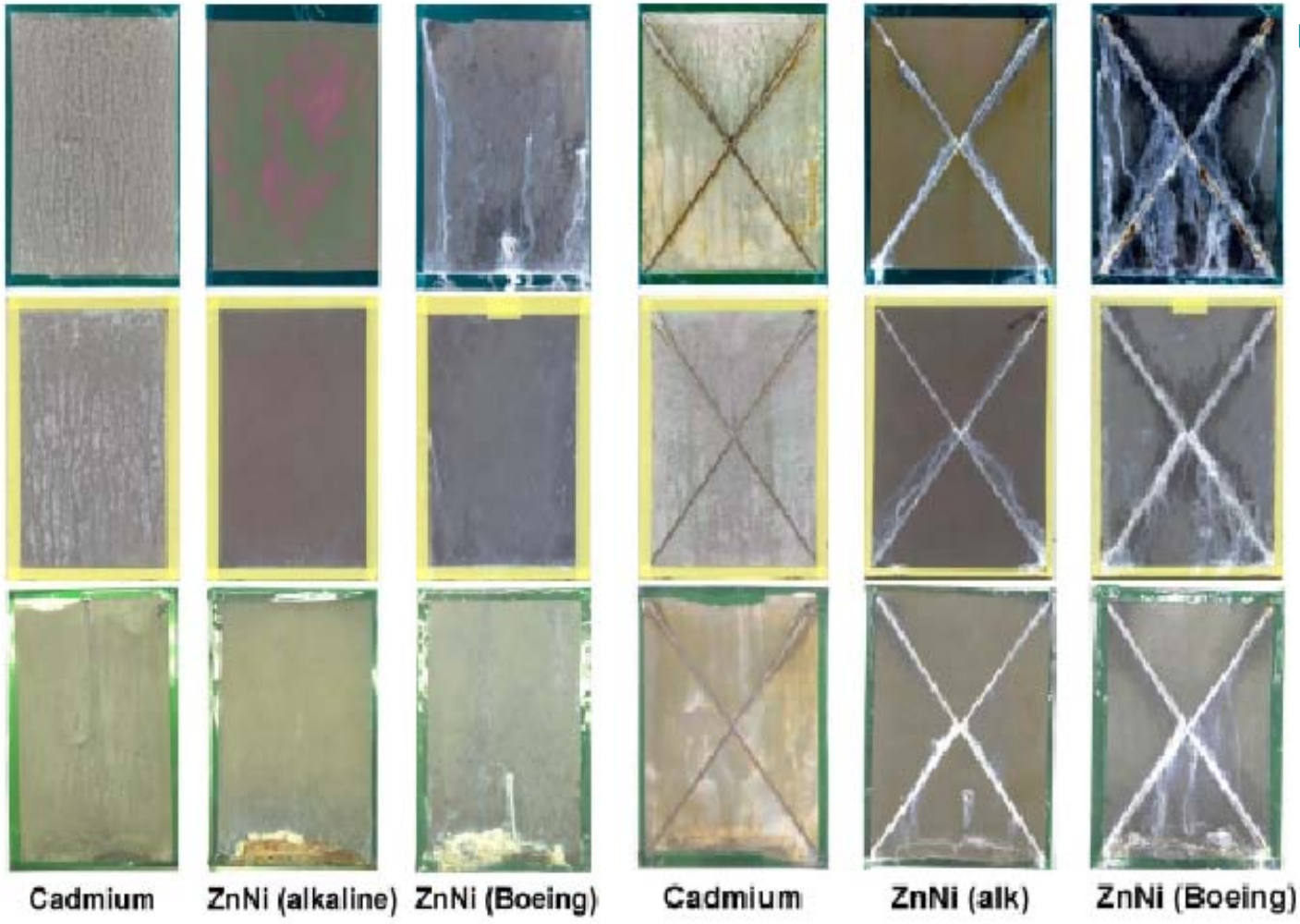
- Alloy chemistry
  - Difficult to ensure reproducibility and uniformity, especially on complex shapes
- Embrittlement

klegg@rowantechnology.com

Data available

Data available from Boeing, JGPP report
http://www.jgpp.com/projects/cadmium/jtr.html
http://www.materialoptions.com/w2g/cgi/kmcgi.exe?O=DIR0000000I6D&V=0

Corrosion

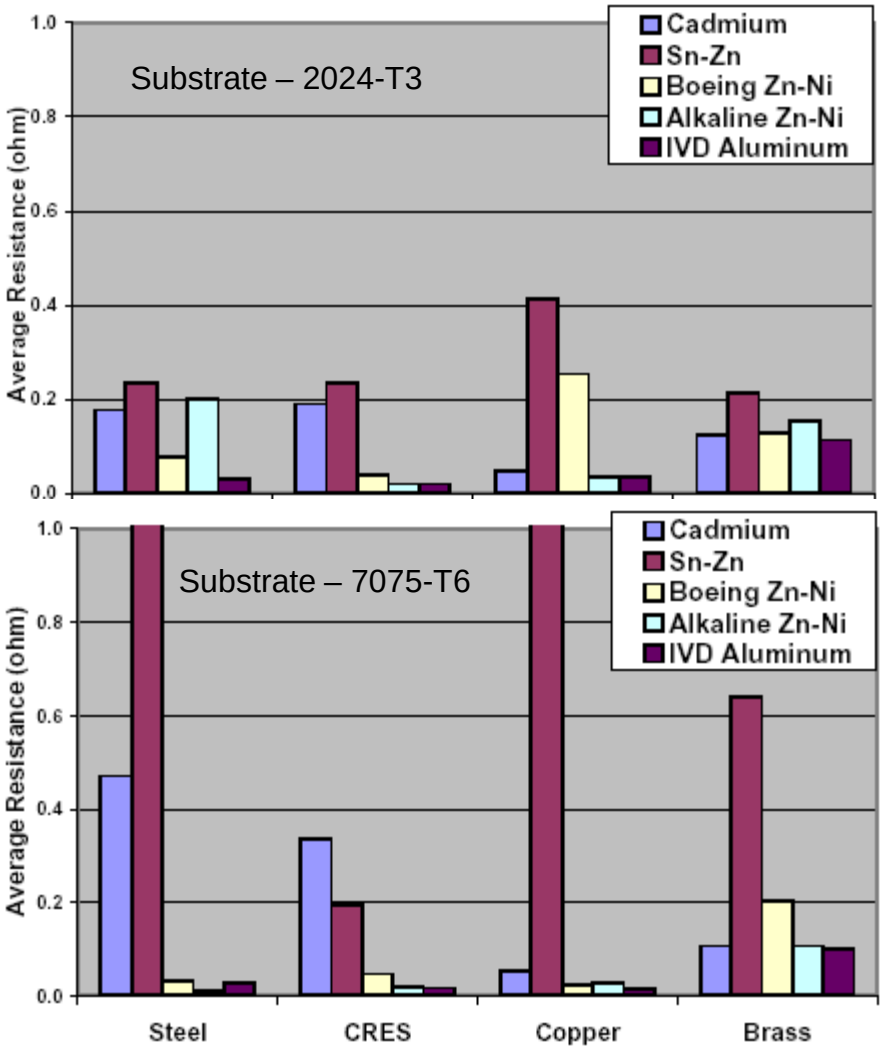


- Alkaline Zn-Ni best alternative in scribed tests

klegg@rowantechnology.com

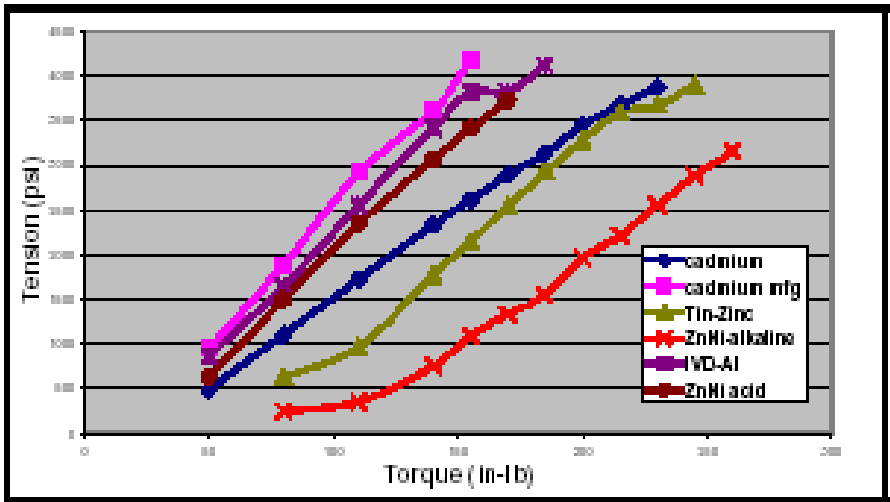
Galvanic corrosion

- Generally acceptable against common materials

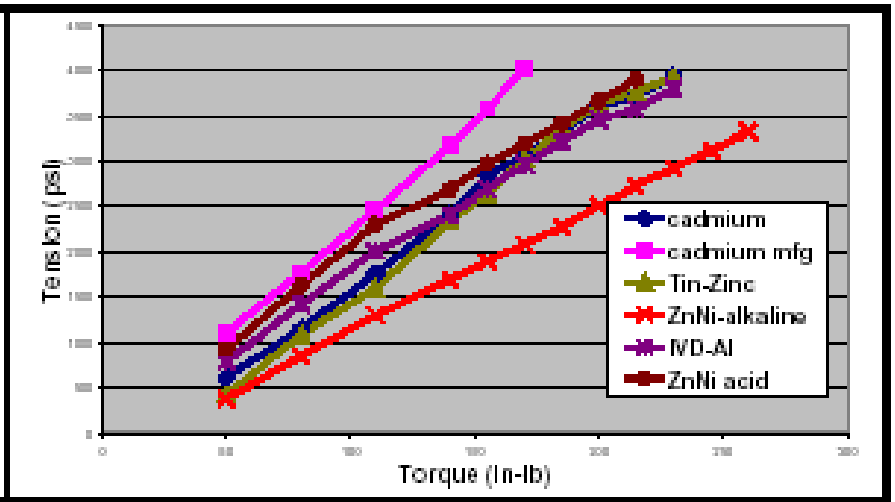


Torque-tension

- Alkaline Zn-Ni quite different from Cd
  - Difficult to run onto bolts
  - Note, however, test done with no lubricant, so may be fine with dry lube



First Cycle



Fifth Cycle

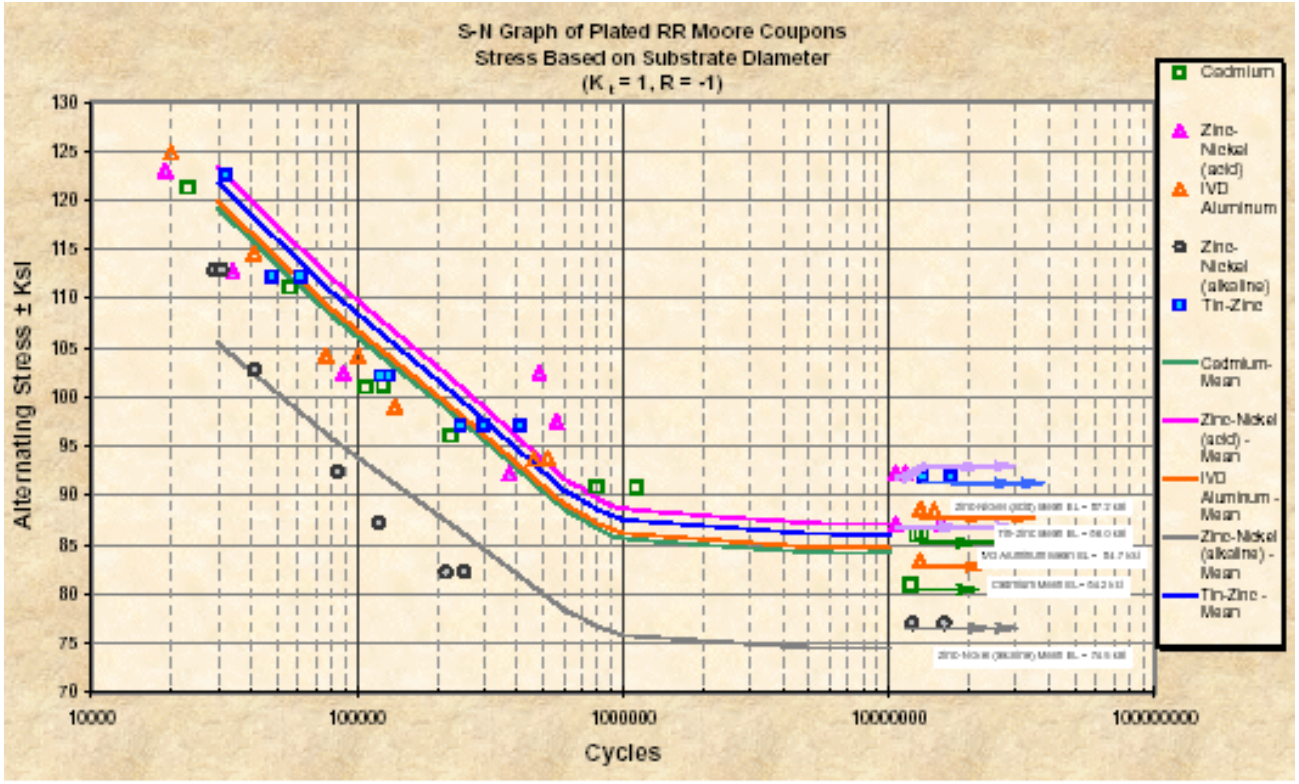
klegg@rowantechnology.com

Embrittlement

- Zn-Ni embrittles on deposition
  - Zn-Ni (acid and alkaline) can be H baked with the normal 375°F for 23 hour bake

klegg@rowantechnology.com

Fatigue



- Alkaline Zn-Ni has significant debit
  - Endurance limit - 11%
  - Some substrate issues
  - Retesting recommended

klegg@rowantechnology.com

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Developments needed

- Extension to high strength steels
  - New JTP for HSS under way – Boeing, JGPP
- Brush plating
  - Is Zn-Ni a good repair for IVD or electroplated Al?

klegg@rowantechnology.com

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High strength stainless steel

S-53 – new steel developed by QuesTek Innovations LLC

Keith Legg 847-680-9420
www.rowantechnology.com

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High strength stainless steel

- Developed using Materials by Design
  - Design using a variety of models and databases
- Normal development time for a steel
  - 10 years and hundreds of heats
- S-53 developed in half a dozen heats
  - Aim – meet the mechanical specs of 300M, but with the corrosion resistance of 15-5PH stainless
  - Developed under SERDP funding
  - Now in ESTCP program to validate at Ogden

klegg@rowantechnology.com

Advantages and limitations

Advantages

- No coating to come off
- Eliminates corrosion
  - Primary cause of landing gear overhaul and parts condemnation
- Avoids SCC
  - Primary mechanism for major landing gear failure

Limitations

- Cannot be used uncoated against Al

klegg@rowantechnology.com

Developments needed

- Full validation of properties and performance
- Development of materials database
- Licensing to steel producers so commercially available
  - QuesTek's intent is licensing to several steel companies (QuesTek is a steel developer, not a producer)

klegg@rowantechnology.com

Data available

Extensive data will become available over next 2 years from ESTCP program

Keith Legg 847-680-9420
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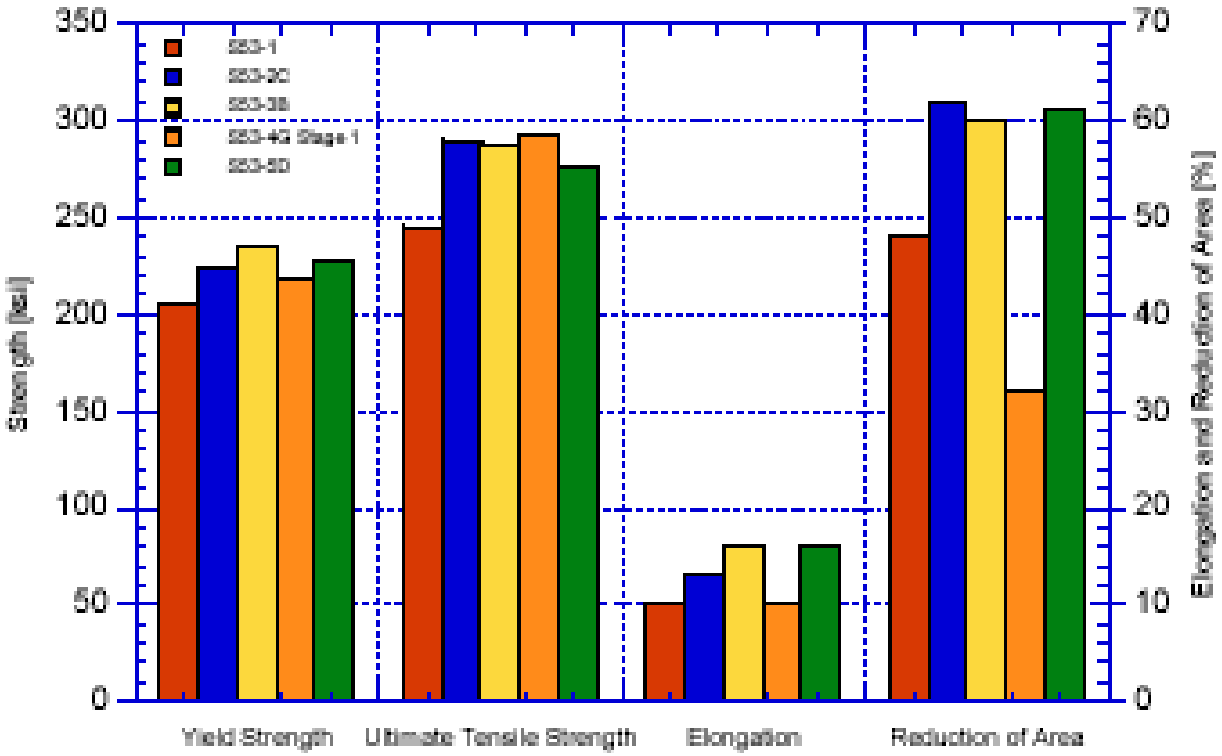
Summary of S-53 heats



- Note: Edisonian method takes several hundred heats!
- Meets 300M properties
  - Corrosion resistance = 15-5 PH stainless
  - Much better K_{IC} (88 √")
  - K_{ISCC} (50-60 √")

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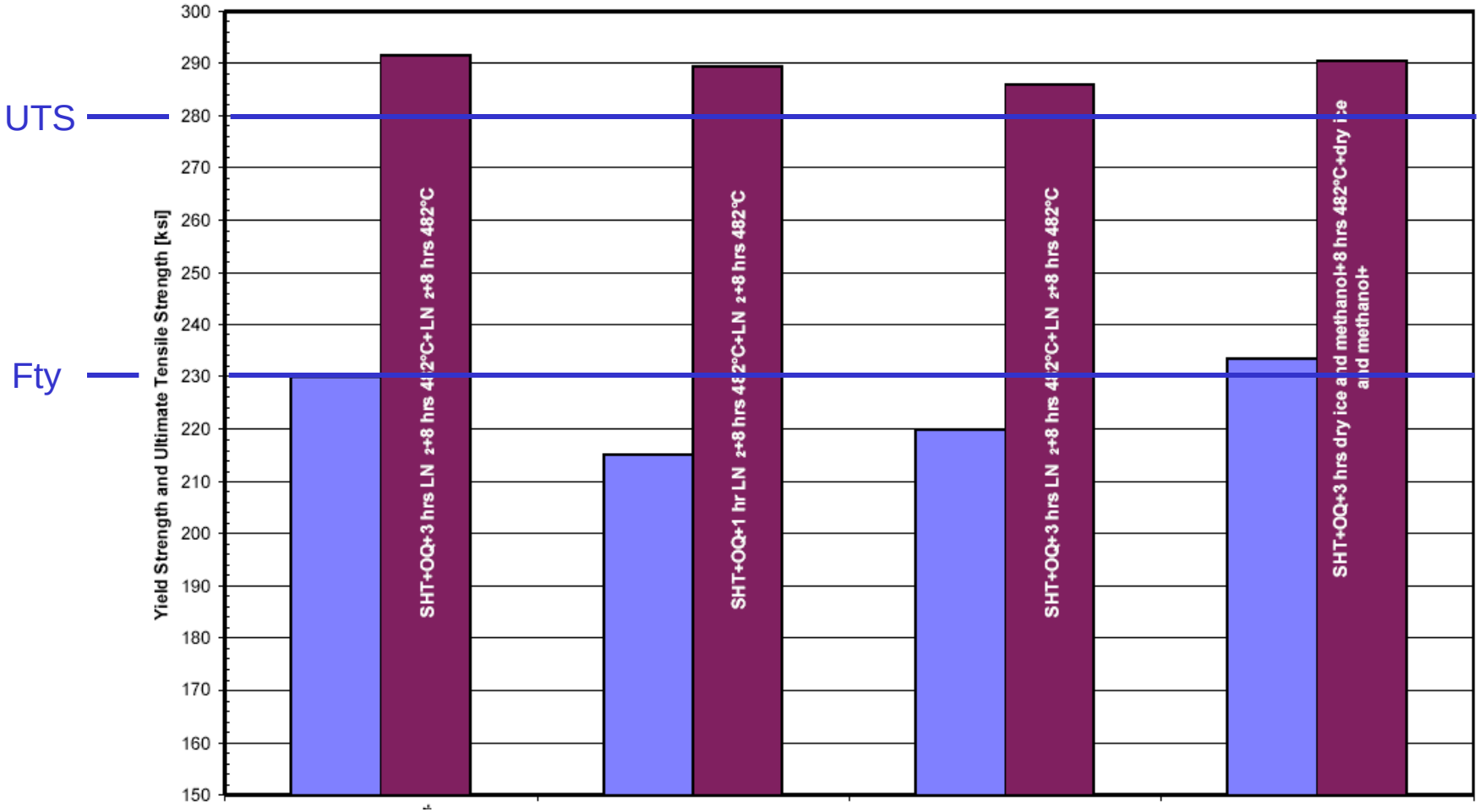
HSSS properties



klegg@rowantechnology.com

Current status

- Appears to be mechanically equivalent to 300M but much better fracture strength and SCC
- Being tested and validated at Hill AFB
- Work to be complete in 3005
- Will obtain data needed for qualification
  - Not MIL Handbook 5 (requires 10 heats at $300,000/heat)
  - Will do three heats to 20,000 lb
    - Then use AIM method (Accelerated Insertion of Materials) to interpolate between and extend lab data using modeling data

Conclusion

- Al is the best overall option, but deposition methods are not straight “drop-in”
- High strength stainless exciting new development
  - Will be 2 or 3 years before it is fully qualified at Ogden
  - Even then, no MIL Handbook 5 numbers
  - Modeling will tell us more about this steel than we know about most others
- There are niche products for other Cd alternative applications