COVENTYA

ASETSDefense Workshop

2016 December 6 – 8

Beyond the Surface

Hard Chrome by Trivalent Chromium : an alternative to Hexavalent Chrome for functional plating

Reported By:

Brad Durkin

Director International Product Management

COVENTYA Group

Written by: Many – credits coming

COVENTYA

Technology Development is Currently Focused in 2 Paths

European Team:

- Research project at the IRT-M2P in order to develop an alternative to Cr^{VI} process based on Cr^{III} electrolyte

USA Team:

- Demonstrate & validate Cr(VI)-Free Hard Chrome Electroplating to meet performance specifications of coatings produced from current hexavalent chromium plating processes.
- Project builds on past Cr(III) activities developed under multiphase **C**ommercial **T**echnologies for **M**aintenance **A**ctivities (CTMA) project – a joint partnership **N**ational **C**enter for **M**anufacturing **S**ciences (NCMS) and DOD.

PARTNERS OF THE EUROPEAN HCTC PROJECT – EVALUATION EX DBA 1318

Industrial Partners

SAFRAN AEROSPACE · DEFENCE · SECURITY
PSA PEUGEOT CITROËN
RENAULT
AIRBUS HELICOPTERS
COVENTYA
UTC Aerospace Systems
nexter SYSTEMS
ALSTOM Transport
nordchrome LEADER IN SURFACE TECHNOLOGY
Academi
chrome dur INDUSTRIEL
L'ELECTROLYSE
CCN GROUP
bonnans.sa
Micronics Systems
UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR
Institut UTINAM
cnrs

Sub contractant

FARADAY TECHNOLOGY, INC.

Technology Development is Currently Focused in 2 Paths

European Team:

- Research project at the IRT-M2P in order to develop an alternative to Cr^{VI} process based on Cr^{III} electrolyte

USA Team:

- Demonstrate & validate Cr(VI)-Free Hard Chrome Electroplating to meet performance specifications of coatings produced from current hexavalent chromium plating processes.
- Project builds on past Cr(III) activities developed under multiphase **C**ommercial **T**echnologies for **M**aintenance **A**ctivities (CTMA) project – a joint partnership **N**ational **C**enter for **M**anufacturing **S**ciences (NCMS) and DOD.

CTMA Program Overview

Chrome deposits plated from first generation electrolyte Faraday (EX DBA 1411) exhibited equivalent or improved performance vs Cr(VI)

- Hardness
- Wear
- Fatigue

Limitations Included

- Chemistry difficult to control/replenishment/maintain
- Narrow plating window – not production practical
- Not REACh compliant – contains Boric Acid

New Electrolyte Developed By COVENTYA & for past 2+ years under various evaluations

- COVENTYA EX DBA 1318 – Patent pending

HARD CHROME BY TRIVALENT CHROMIUM : AN ALTERNATIVE TO HEXAVALENT CHROME FOR FUNCTIONAL PLATING

PRESENTED SURFIN 2016

J. GURT-SANTANACH, J. TARDELLI, K. WOJCZYKOWSKI, L. THIERY, N. POMMIER, J.Y. HIHN, J. FRAYRET

PASSERELLE DE L'INNOVATION

IRT m2p
INSTITUT DE RECHERCHE TECHNOLOGIQUE MATÉRIAUX MÉTALLURGIE ET PROCÉDÉS

COVENTYA

USA Project Team

Erik Hangleland-RDECOM EALSP

Mark Feathers-AMCOM Program Manager

- Michael Johnson-AMCOM CGI

Jeremy Smith-Corpus Christi Army Depot

Ricky McNally-Aviation and Missile Research Development and Engineering Center-Huntsville

Bert Hernandez-Aviation and Missile Research Development and Engineering Center-CCAD

Vic Champagne-ARL

Project execution-Faraday Technology Inc

- **FARADAY:** E.J. Taylor, Maria Inman, Tim Hall, Rajeswaran Radhakishnan, Jing Xu, Stephen Synder
- **Boeing:** Steve Gaydos, Bruce Griffin, Sundra Jean-Pierre (JP) Ndongala
- **COVENTYA:** George Bokisa, & Brad Durkin
- **UTRC:** Mark Jaworowski, Tianli Zhu

FARADAY TECHNOLOGY, INC.

GARMYCr:
Development and Demonstration of FARADAYIC TriChrome at Army Depot

Faraday Technology, Inc.

Sponsored by:
US AMCOM
(Pueblo Economic Development Corp)

BOEING

COVENTYA

United Technologies Research Center

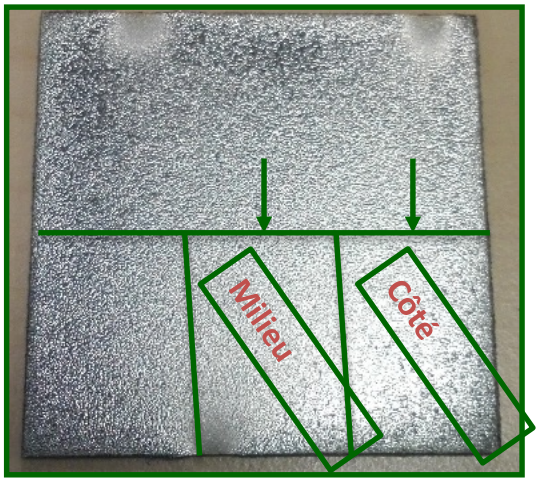
SUMMARY: REACH Compliant Chemistry Preliminary Coatings Overview Property Comparison

Characteristic	Faraday with funding from NCMS-CTMA	Faraday with funding from IRT M2P and the U.S. Army
Substrate	4130 Steel	4130 Steel
Bath	EX DBA 1411	EX DBA 1318
Bath pH	2.5	5.3
REACH-compliant	Contains boric acid	Boric acid free
Current Efficiency	~30%	~9%
Visual Appearance	Matte	Bright
Plating Rate	Up to 5 mils/hr	Up to 1.5 mils/hr
Thickness (AMS 2460, 3.4.1)	Equivalent to Cr^{+6}	Equivalent to Cr^{+6}
Porosity (AMS 2460, 3.4.4)	Equivalent to Cr^{+6}	Equivalent to Cr^{+6}
Micro-Hardness (AMS 2460, 3.4.3)	Equivalent to Cr^{+6}	Equivalent to Cr^{+6}
Corrosion Protection (ASTM B117)	Superior to/Equivalent to Cr^{+6}	Superior to/Equivalent to Cr^{+6}
Fatigue (ISO 1143, ASTM E468)	Superior to/Equivalent to Cr^{+6}	Superior to/Equivalent to Cr^{+6}
Wear (ASTM D4060)	Slightly Greater than Cr^{+6} (after bake)	Equivalent/Superior to Cr^{+6} (as plated) Greater than Cr^{+6} (after bake)
Adhesion (ASTM B 571)	Yes (after bake)	Yes (after bake)

FARADAY TECHNOLOGY, INC.

SUBSTRATE

- Substrates
  - Representative of the final use

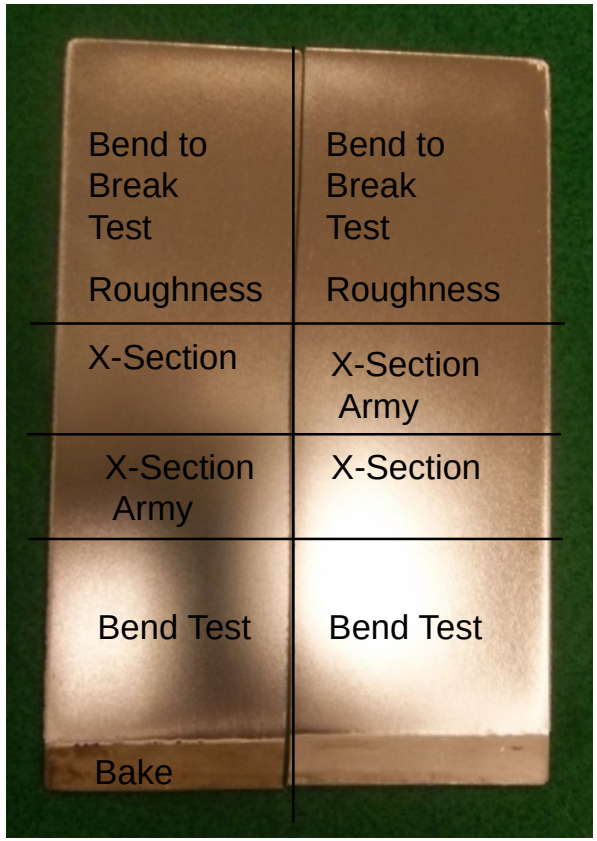


15CDV6 coupons
(quenched and tempered steel)
Mechanical strength : 980 to 1180 MPa

15CDV6 & XC 48 steel cylinders

Alloy 4130 Panels
Sectioning For Optimization Testing

- Thickness (AMS 2460, 3.4.1)
  - Cross-section and Magnetic Probe
- Hardness (AMS 2460, 3.4.3)
  - Microhardness via cross-section
    - As-plated and post 375°F (190°C) bake for 24 hr
- Corrosion Resistance (ASTM B117)
- Microstructure
  - Cross-section
- Porosity (AMS 2460, 3.4.4)
  - Ferro porosity test
- Preliminary Bend to Break (AMS 2460, 3.4.2)
- Roughness
- Plating Performance:
  - Current Density, Current Efficiency, Plating Rate

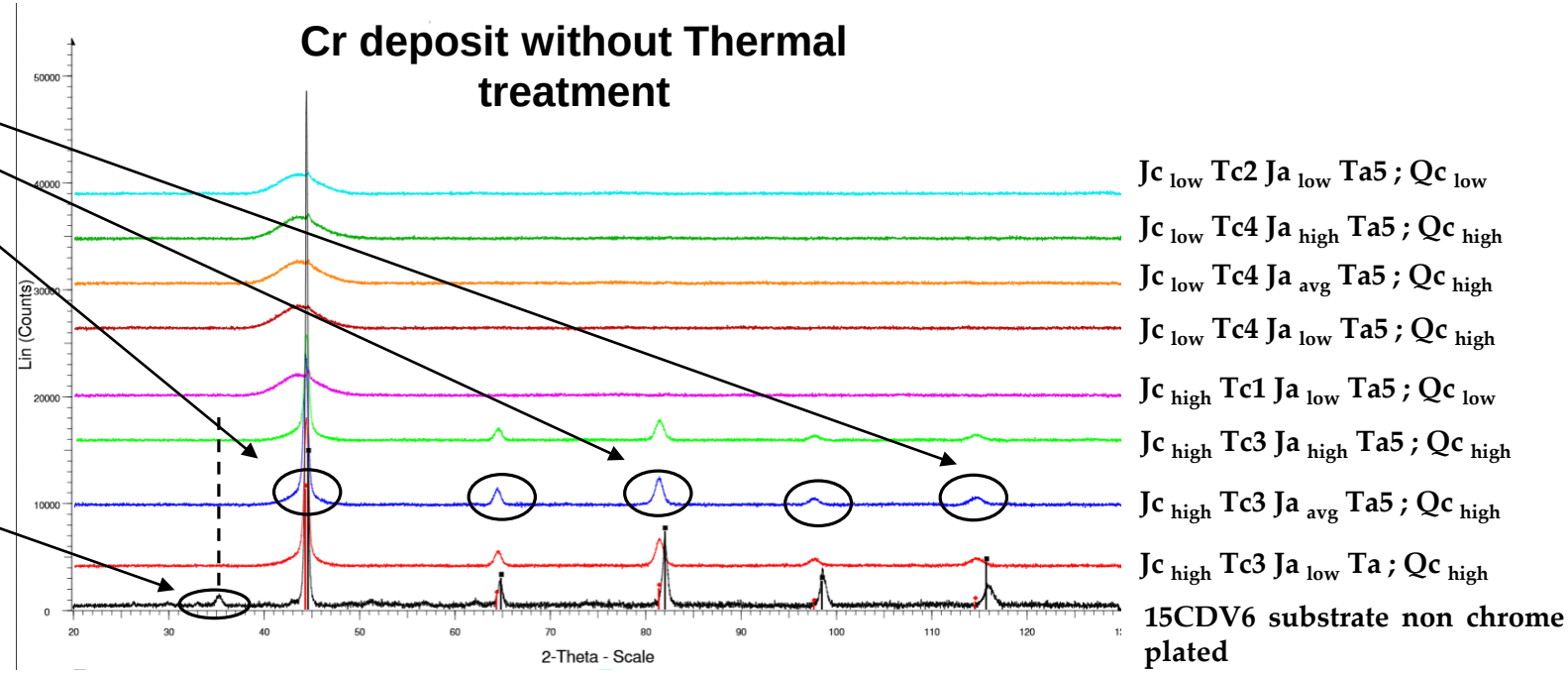


FARADAY TECHNOLOGY, INC.

XRD analysis without Thermal Treatment

Cr low crystallinity

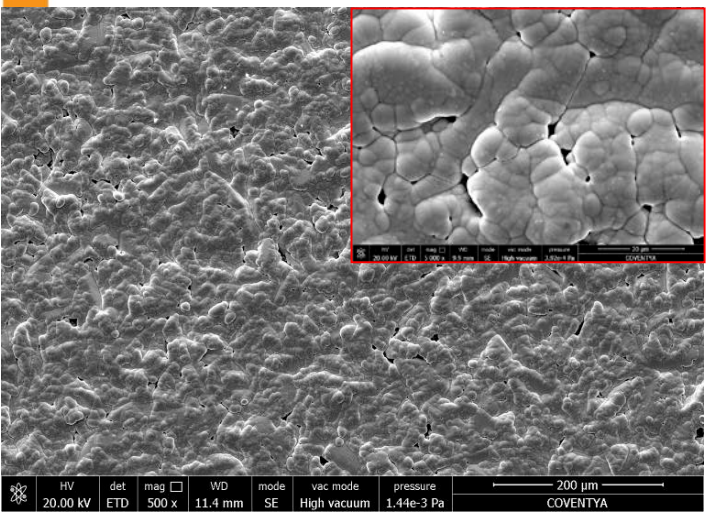
Peak of the substrate Not found for every sequence



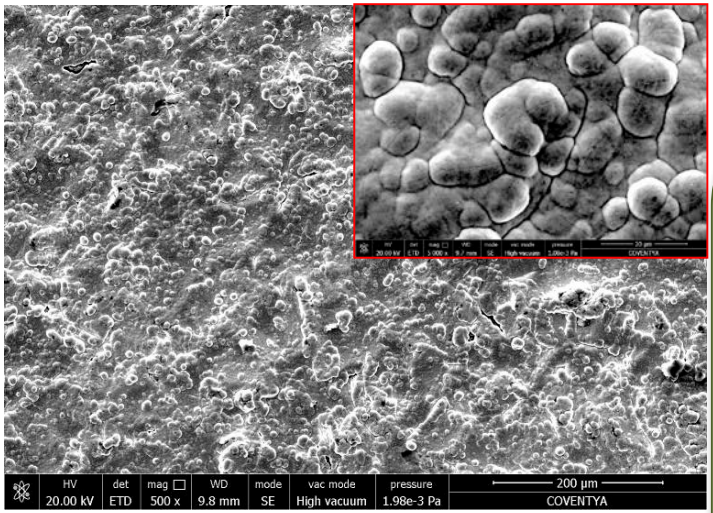
- **Amorphous deposits without thermal treatment;**
  → Unless for deposits obtained with Jc $_{high}$ and Qc $_{high}$ for which Cr is slightly crystalline

SURFACE OBSERVATIONS -EX DBA 1318 DEPOSIT

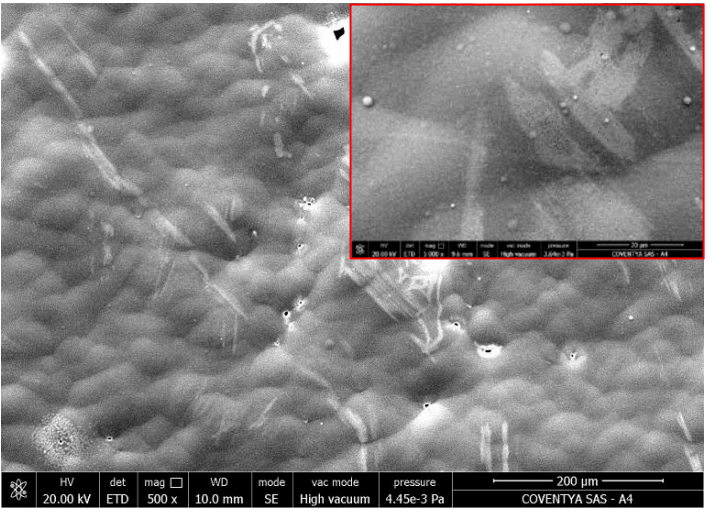
Cr^{III} - 1h*



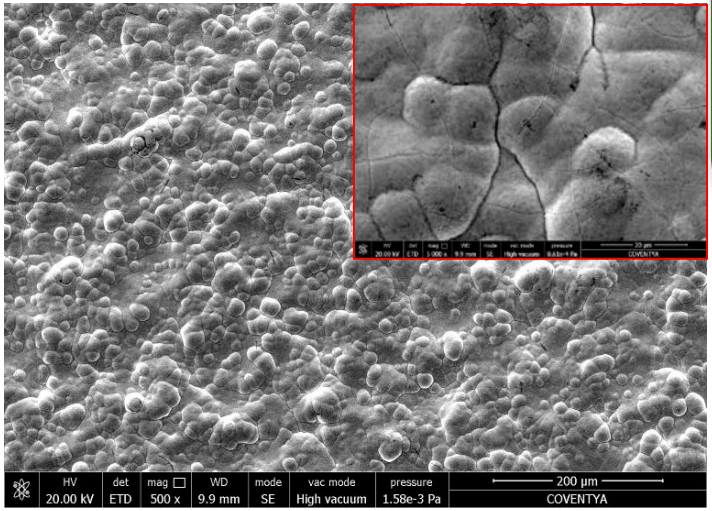
Cr^{VI} – 1h*



Cr^{III} - 5h*



Cr^{VI} - 5h*



* : plating time

<u>Differences between Cr^{III} and Cr^{VI}</u>

→ Coating slightly porous with Cr^{III}

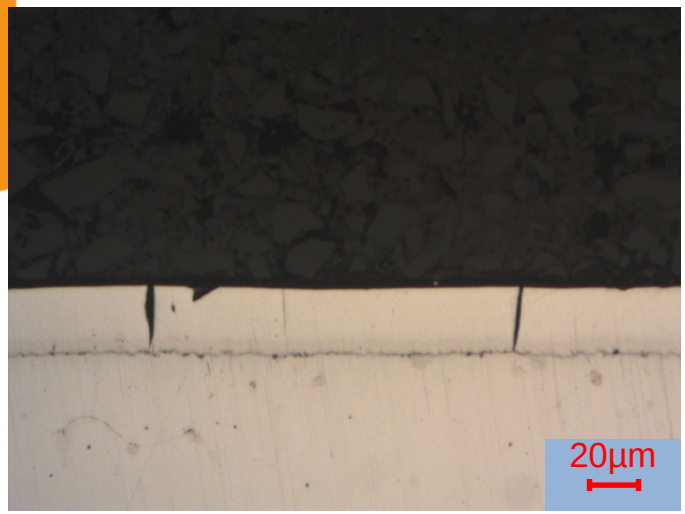
→ Higher roughness with Cr^{VI}

→ Micro-cracks with Cr^{VI}

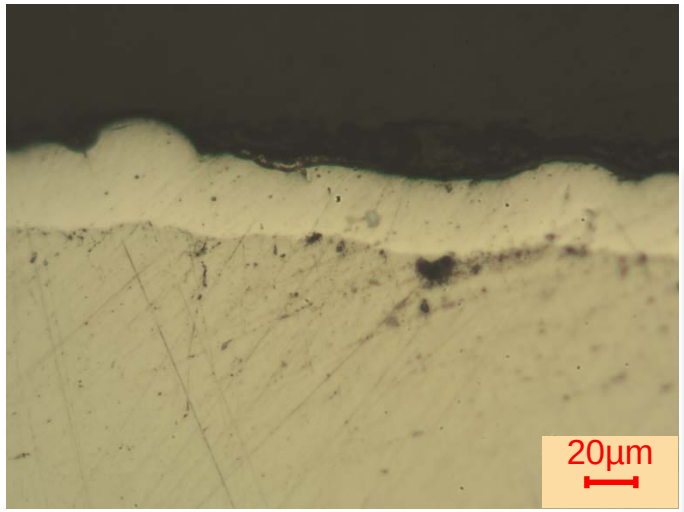
→ Same nodule size

CROSS SECTION OBSERVATIONS EX DBA 1318 DEPOSIT

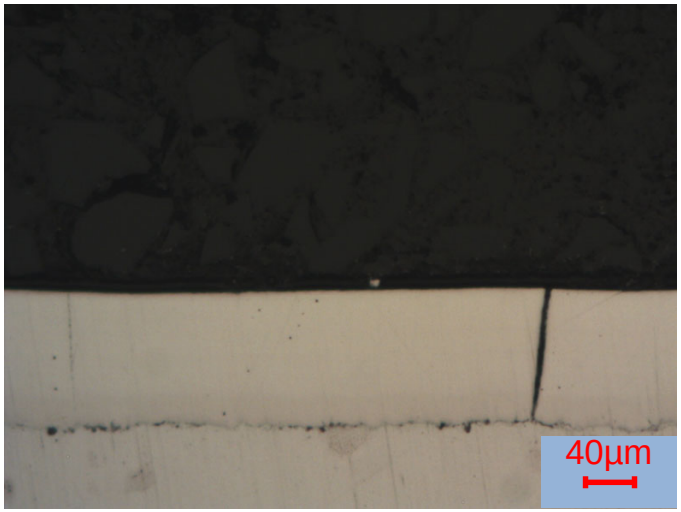
Cr^{III} - 1h*



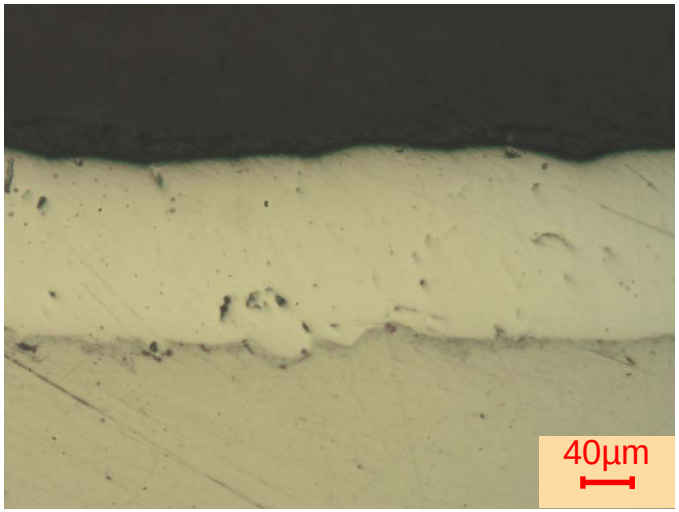
Cr^{VI} - 1h*



Cr^{III} - 5h*



Cr^{VI} - 5h*



* : plating time

Differences between Cr^{III} and Cr^{VI}

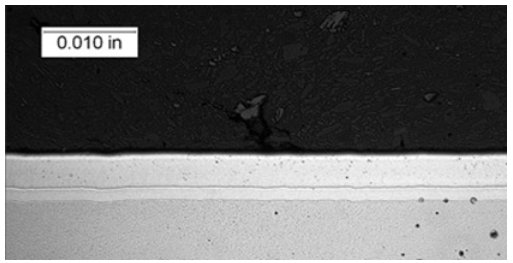
→ **Micro-cracks for Cr^{VI}**
→ **Macro-cracks for Cr^{III}**

Cr(VI) /EX DBA 1318 Cr(III) Comparison: Porosity/Hardness/Microstructure/Salt Spray

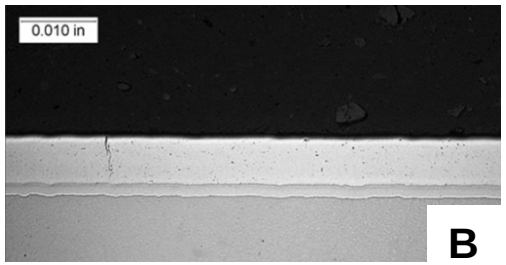
Hexavalent Chrome Baseline

AMS 2460, 3.4.3

(140 µm)
982 HV

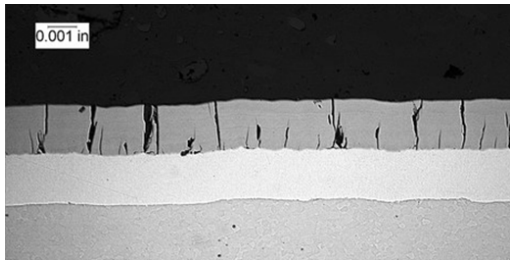


(183 µm)
907 HV

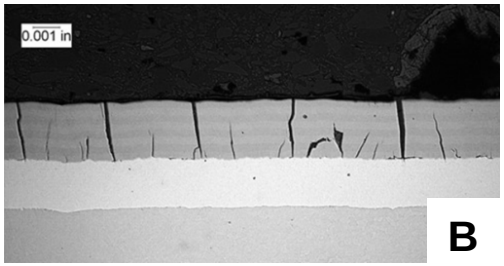


Trivalent Chrome Coating

(44 µm)
900 HV



(56 µm)
888 HV



All Samples Have a Ni Sulfamate Underlayer
B indicates that the sample underwent a a Hydrogen Embrittlement Bake at 375° F (190° C) for 24 ± 4 hr

FARADAY TECHNOLOGY, INC.

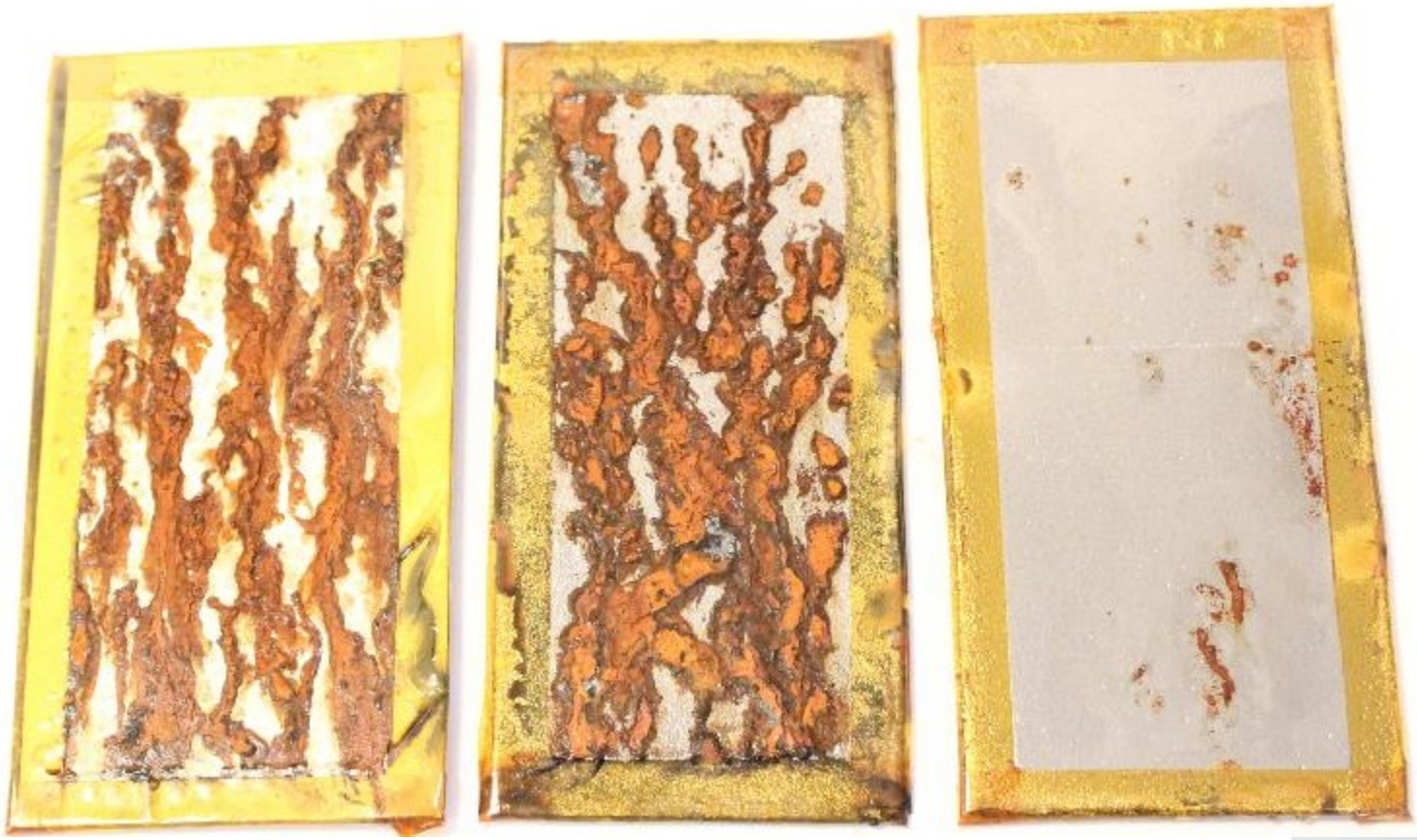
COATING CHARACTERIZATION
EX DBA 1318 DEPOSIT

- Corrosion protection
  - Neutral Salt Spray Test: ISO 9227 after 96h

Cr^{VI} deposit 40µm

Cr^{III} deposit 40µm

Underlayer Ni sulfamate ~ 20µm + + Cr^{III} deposit – 40µm

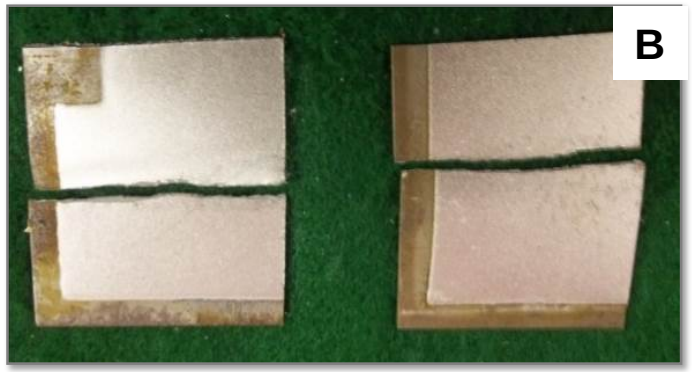


Cr(VI) / EX DBA 1318 Cr(III) Comparison: Bend To Break Test (AMS 2460, 3.4.2)

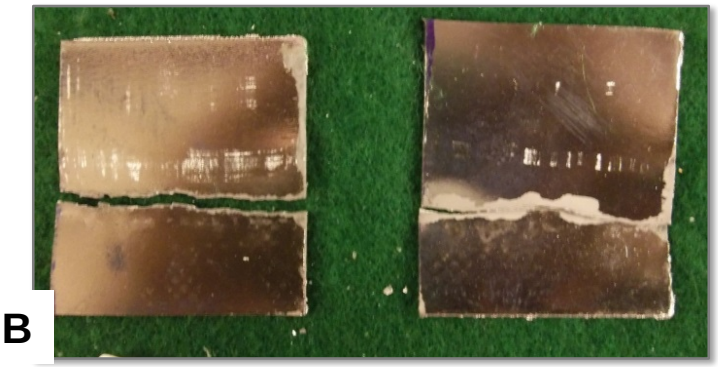
Hexavalent Chrome Baseline

Trivalent Chrome Coating

Bend to Break Test



Bend to Break Test



B indicates that the sample underwent a a Hydrogen Embrittlement Bake at 375° F (190° C) for 24 ± 4 hr

COATING CHARACTERIZATION
EX DBA 1318 DEPOSIT

<u>Grinding test</u>

Abrasive wheel : Corindon (ref 38a60lvbe)

Rotation speed : 1200 rpm

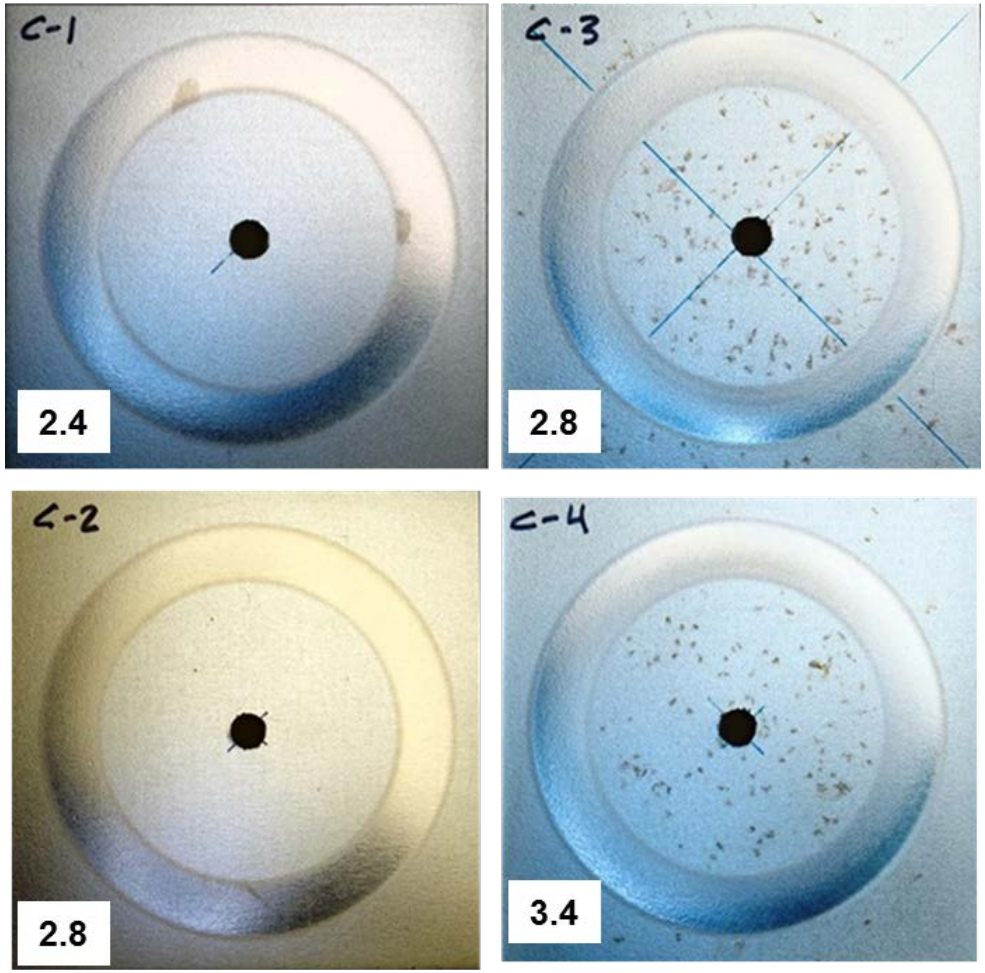
Part rotation speed : 200 rpm

Abrasion speed : 25 m/s

Cr(VI) /EX DBA 1318 Cr(III) Comparison: Taber Abrasion (ASTM-D-4060)

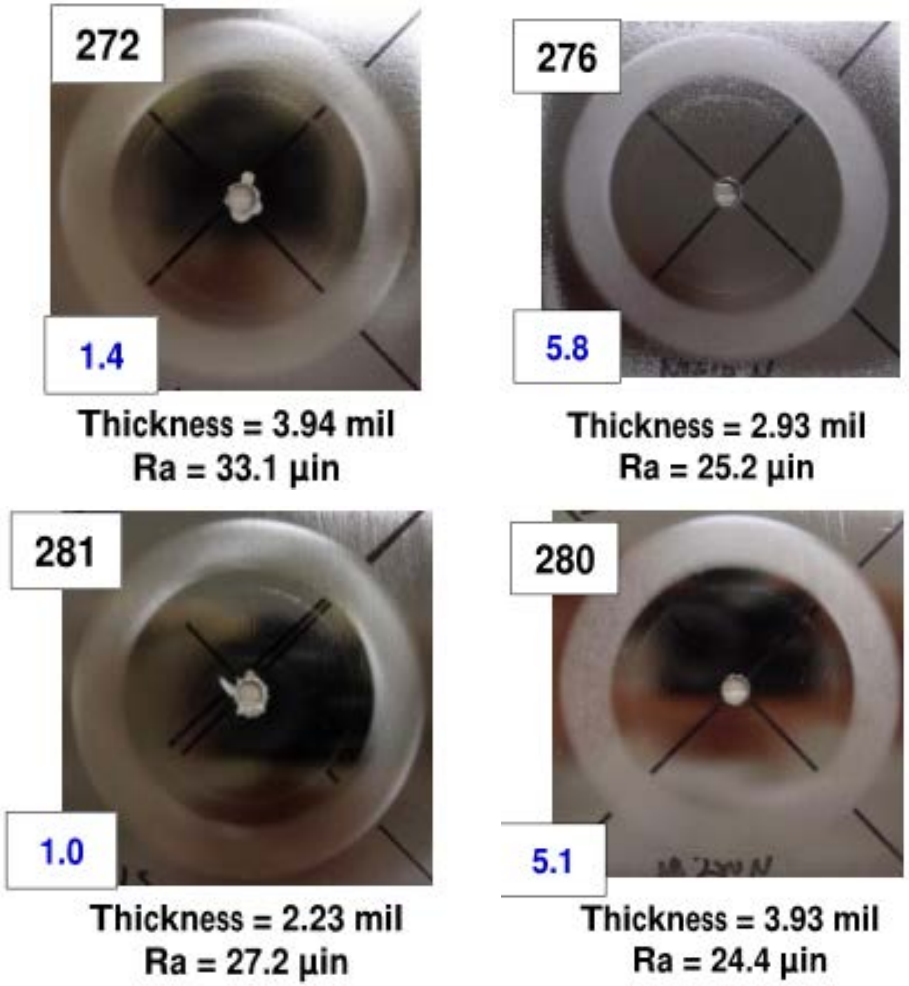
Hexavalent Chrome Baseline

As-Plated | Post Bake



Trivalent Chrome Coating

As-plated | Post Bake



ASTM D 4060 with a 1,000-gram load, with the following exception: the **CS-17 wheels** were resurfaced every 1,000 cycles whereas ASTM D 4060 requires wheel resurfacing every 500 cycles.

Post Bake 375˚ F/24 hr bake

FARADAY TECHNOLOGY, INC.

COATING CHARACTERIZATION
EX DBA 1318 DEPOSIT

Taber Abrasion test

- According to ASTM D-4060
  - **Abrasive wheel CS-10** – harder surfaces used to relate EN to Hard Chromium
  - 10,000 cycles, Load 1000 grams

Sample	CrIII - 01	CrIII - 02	CrVI - 01	CrVI - 02
Treatment	Pulse sequence		Treated at the applicator (DC)	
Heat treatment	No	24h 190° C	24h 190° C	24h 190° C
Average thickness center (µm)	27 – 30		40	
Weight loss (mg)	16.6	35.3	23.7	23
Wear Index (TWI)	**1.66**	**3.53**	**2.37**	**2.3**

- Value around 1.0 to 2.0 TWI without heat treatment
- Increase of wear index with heat treatment for CrIII deposits

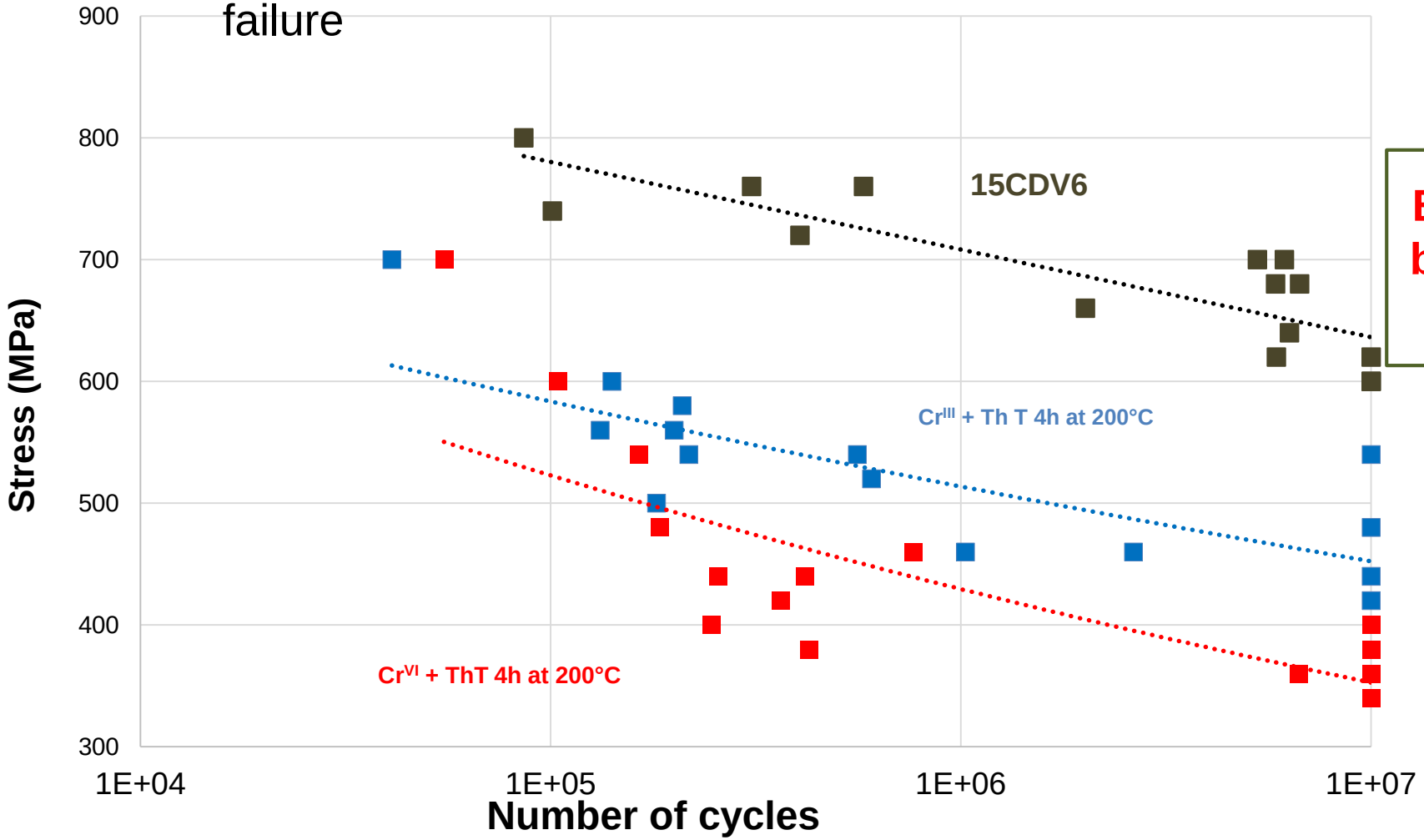
COATING CHARACTERIZATION
EX DBA 1318 DEPOSIT

Fatigue tests (rotative bending) ISO 1143:2010

15 CDV 6 (Moore type) samples

Frequency : 50 Hz

Stress vs Number of cycles until 1^{E}+07 cycles without complete failure



Better fatigue behavior than hex Chrome

OVERVIEW OF THE COMPARATIVE PROPERTIES

	HEXAVALENT CHROME	EX DBA 1318 HARD CHROME
Ability to plate high thickness	Yes	Yes (up to 400 µm tested)
Structure	Micro cracked	Presence of through cracks – Increase with heat treatment
Hardness	Decreases with temperature	Increases with temperature
Fatigue	Good	Superior to Hex Chrome
Wear resistance	Good	Comparable/Improved to Hex Chrome without heat treatment
Corrosion protection	Medium	Superior to Hex Chrome with a Ni underlayer

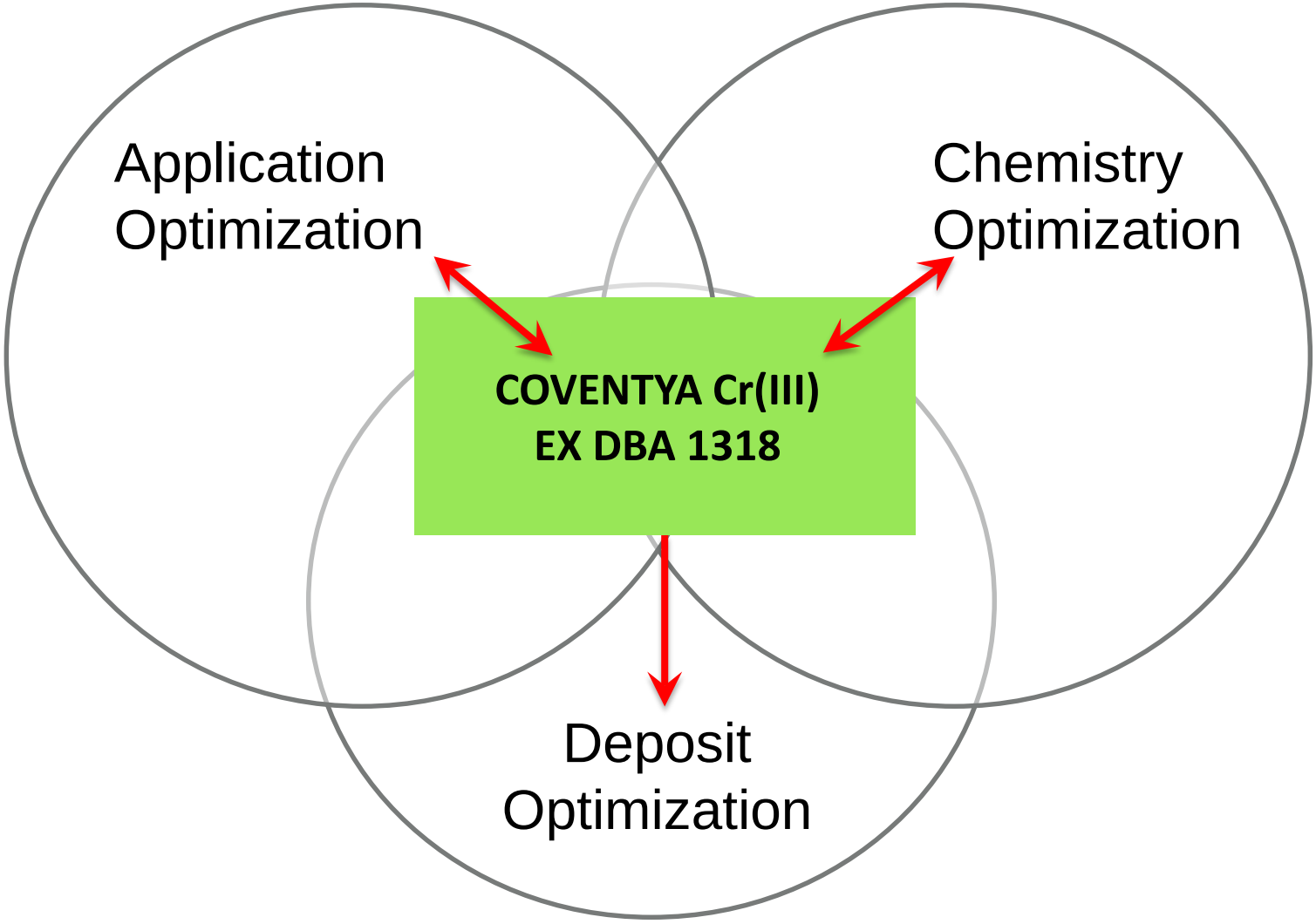
Our Conclusion to Date:

Hard Chromium Deposits from Cr(III) Electrolytes Have Many Similar Deposit Characteristics

– But Requires Some Continued Evolution and Development As a Complete Cr(VI) Replacement Technology

Optimization of EX DBA 1318 Continues……

EX DBA 1318 Cr(III) Development & Optimization Overview



COVENTYA

Opportunities:
Chemistry Optimization

For Cr(VI) electrolytes, 3 to 4 chemistry species to control impacting solution performance, and deposit performance

- Industry has had since 1920's to define, refine and understand this chemistry platform.

For Cr(III) electrolytes, typically 8 – 10+ chemistry species to control impacting solution performance and deposit performance.

- Application for thick deposits <10 years old – we have much more to learn toward optimization of the technology platform.
- R&D continues to evaluate various chemistry additives to improve system and deposit performance.
- New discoveries will continue to evolve the chemistry/technology platform.

EX DBA 1318 : Cr^{III} BORIC ACID FREE ELECTROLYTE

- Comparative operating parameters Cr^{VI} vs Cr^{III}

Parameter	Electrolyte Cr^{VI}	EX DBA 1318 : Cr^{III}
Chrome metal concentration	100 – 150 g/L	17 – 22 g/L
Sulfate concentration	2 – 5 g/L	50 – 65 g/L
Complexing agent	No	180 – 230 g/L
Catalyst	Yes	No
Boric acid	No	No
Proprietary Additives	No	Yes
pH	< 1	4.5 – 6
Current density (A/dm²)	20 - 90	40 – 60
Temperature (°C)	55 - 65	35 - 45
Anodes	Pb/PbSn / Pb alloys	Inert anodes – Graphite / DSA

COVENTYA

Opportunities:
Chemistry Optimization

For Cr(VI) electrolytes, 3 to 4 chemistry species to control impacting solution performance, and deposit performance

- Industry has had since 1920's to define, refine and understand this chemistry platform.

For Cr(III) electrolytes, typically contain 8 – 10+ chemistry species to control - impacting solution performance and deposit performance.

- Application for Cr(III) thick deposits <10 years old – we have much more to learn toward optimization of the technology platform.
- R&D efforts continue evaluation various chemistry additives to improve system and deposit performance.
- New discoveries will continue to evolve the chemistry/technology platform.

Opportunities:
Application Development

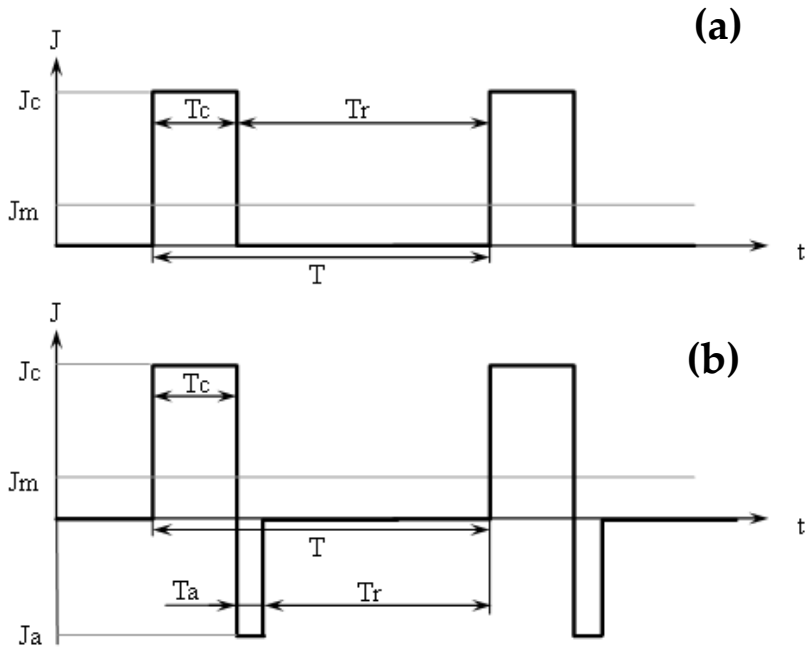
Technique of electroplating have differences vs Cr(VI) Hard Chrome technology

- More attention to racking and plating part configuration/orientation in tank vs Cr(VI) systems – anode to part orientation, shields, etc.
- Author opinion – difficult today for all HC job shop platers to replace Cr(VI) with this first generation technology – but application specific job shops could easily implement – eg., for hydraulic cylinders, shock rods, tools, similar types applications.

Methods rectification impact on deposit properties

- DC which is common with Cr(VI) vs Benefits of Looping/Pulsing Waveforms (direct/direct-reverse) with Cr(III) (so far).
- Determine other combinations to evaluate and impact deposit performance.

Pulse Current Principle



With :
-**T :** Period,
-**Tc :** Duration of cathodic pulse
- **Jc :** Cathodic peak current density,
-**Ta :** Duration of anodic pulse
- **Ja :** Anodic peak current density
- **Tr :** Rest time
- **Jm :** Average current density on period .

$$\mathbf{Jm} = \frac{(\mathbf{Jc} * \mathbf{Tc}) + (\mathbf{Jr} * \mathbf{Tr})}{\mathbf{Tc} + \mathbf{Tr}}$$

↓

Anodic case : take Ta & Ja into account.

Type of pulse current
- **C.P.S :** Simple pulse current (a),
- **C.P.I :** Pulse with reverse polarization (b).

COVENTYA

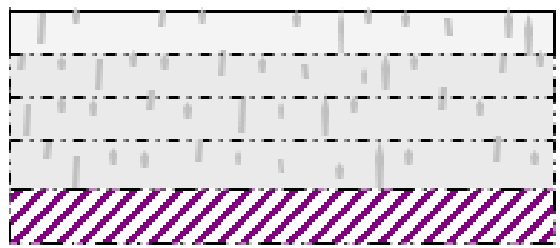
Controlling Cracking/Crack Density

Layered chrome deposit from Cr^{+3} bath with discontinuous cracks achieved by waveform looping.

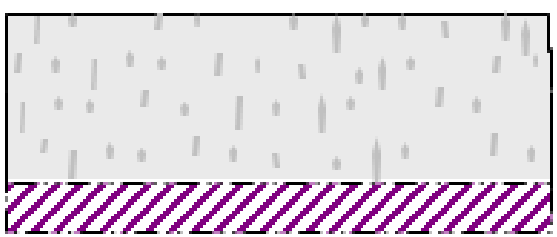
X-section perspective

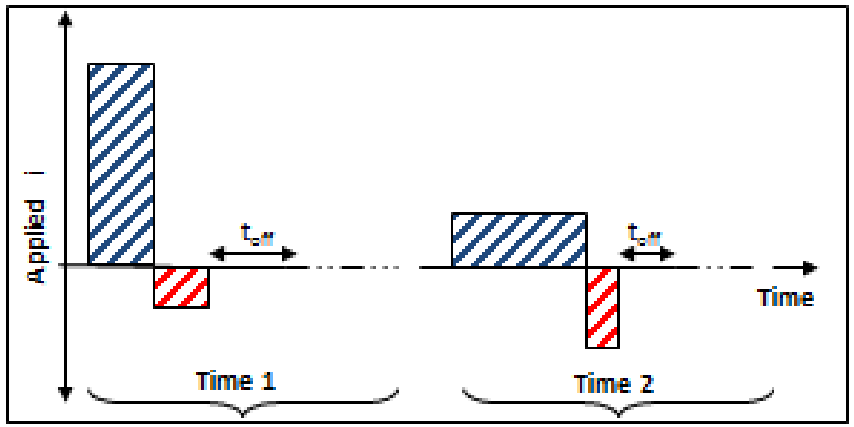
1. Beginning stage of the Cr^{3+} deposit

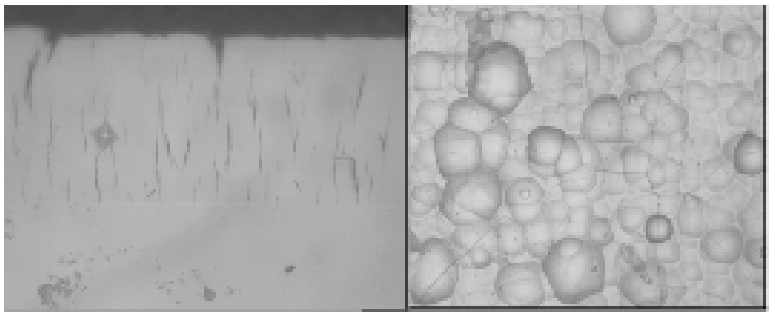
2. Further progression of the Cr^{3+} deposit



3. Final stage of the Cr^{3+} deposit without continuous cracks







	# Through-cracks
Baseline w/o looping	280
With looping	50

FARADAY TECHNOLOGY, INC.

Opportunities:
Application Development

Surface Preparation considerations –

- Cr(VI) process lines traditionally have limited surface prep steps/activations
- Cr(VI) electrolytes very acidic (<1 pH), many HC applications also incorporate surface prep of reverse etching in Cr(VI) electrolyte – which is not possible with Cr(III) – damaging to chemistry
- Cr(III) electrolyte operating pH 4.5 – 6 so far requires modification of traditional HC process line surface prep strategy
- High Strength and hardened steel substrates require electrolytic type activations in place of reverse etching technique.
- More aggressive acid activations required based on substrate type

Opportunities:
Deposit Optimization

Impact of post plating bake for hydrogen embrittlement / or other heat treatments

- Due to carbon in alloy, forms chrome-carbide which hardens deposit – up to 1700 HV_{100} - look at ways to minimize carbon in alloy
- Taber Wear Index increases after Heat treatment – which might not represent "true wear" of the deposit.

Adhesion – Related to Surface Prep, Chemistry Optimization, Application development

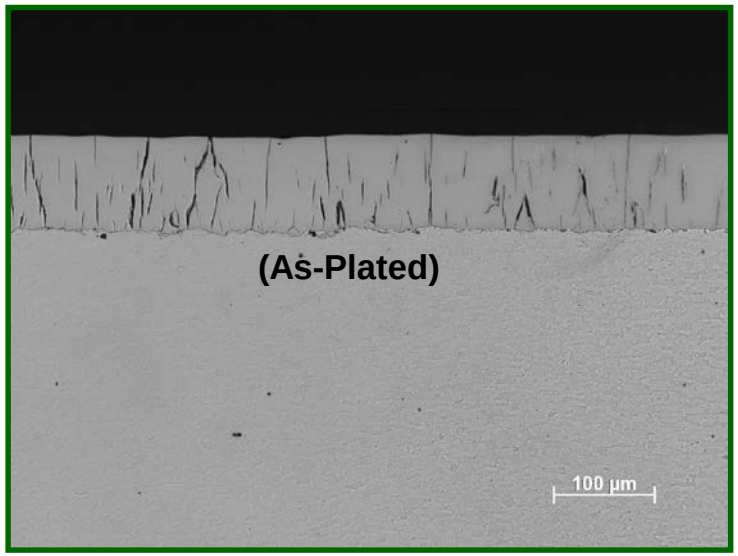
- Current work incorporating nickel base layer to maintain consistent surface to mitigate ferrous substrate impact

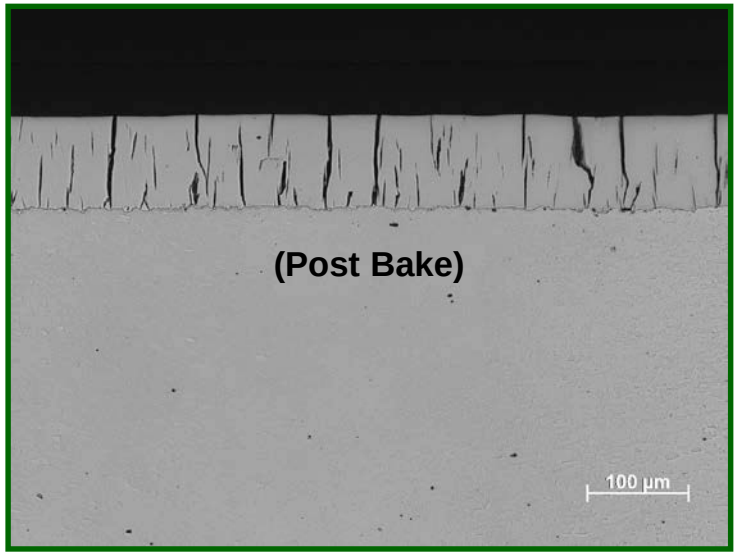
Macro-cracking vs Micro-cracking – tendency for through-cracks to substrate

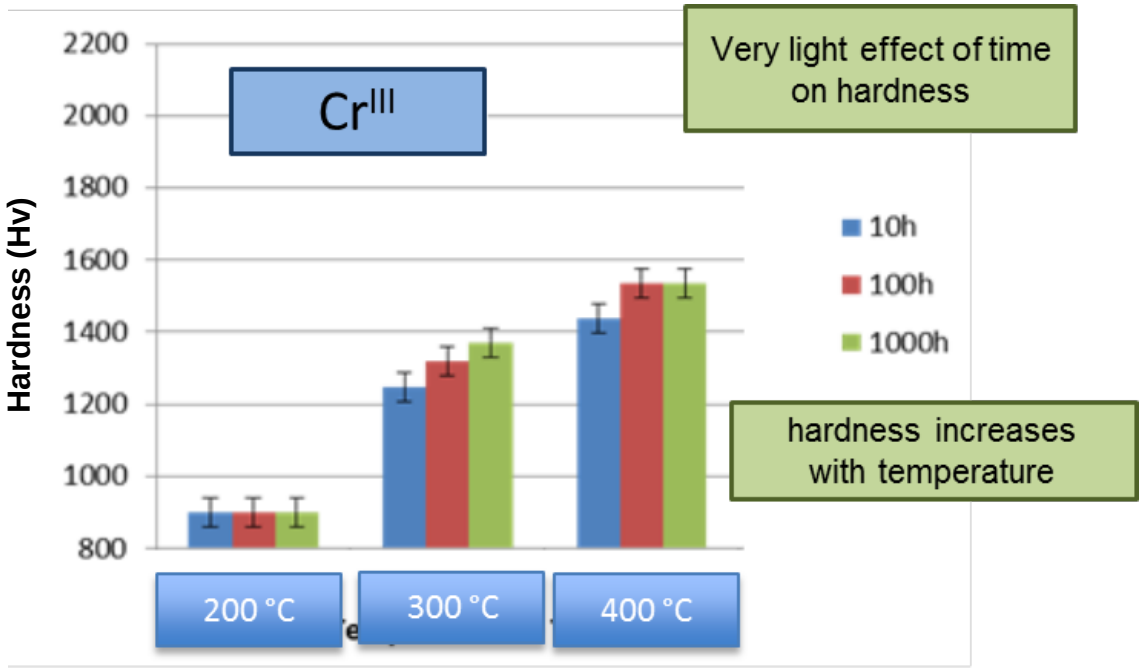
- Deposit stress investigations to impact
- Alloy carbon & oxygen content – control with rectification and chemistry optimization
- Optimize additives in chemistry – identify new chemistry species to impact carbon & stress

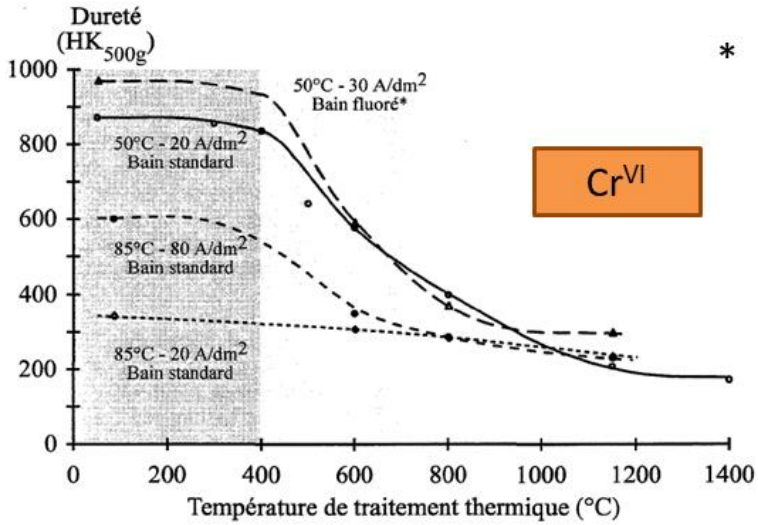
EX DBA 1318 Cr(III): Baking Effect on Microstructure/ Hardness (AMS 2460, 3.4.3)

LC1318-2-DS-1021-120









FARADAY TECHNOLOGY, INC.

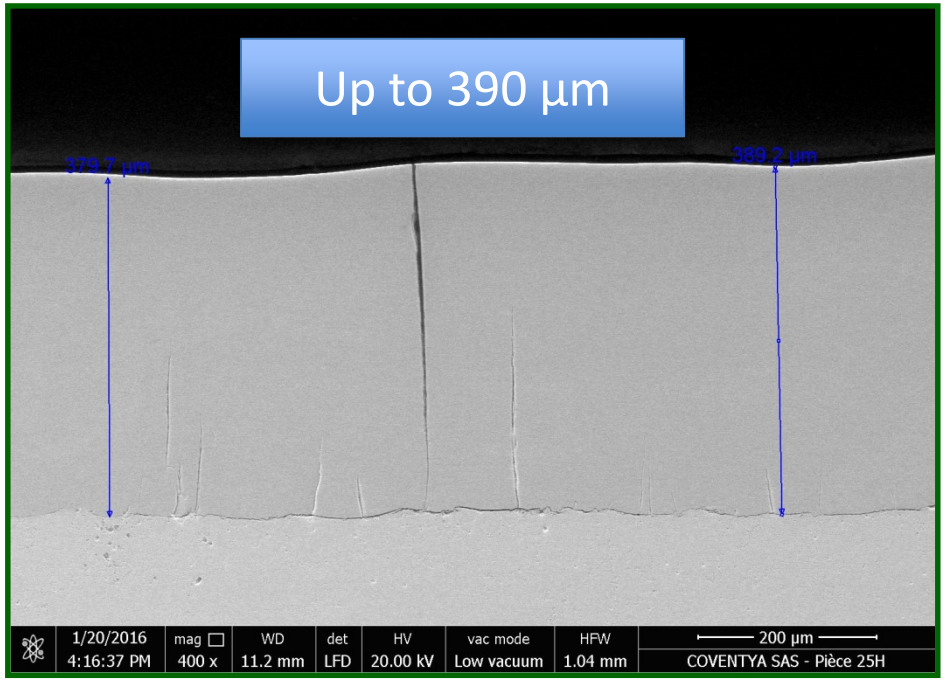
CHEMICAL CONTENT AND COATING SYSTEMS

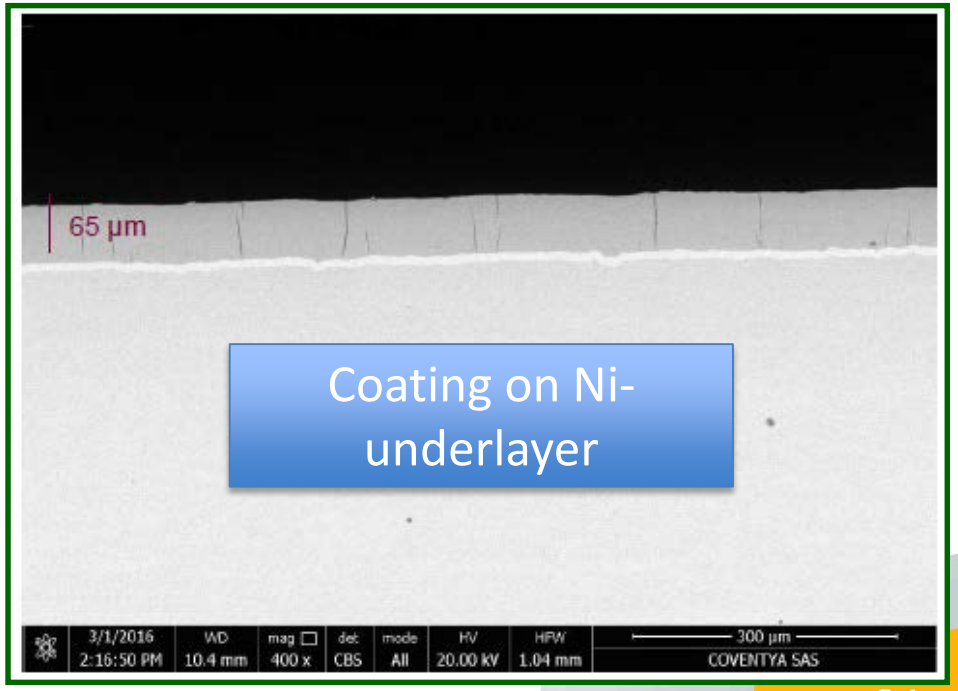
Initial screening composition of coatings (Cr^{III} and Cr^{VI}) by EDS

Process	Deposit thickness	Content (%mass)			
		Cr	Fe	O	C
Cr^{III}	60µm	83.8	< 0.2	10.9	5.2
Cr^{VI}	60µm	95.8	< 0.1	3.5	<1

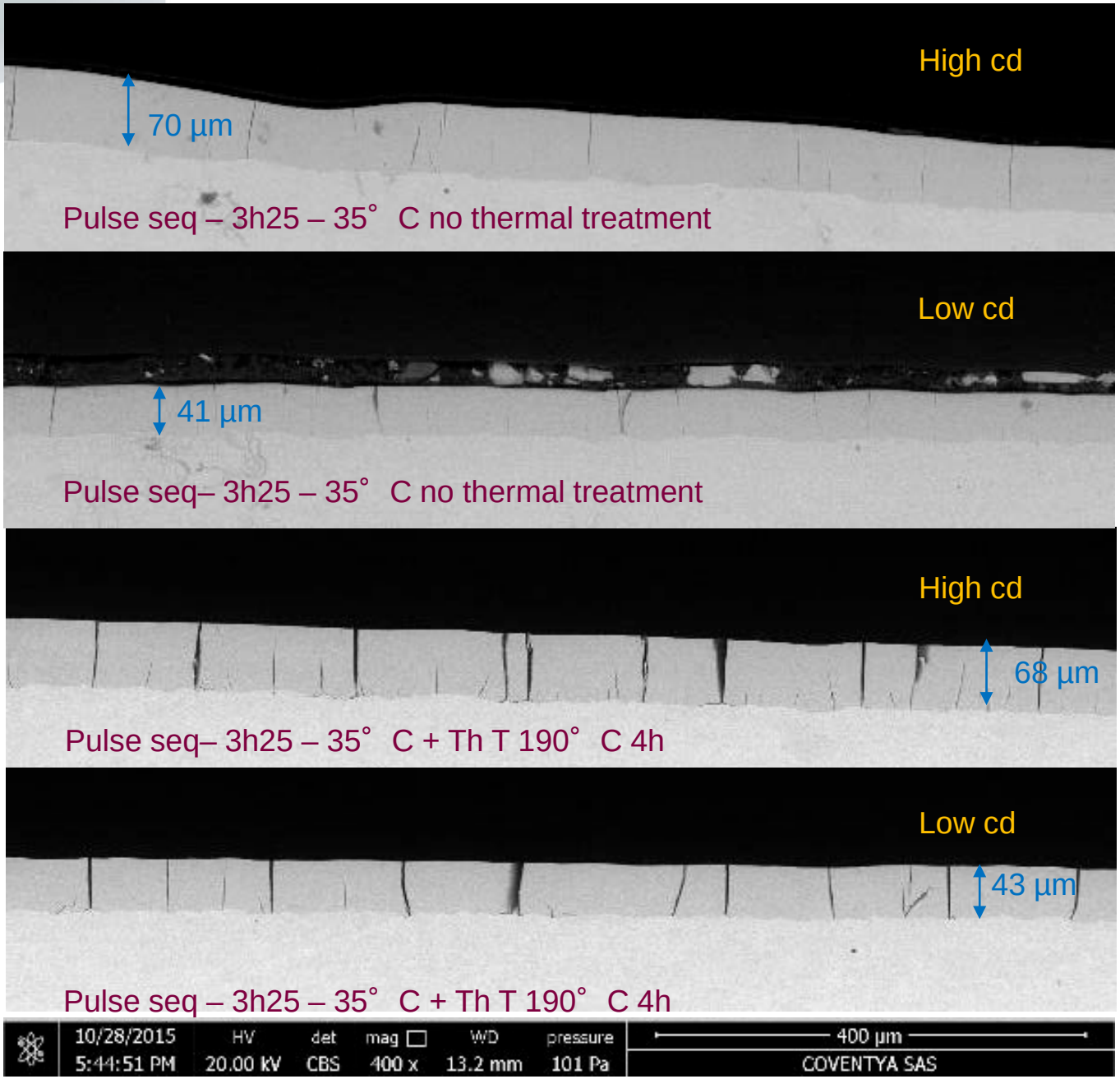
→ The carbon content is higher with the Cr^{III} solution

→ The carbon comes from the organic complex used to stabilize the Cr^{III}





THERMAL TREATMENT INFLUENCE



~ 1-3 macro-cracks/mm

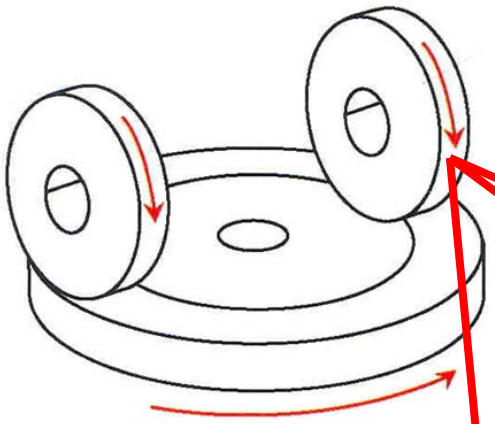
~ 0-3 macro-cracks/mm

~ 9 macro-cracks/mm

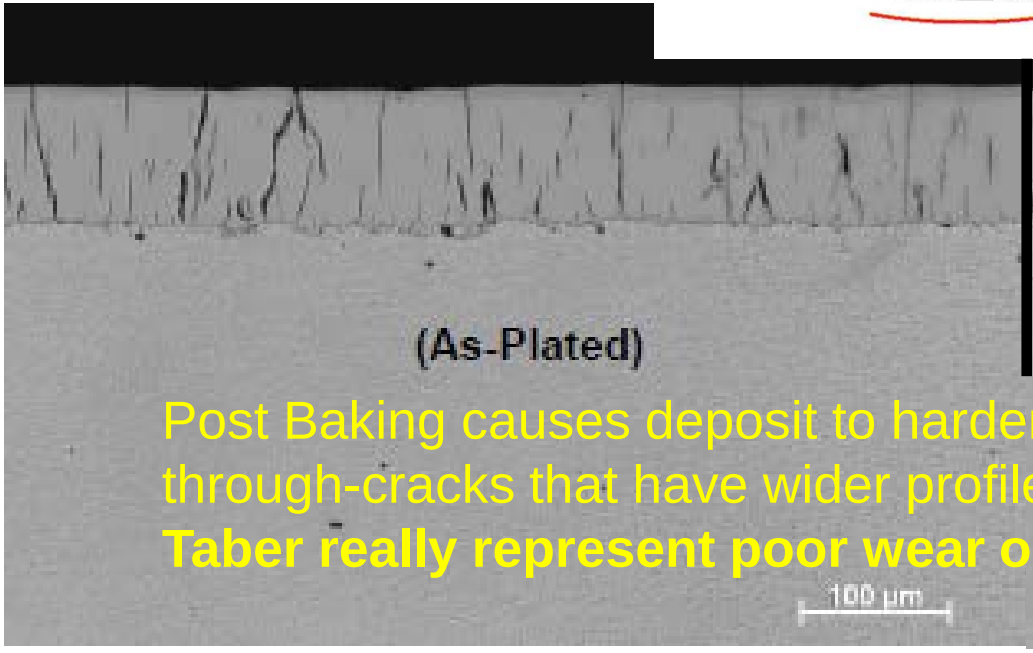
~ 10 macro-cracks/mm

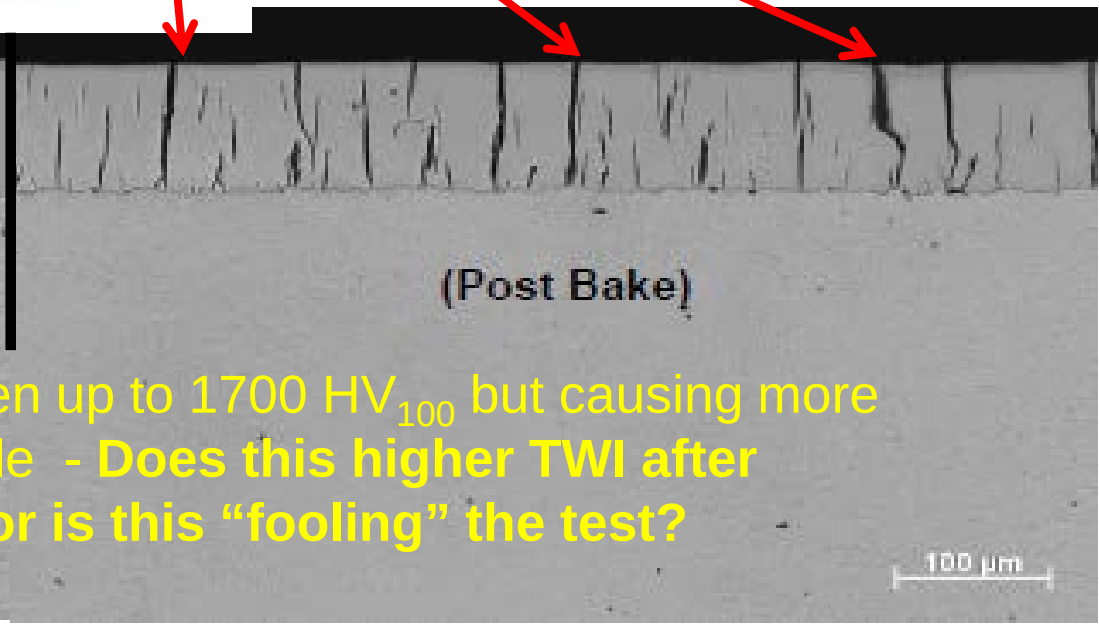
COVENTYA EX-DBA-1318 Cr(III) Cross Section - Proposed Mechanism for higher TWI after Heat treatment

Taber Wear Test (TWI)



Edges of through -cracks which have widened from HT fracture due to their higher brittleness - cause more mg deposit loss (chips) and higher resulting TWI – Adhesion to base is good





Post Baking causes deposit to harden up to 1700 HV_{100} but causing more through-cracks that have wider profile - **Does this higher TWI after Taber really represent poor wear or is this "fooling" the test?**

Opportunities: Deposit Optimization

Impact of post plating bake for hydrogen embrittlement / or other heat treatment

- Due to carbon in alloy, forms chrome-carbide which hardens deposit – up to 1700 HV_{100}
- Taber Wear Index increases after Heat treatment – which is likely related to tops of through cracks fracturing during test

Adhesion – Related to Surface Prep, Chemistry Optimization, Application development

- Improved surface prep sequences vs traditional Cr(VI) approach.
- Current work USA team incorporating nickel base layer to maintain consistent surface to mitigate substrate impact

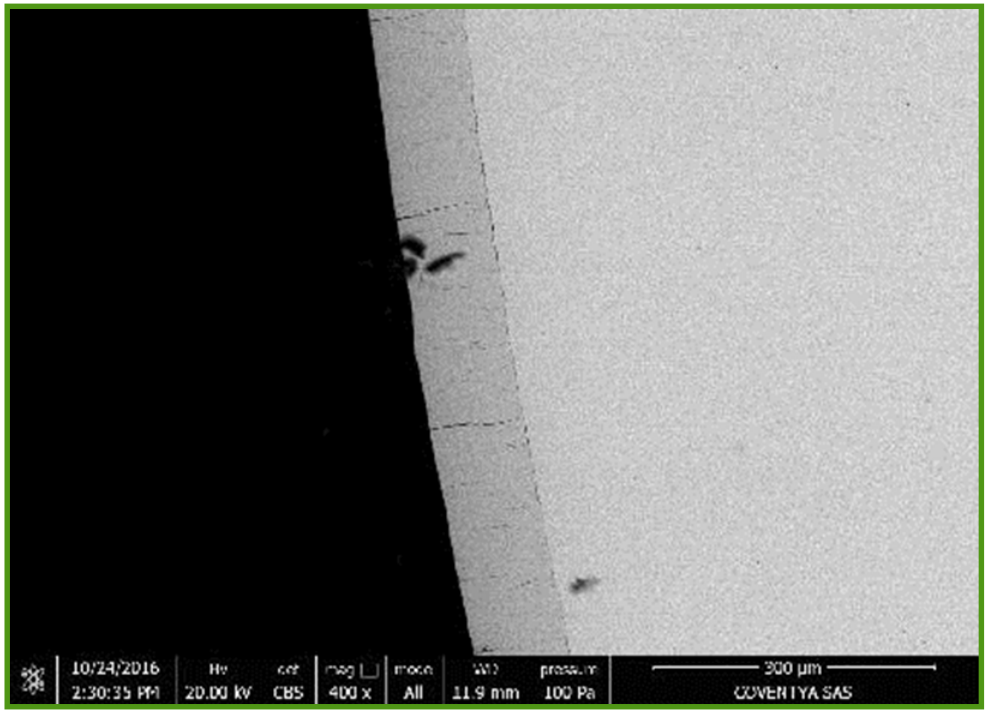
Macro-cracking vs Micro-cracking – tendency for through-cracks to substrate

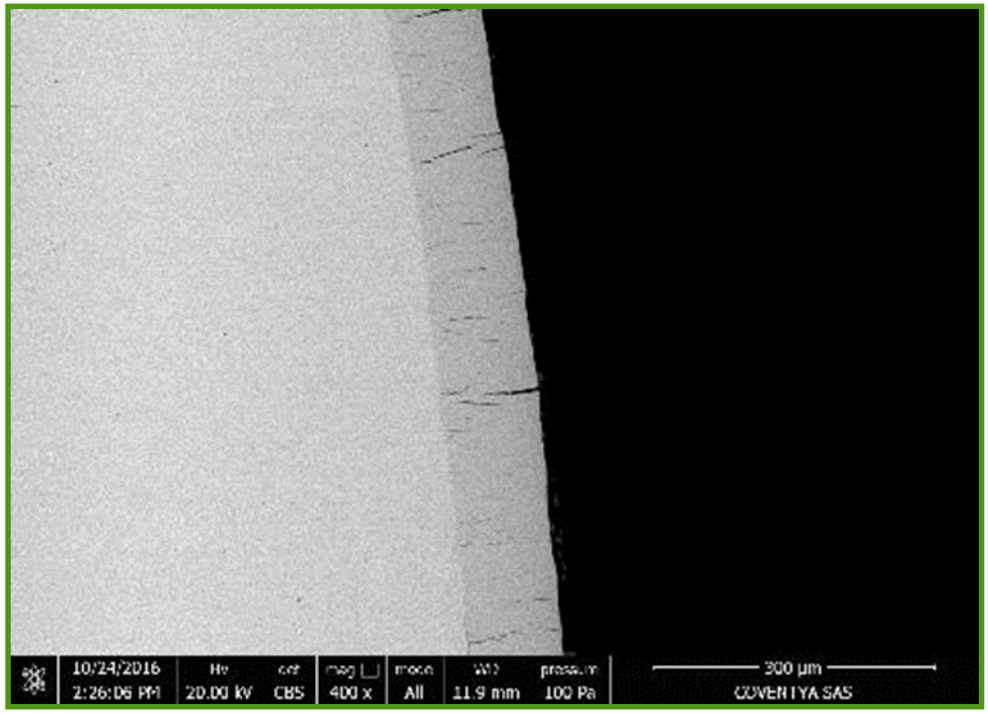
- Deposit stress investigations to impact – University of Houston program.
- Alloy carbon & oxygen content – control with rectification and chemistry optimization – deposit studies continue
- Optimize additives in chemistry – identify new chemistry species to impact carbon & stress – R&D process.

EX DBA 1318 Cr(III) Status

Through-cracking

- Possibility to minimize cracks as deposited – chemistry & operating conditions optimization



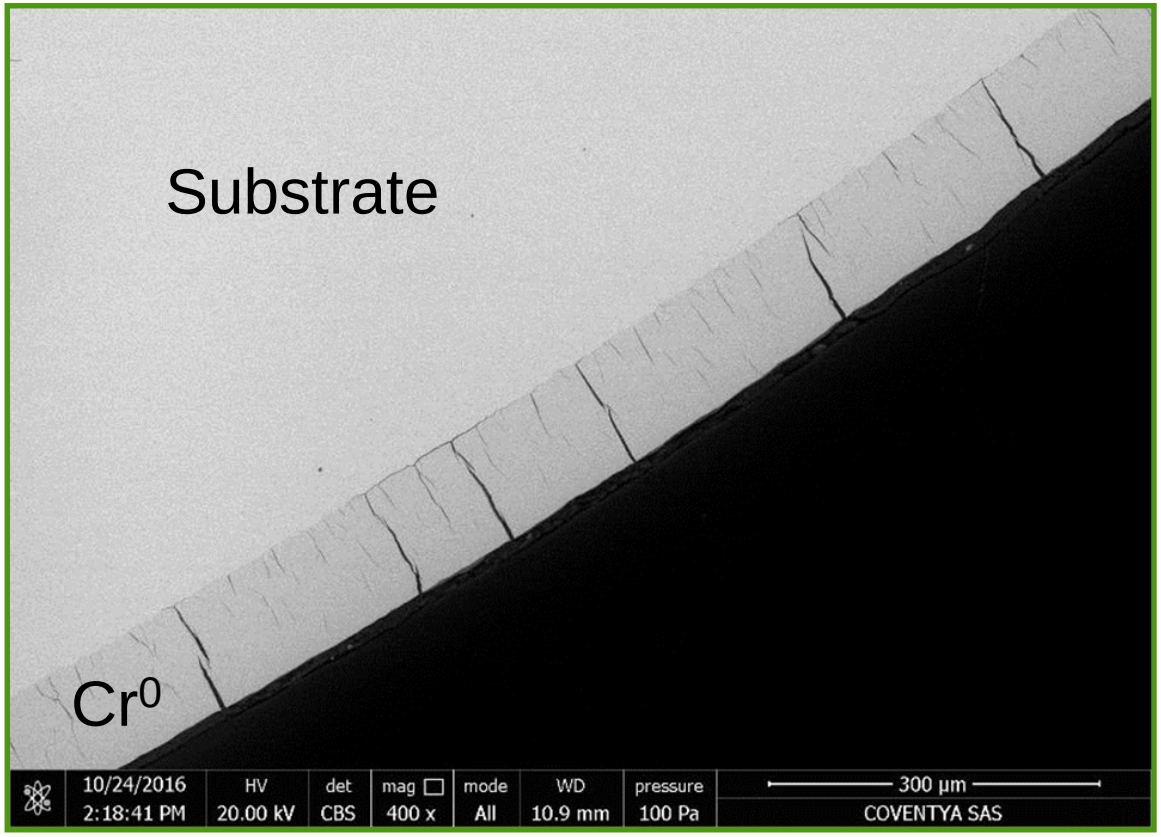


- Other additives evaluation to verify impact through-cracking

COVENTYA

Post Plating Heat Treatment Impact

- After thermal treatment presence of through-cracks exist due to carbon inclusion.
- Adhesion to substrate verified good despite cracking.
- Early tests predict its possible to target a microstructure more similar to CrVI – fewer through-cracks and thinner cracks after HT with various optimizations



COVENTYA

Summary (To Date)

Over past year, programs have demonstrated progress toward Cr(VI) replacement with Cr(III) technology

- Deposits meet many application demands
- Stability of technology – many 1000's of AH/L with replenishments
- REACh Compliant technology basis for future work

Optimization programs will continue as outlined

- Application & Chemistry to impact deposit

Outside of Aerospace/Military applications – deposit samples have been produced for other Industrial applications and are being characterized as Cr(VI) replacement.

Development of this Technology platform still in Infancy – over the next 4 – 7 years will see many improvements

- HC technology Cr(VI) has been evolved for 90+ years

Project USA Team Activities

Testing Status

- **Testing Recently Undertaken**
  - Boeing
    - Grinding
  - Faraday
    - Taber Abrasion
- **Testing to be Initiated/Completed in the Next Period**
  - U. Minnesota
    - Carbon content
  - Faraday
    - Taber Abrasion
  - UTRC
    - Hardness
  - U. Houston
    - In-situ stress Cr^{6+}
- **Testing to be Initiated in the Near Future**
  - MBD
    - Fatigue
  - Boeing
    - Hydrogen Embrittlement

FARADAY TECHNOLOGY, INC.

Slide 15

COVENTYA

COVENTYA

Special thanks to all the team members for their support & efforts.

THANK YOU FOR YOUR ATTENTION!
QUESTIONS?

Further Contact Information About Talk:

Email: b.durkin@coventya.com

COVENTYA