ASETSDefense
Martin Beneke
Sonja Nixon

Chromate free surface pre-treatments for aluminium alloys

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Drivers for chromate replacement

- ***Airbus Environmental aims: Remove hazardous (CMR) substances from a/c and plants***
  - ***Airbus ACF (Airbus Chromate Free) program started in 2002***
- ***REACH*** regulation: ***R****egistration,* ***E****valuation,* ***A****uthorisation and* ***R****estriction of* ***C****hemicals*

CrO_3, official REACH sunset date: 9/2017

Chemical name(s): Chromium trioxide
EC No.: 215-607-8
CAS No.: 1333-82-0

CrO_3 is used e.g. for CAA, CrVI CCC, Acidic Pickling processes, Hard Chrome plating, etc.

ECHA
EUROPEAN CHEMICALS AGENCY

Committee for Risk Assessment (RAC)
Committee for Socio-economic Analysis (SEAC)

Opinion

on an Application for Authorisation for

Chromium trioxide use: Surface treatment for applications in the aeronautics and aerospace industries, unrelated to Functional chrome plating or Functional chrome plating with decorative character

ECHA/RAC/SEAC: AFA-O-0000006490-77-04/D

Consolidated version

Date: 16 September 2016

CTAC: Chromium Trioxide Authorization Consortium

- **Aim: Use of CrO_3 after the sunset date**

RAC and SECA recommendation for final decision of European Commission:

„Taking into account the information provided in the application for authorisation prepared by the applicant and the comments received on the broad information on use the duration of the review period for the use is recommended to be **seven years**."

CrO_3 banned and full implementation of replacements in manufacturing and supply chain latest end 9/2024 necessary!

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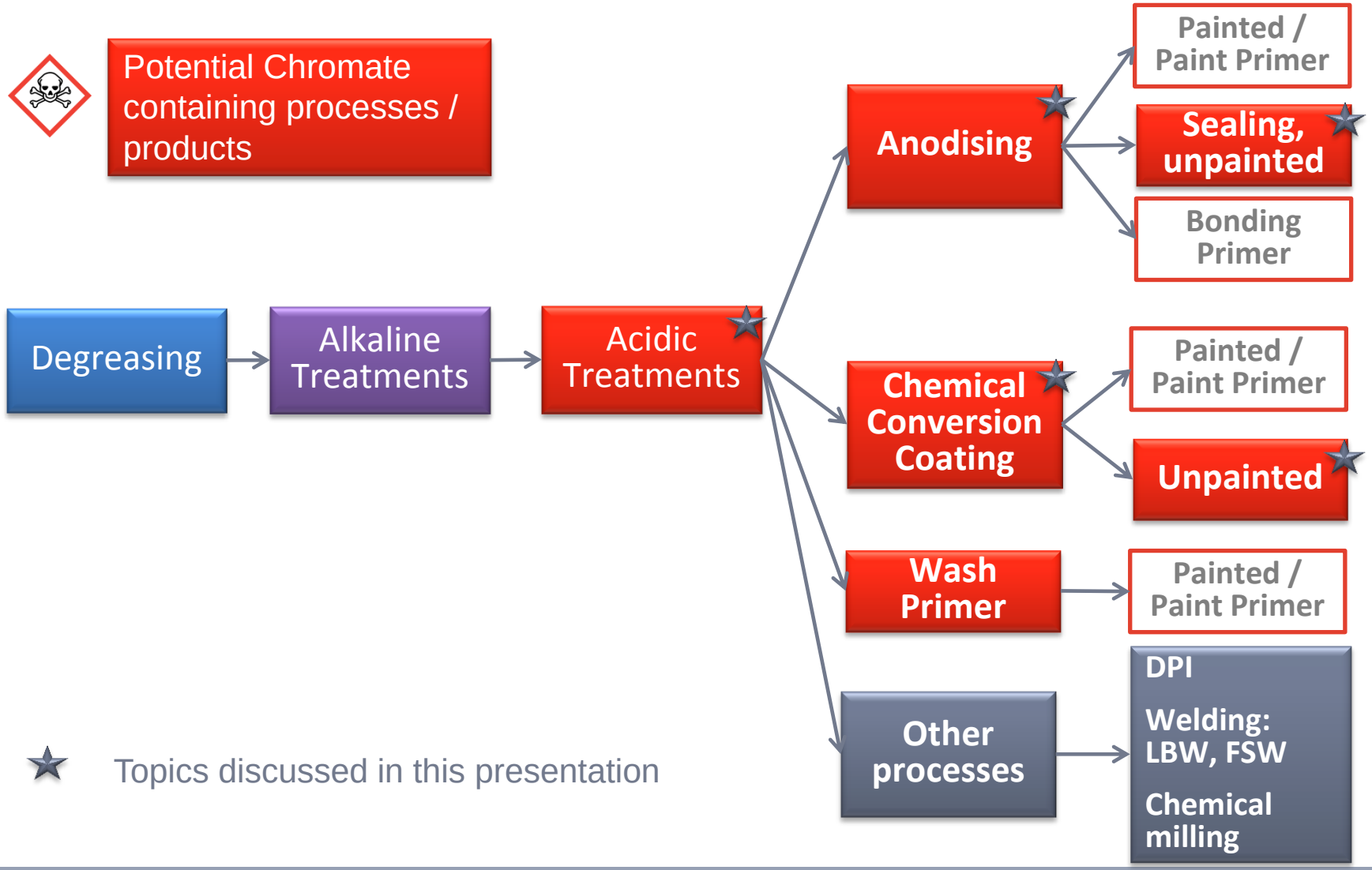
Surface pre-treatment of aluminium alloys



★ Topics discussed in this presentation

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Anodising CAA Replacement

CAA Cr VI

1:1 Replacement solution

n/a

Corrosion Protection

Structural Bonding

TSA

PSA

Painted parts

Unpainted parts

Basic Primer Application, Unsealed TSA

plus Post Treatment, Sealing Process

Bonding Primer

Chromate free CCC options are available

CAA: Chromic Acid Anodising
TSA: Tartaric Sulphuric Acid Anodising
PSA: Phosphoric Sulphuric Acid Anodising
CCC: Chemical Conversion Coating

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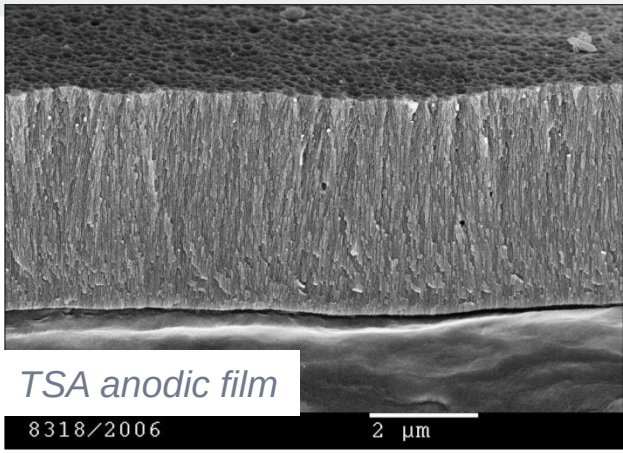
CAA replacement: TSA Anodic Pre-treatment (2006)

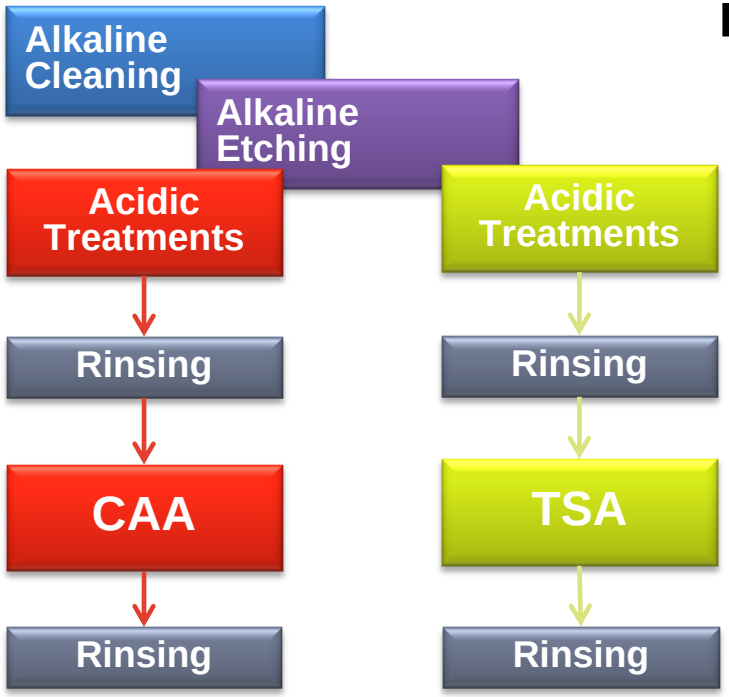
Tartaric Sulphuric Acid Anodising compared to CAA

- eco-efficient alternative to CAA fulfilling the same requirements
- TSA is standard for A350 (CAA was only temporarily accepted)
- 120 Supplier world wide qualified to TSA AIPS 02-01-003
- 10 years manufacturing experience with time reduction by ~ 30%



TSA anodic film

CAA key process parameter	
Film thickness	2-5 µm
Temperature	40 °C
Process time	45 min
Voltage	40 V or 21 V
Chromic Acid content	30-100 g/l



TSA key process parameter	
Film thickness	2–7 µm
Temperature	37 – 43 °C
Process time	20 – 25 min
Voltage	13 – 15 V
Tartaric Acid content	80 g/l
Sulphuric Acid content	40 g/l

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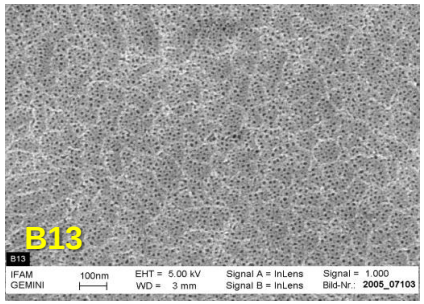
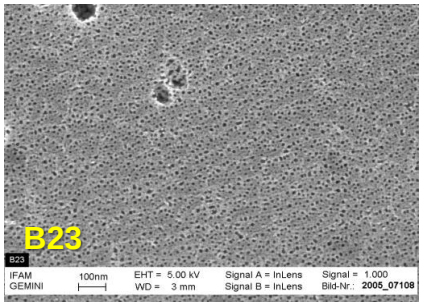
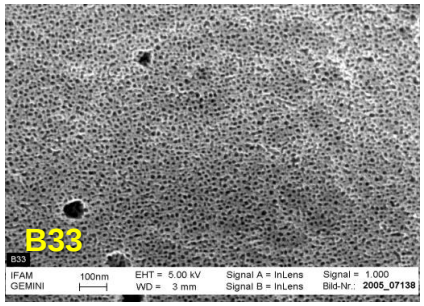
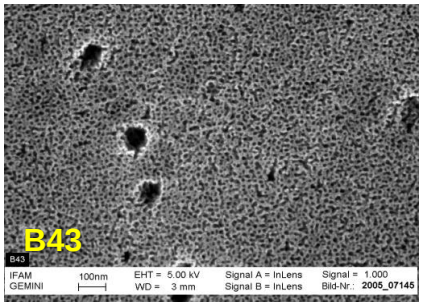
TSA process development

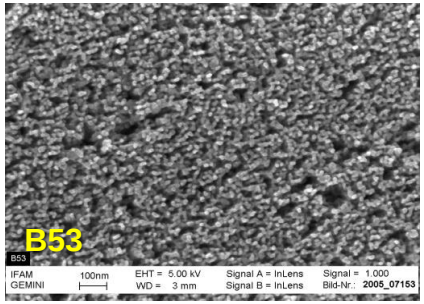
Morphology and thickness dependence in relation to TSA process parameters

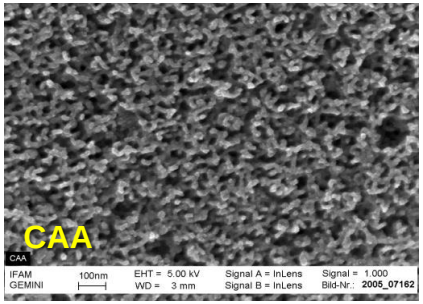


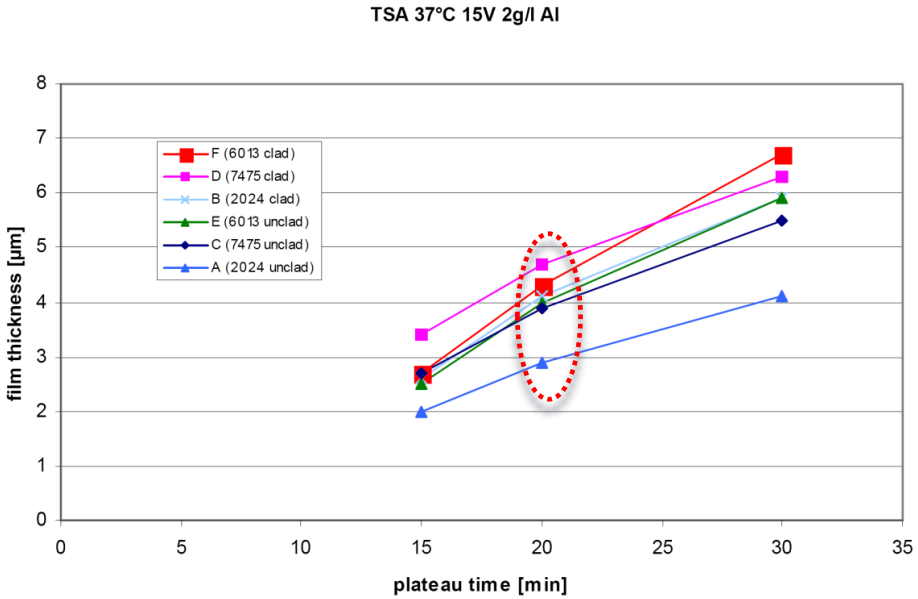












Sample	Alloy	Process parameter	Oxid thickness
B13	2024 bare	**13V; 5+20min; 37°C**	**1.8 µm**
B23	2024 bare	**15V; 5+30min; 37°C**	**3.1 µm**
B33	2024 bare	**15V; 5+20min; 43°C**	**3.2 µm**
B43	2024 bare	**18V; 5+30min; 43°C**	**4.6 µm**
B53	2024 bare	**13V; 5+25min; 50°C**	**5.0 µm**
CAA	2024 bare		**3.3 µm**

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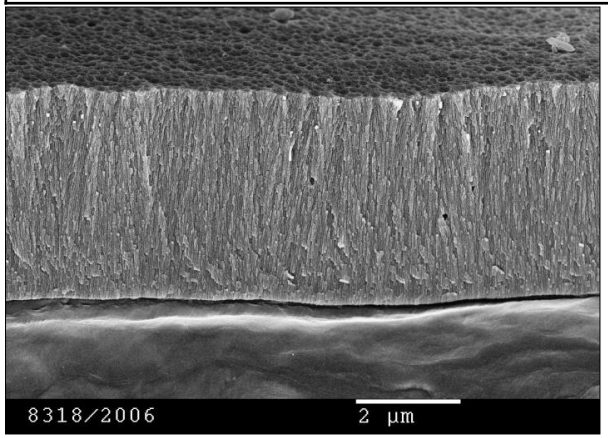
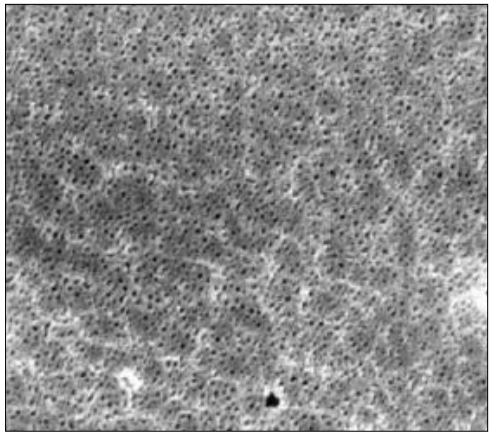
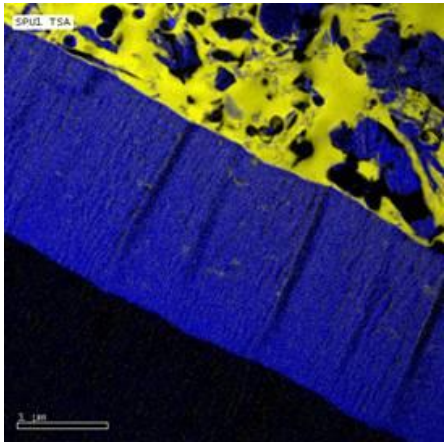
TSA development in relation to Adhesion and FFT results

Airbus CrVI based EP Primer							
				Adhesion		Filiform Corrosion	
Sample	Alloy	Anodizing Process (TSA)	Oxide Film thickness	GT after 0h	GT after 168h H2O	Max [mm]	Average of 5 Fila [mm]
B12	2024 bare	13V; 5+20 min; 37°C	1,8µm	1	0	3	1,4
B15	2024 bare	13V; 5+20 min; 37°C	1,8µm	0	1	4	2,7
B22	2024 bare	15V; 5+30min; 37°C	3,1 µm	1	1	1,5	1,2
B25	2024 bare	15V; 5+30min; 37°C	3,1 µm	1	1	1,5	1
B32	2024 bare	15V; 5+20min; 43°C	3,2 µm	0	0	1	0,7
B35	2024 bare	15V; 5+20min; 43°C	3,2 µm	0	0	2	1,5
B42	2024 bare	18V; 5+30min; 43°C	4,6 µm	0	0	0,5	0,5
B45	2024 bare	18V; 5+30min; 43°C	4,6 µm	0	0	1	1
B52	2024 bare	13V; 5+25min; 50°C	5 µm	1	0	0,5	0,5
B55	2024 bare	13V; 5+25min; 50°C	5 µm	0	0	0,5	0,5
	2024 bare	*CAA*	*3,3 µm*	*0*	*0*	*1,0*	*1,0*

Wide TSA process window available







TSA parameter selection was done in relation to TSA film and corrosion protection performance

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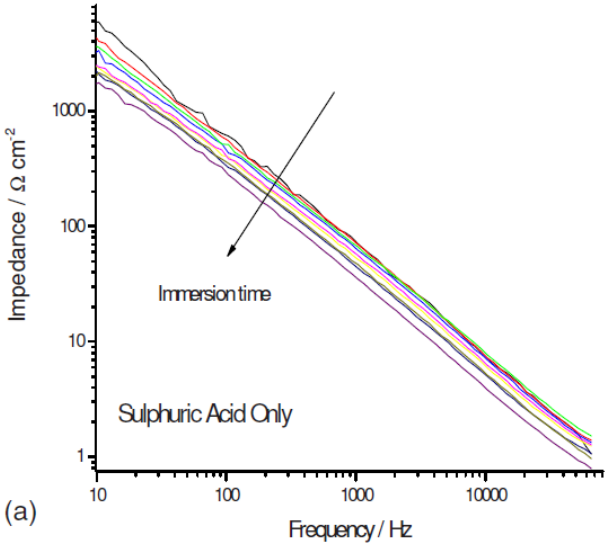
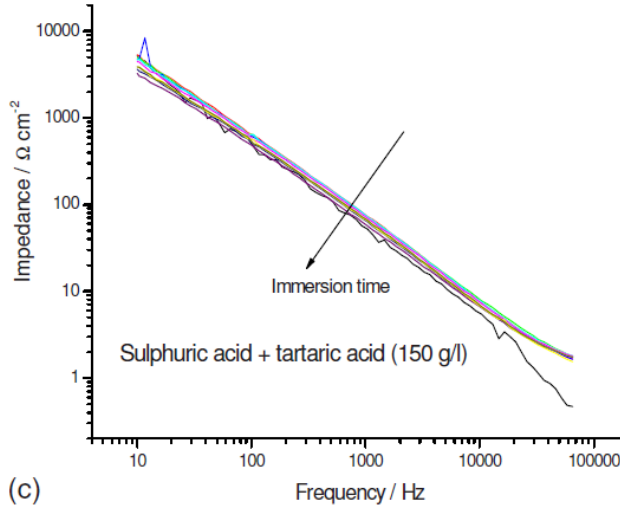
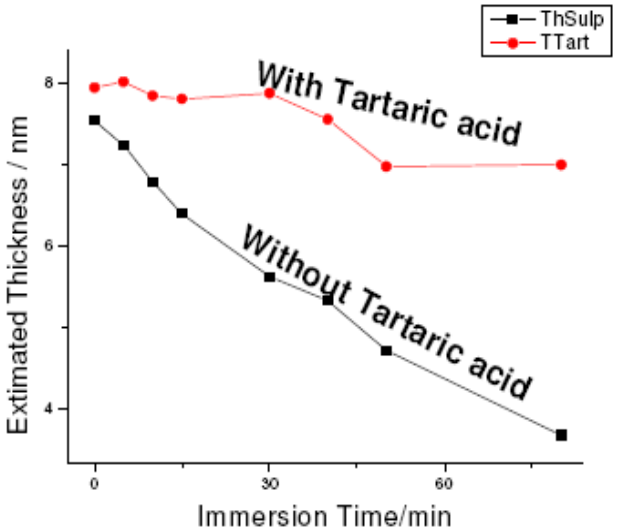
Why TSA? Role of tartaric acid

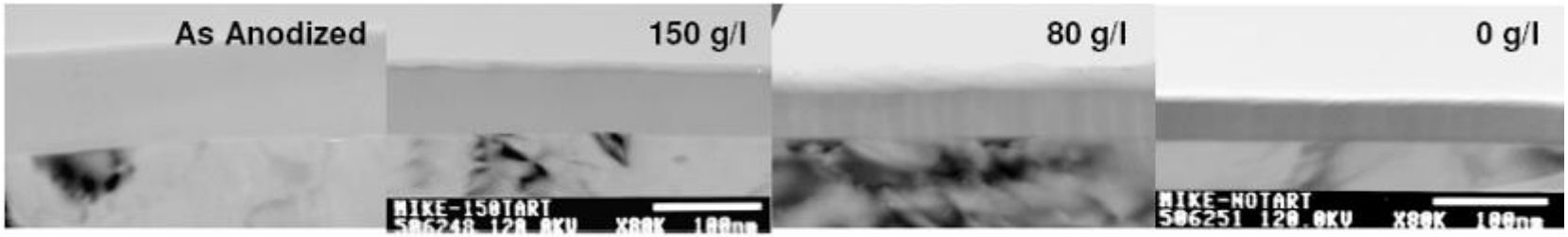
EIS results, currentless time in sulphuric acid and sulphuric/tartaric acid







TEM investigation after dissolution experiments with tartaric acid



Tartaric acid acts as an inhibitor and reduces e.g. the currentless dissolution of the TSA / anodic oxide film:

- **Higher process robustness for manufacturing**
- **Constant and better corrosion protection performance**

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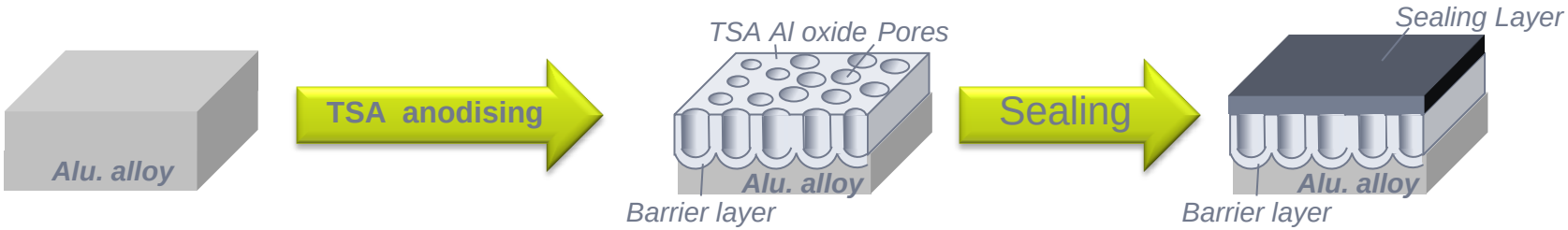
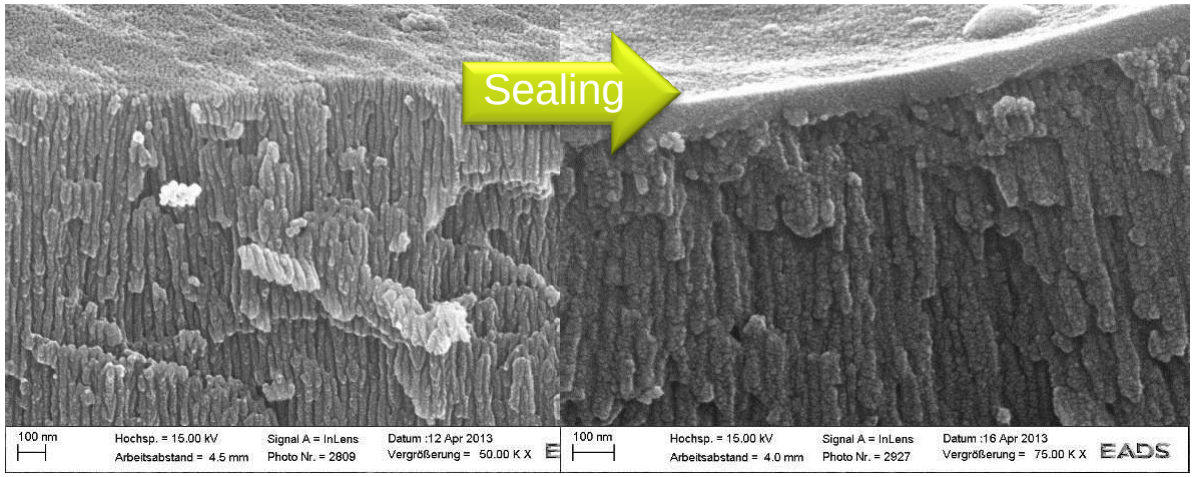
TSA chromate free sealing process – CrIII/Zr CCC

Sealing options:

- **Chemical Conversion Coating, CrIII / Zr CCC process (TCP):**
  - **E.g.: SurTec 650 (~ 20 %, 25 ~ 35°C, 5 ~ 10 min)**





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TSA CrIII/Zr CCC sealing results

TSA Standard
- AIPI 02-01-003
- 5 + 20 min

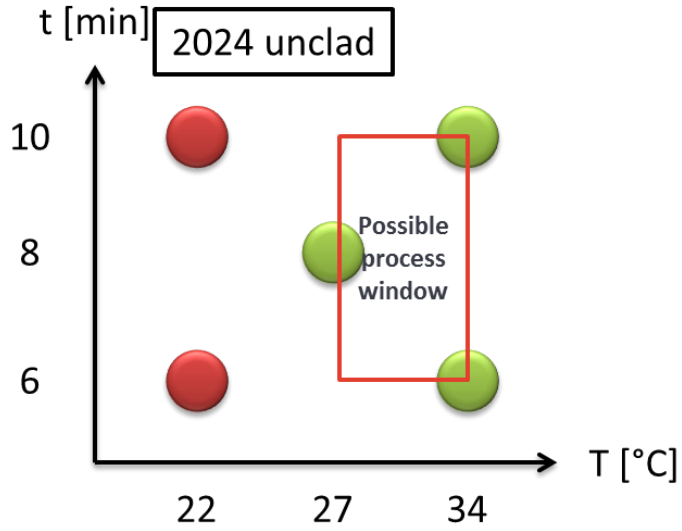
TSA long cycle
- Extended cycle
- 5 + 40 min

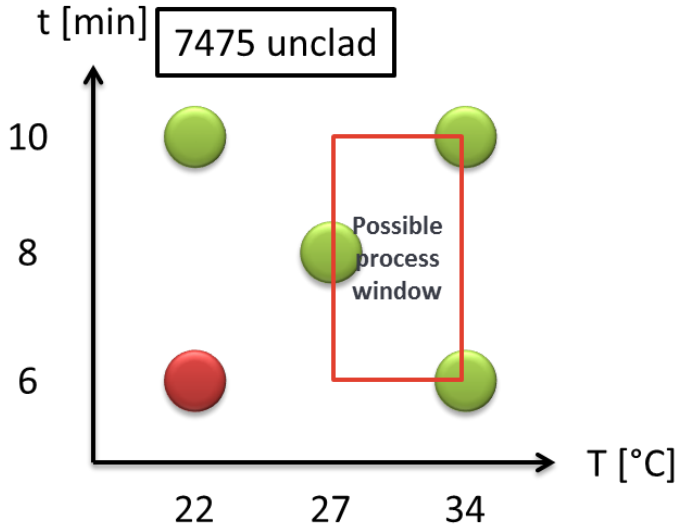
Sealing
- SurTec 650
  - 5 ~ 15 min
  - 25 ~ 35 °C

Post-treatment
- Hot water sealing

Salt spray test
- ISO 9227
- **336 h**

- ISO 9227
- **504h**





- Results validated in shop trials are equivalent to M&P lab experience and meet the requirement of 336h SST
- For extended SST resistance (504h SST), modified TSA long cycle can be used as option
- Long cycle TSA plus 650 met 336h SST without hot water sealing

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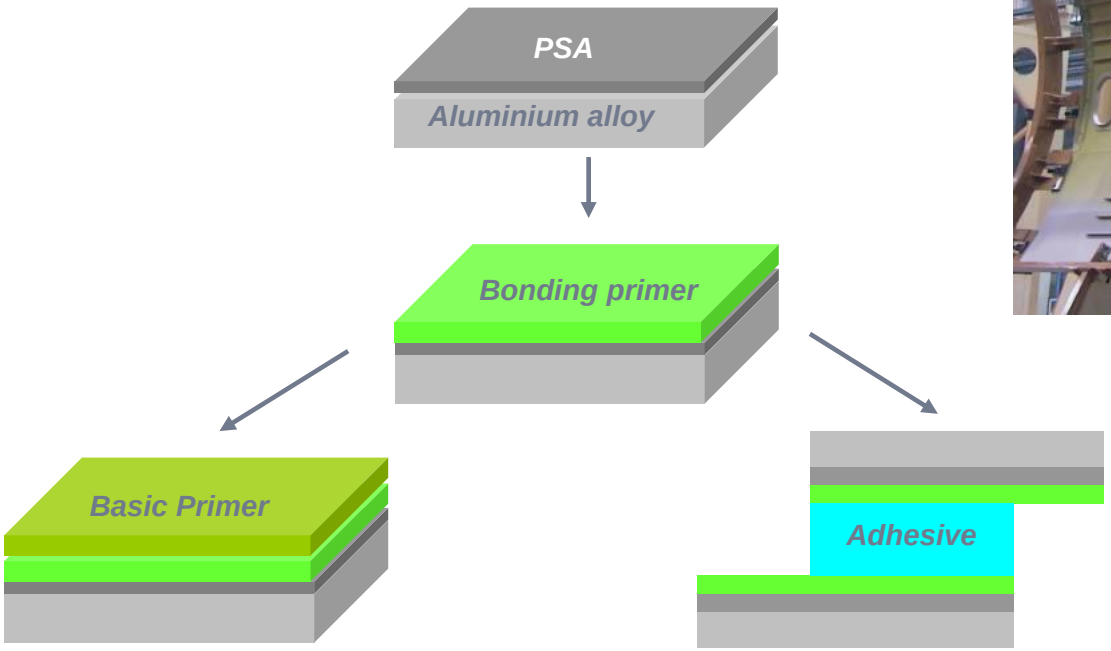
PSA: Anodising for structural bonding (2010)

PSA Phosphoric Sulphuric Acid Anodising for bonded structures

- Anodising (PSA)
- Bonding Primer application
- Structural adhesive
- Basic primer application



Painted surfaces

Bonded structures

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Passive Protection: PSA anodic Pre-treatment

Phosphoric Sulphuric Acid Anodising (PSA)

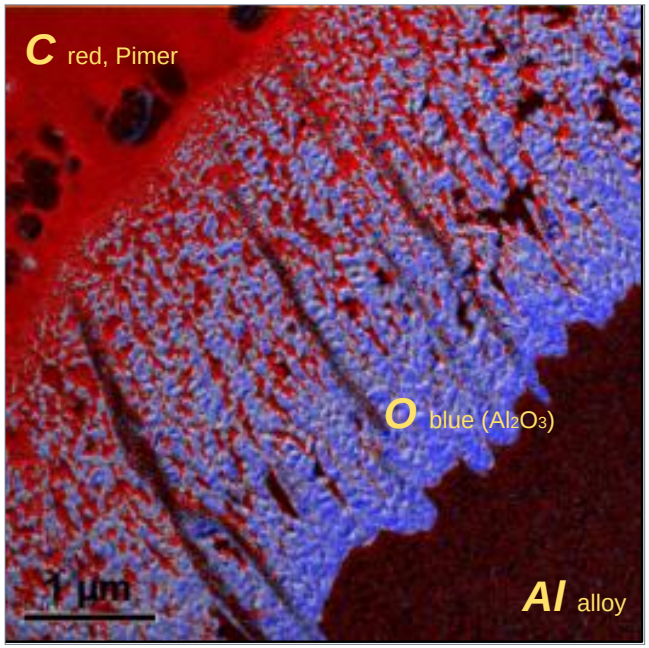
- fulfils the same requirements as CAA in combination for bonding application
- substitution process for surface preparation prior to metal bonding
- reduced process time
- lower voltage and bath temperature

CAA

CAA key process parameter	
Film thickness	2 - 5 µm
Temperature	40 °C
Process time	45 min
Voltage	40 V to 50 V
Chromic Acid content	30 - 100 g/l

PSA

PSA key process parameter	
Film thickness	1 - 5 µm
Temperature	26 - 28 °C
Process time	23 min
Voltage	18 V
Phosphoric Acid content	110 - 125 g/l
Sulphuric Acid content	75 - 80 g/l



PSA is optimised for adhesion:

Good penetration of the Bonding Primer into the PSA anodic oxide for good mechanical interlocking

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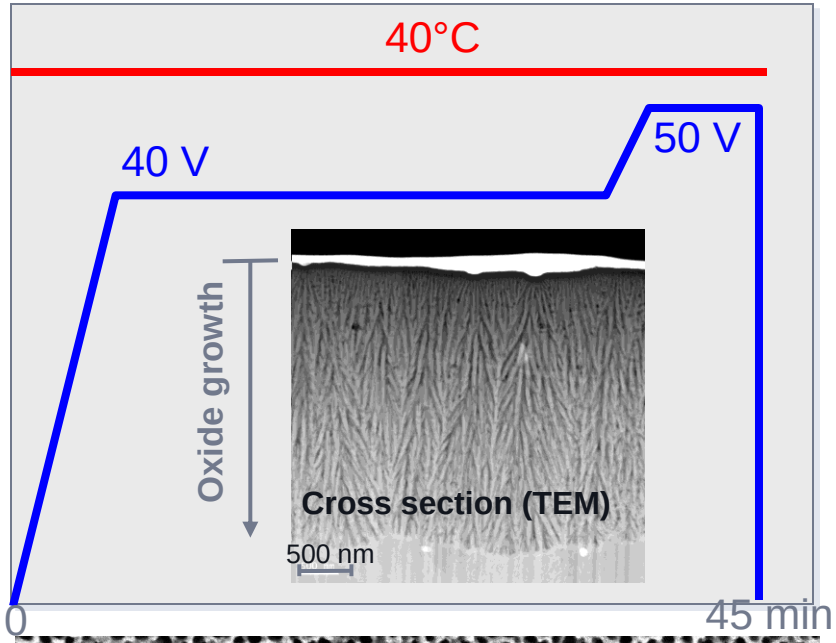
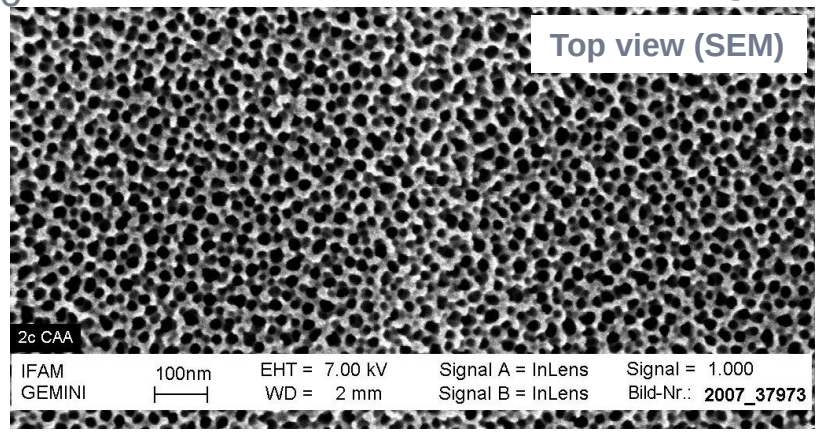
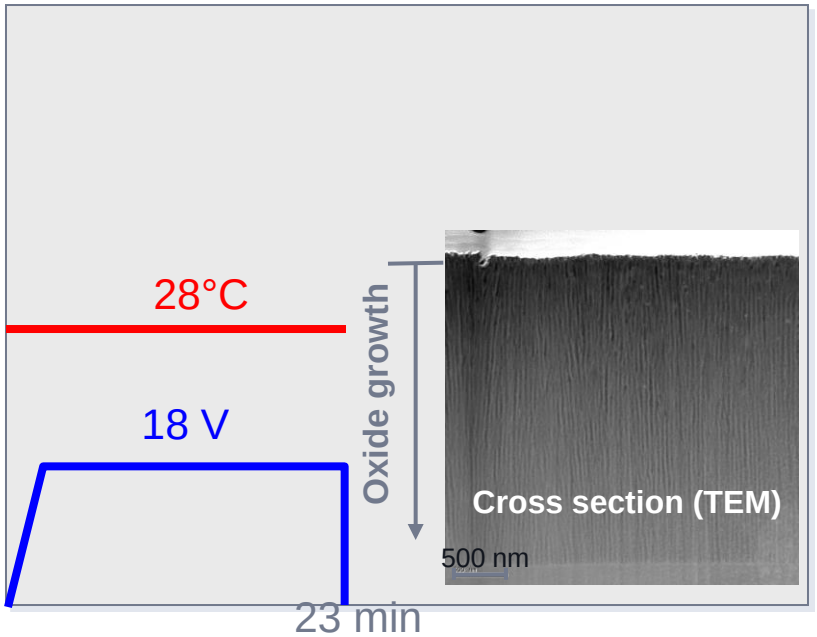
Passive Protection: PSA anodic Pre-treatment

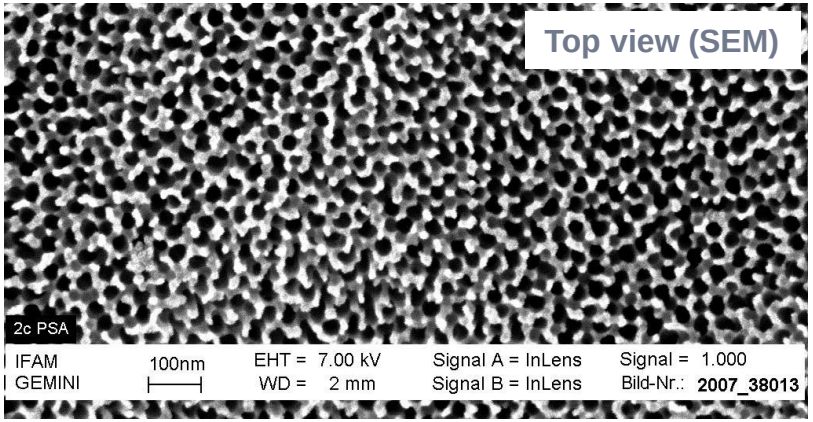
CAA





PSA





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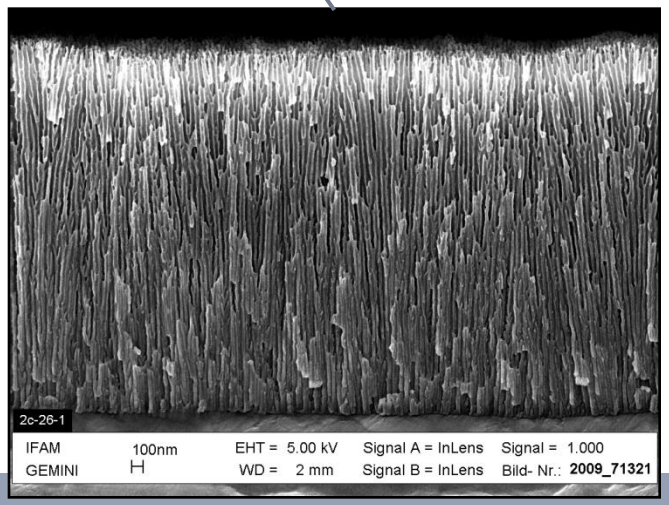
PSA anodic Pre-treatment

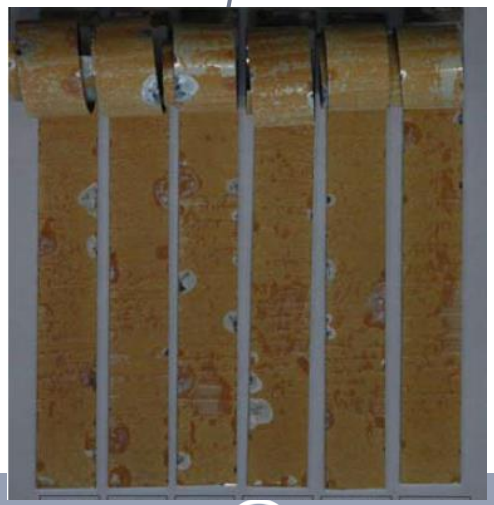
PSA and CAA fulfil the same requirements
for adhesion, corrosion protection and fatigue according to AIPS 02-01-006

	Anodic film properties					Bondingprimer + Paint properties				Bonding properties		Fatigue properties
	Visual aspect	Film thickness	Morphology	Film weight	~~Salt spray test~~	Crosscut test		Filiform	Salt spray test	Adhesive peel test	Bondline corrosion test	Kt1.7
						Dry	Wet					
	visual inspection by naked eyes	SEM, ISO 2360 or ISO 1463	SEM	EN 12373-2	ISO 9227	ISO 2409		EN 3665	ISO 9227	EN 1967	AITM 5-0009	EN 6072 and AIPS 02-01-001, AIPS 02-01-003, AIPS 02-01-006

PSA cannot be adequately sealed

BC 300 days SST: <30% corrosion on 2024 clad





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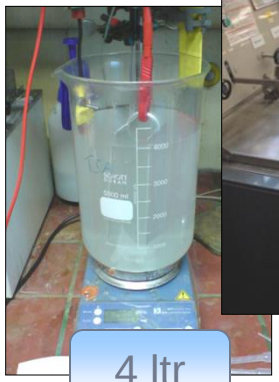
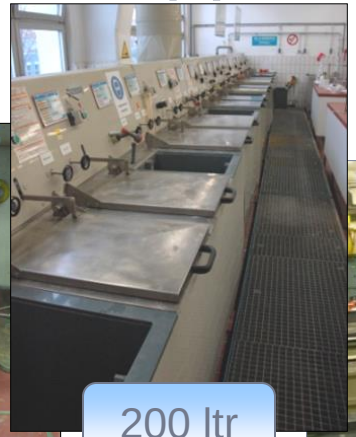
TSA / PSA industrial implementation – from lab to production size

Development (upscaling)

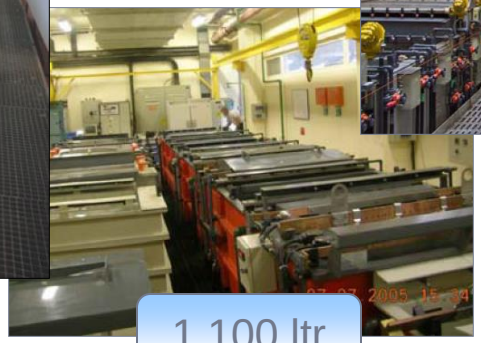


4 ltr



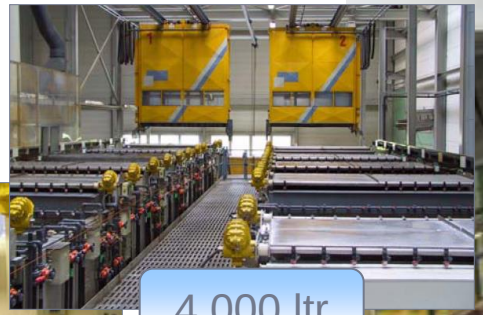
200 ltr

M&P BRE



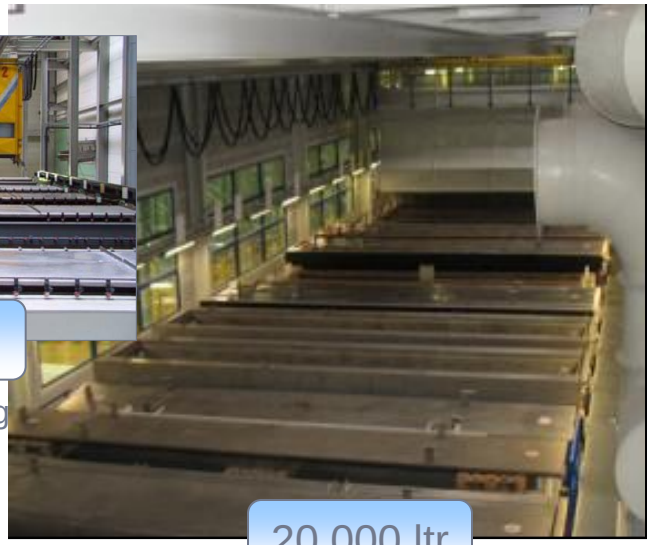
1.100 ltr

IW SUR



4.000 ltr

Manufacturing Nordenham



20.000 ltr

Manufacturing BRE

Implementation Production

20 m³ → 30 m³ → 84 m³ → 125 m³ → 300 m³

already in production
good experience since 2006

implementation in progress

⇨ ***Minimize risk by starting TSA and PSA implementation in small galvanic lines***

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Chromate free conversion coatings

Potential Technologies:

- Silane
- Sol-Gel
- Zr/Ti CCC
- Ce CCC
- TCP, CrIII/Zr technology
- Others: Mn, Mo,…

Best candidate today is the CrIII/Zr technology in relation to standard requirements, 168h SST, Paint adhesion and electrical conductivity.

Lack of CrIII/Zr technology today:

- Process robustness
- SST performance at 168h limit or below
- Optical visibility / quality control
- Overall corrosion protection performance with chromate free paint schemes

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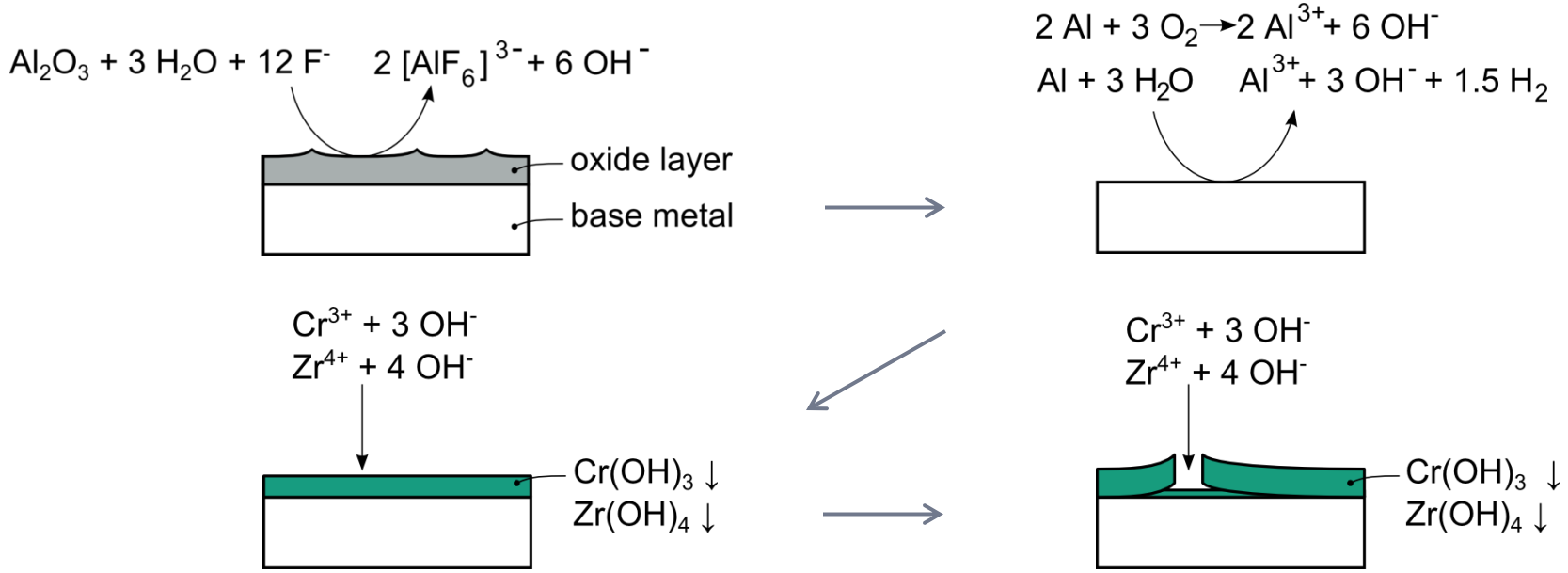
Selected CrIII/Zr process: Basic reactions at the aluminium surface

- **After several screening programs CrIII technology selected as best available technology for corrosion protection**



- Dissolution of aluminium oxide layer, dissolution of aluminium
  - Increase of pH at the metal/electrolyte interface
- Precipitation of $Cr(OH)_3$ and $Zr(OH)_4$
- Crack formation, re-passivation of cracked area

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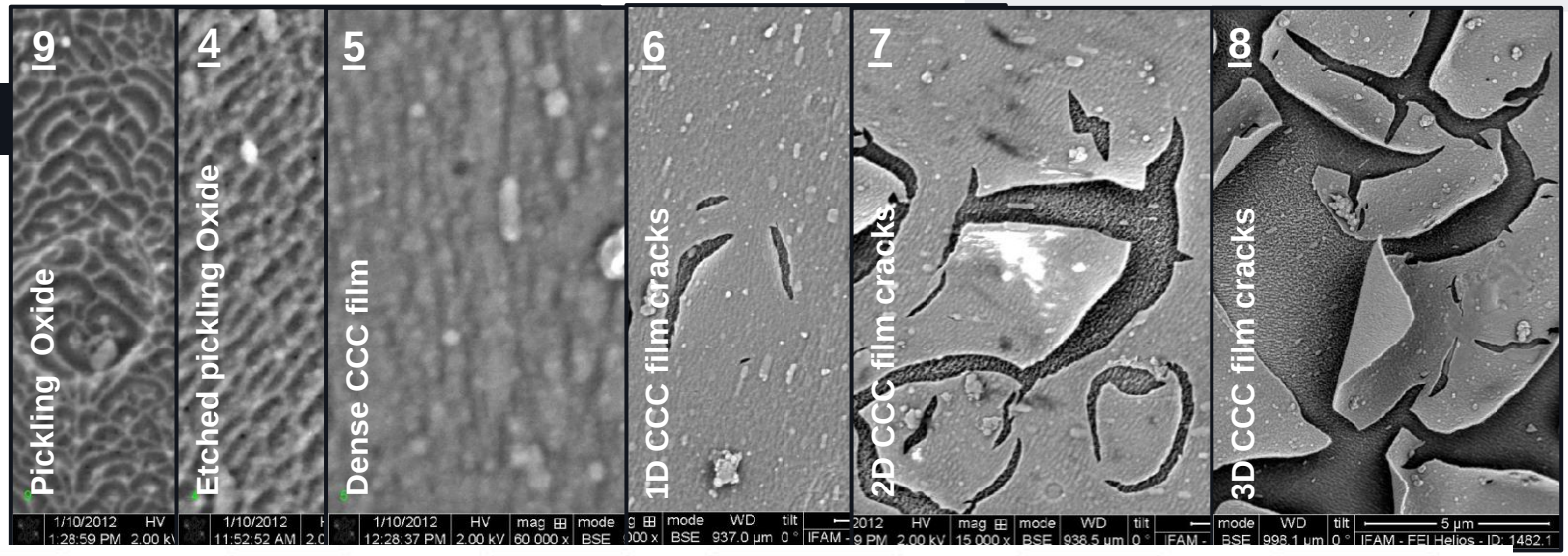
CrIII CCC formation: Relation of Surface properties to SST performance

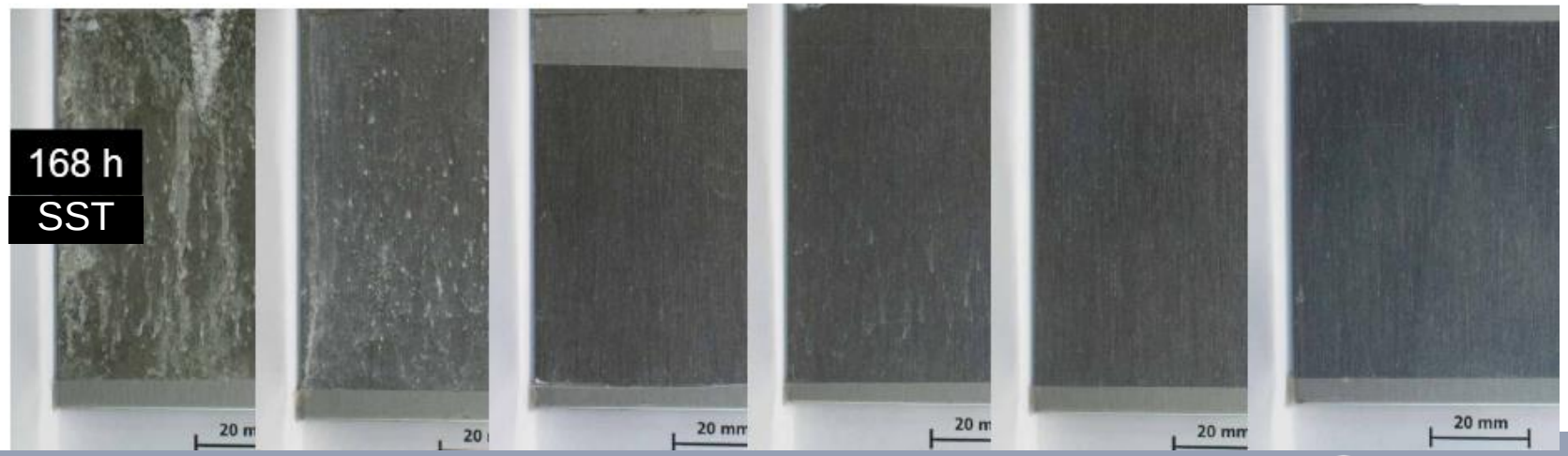
SEM



Treatment time

20 s | 50 s | 3 min | 4:30 min | 6 min | 10 min

168 h SST



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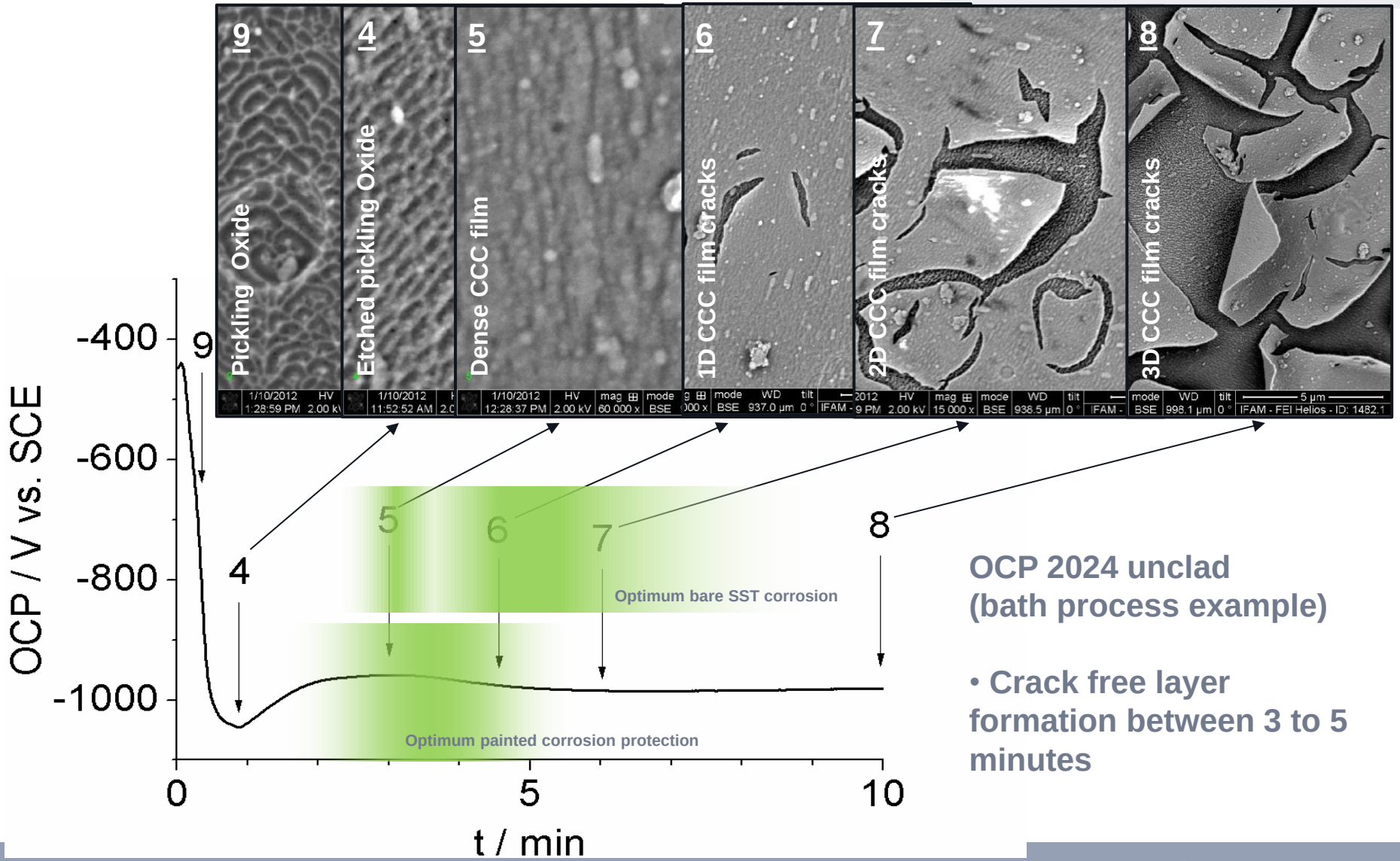
CrIII/Zr CCC: OCP / SEM relation



OCP 2024 unclad (bath process example)

- **Crack free layer formation between 3 to 5 minutes**

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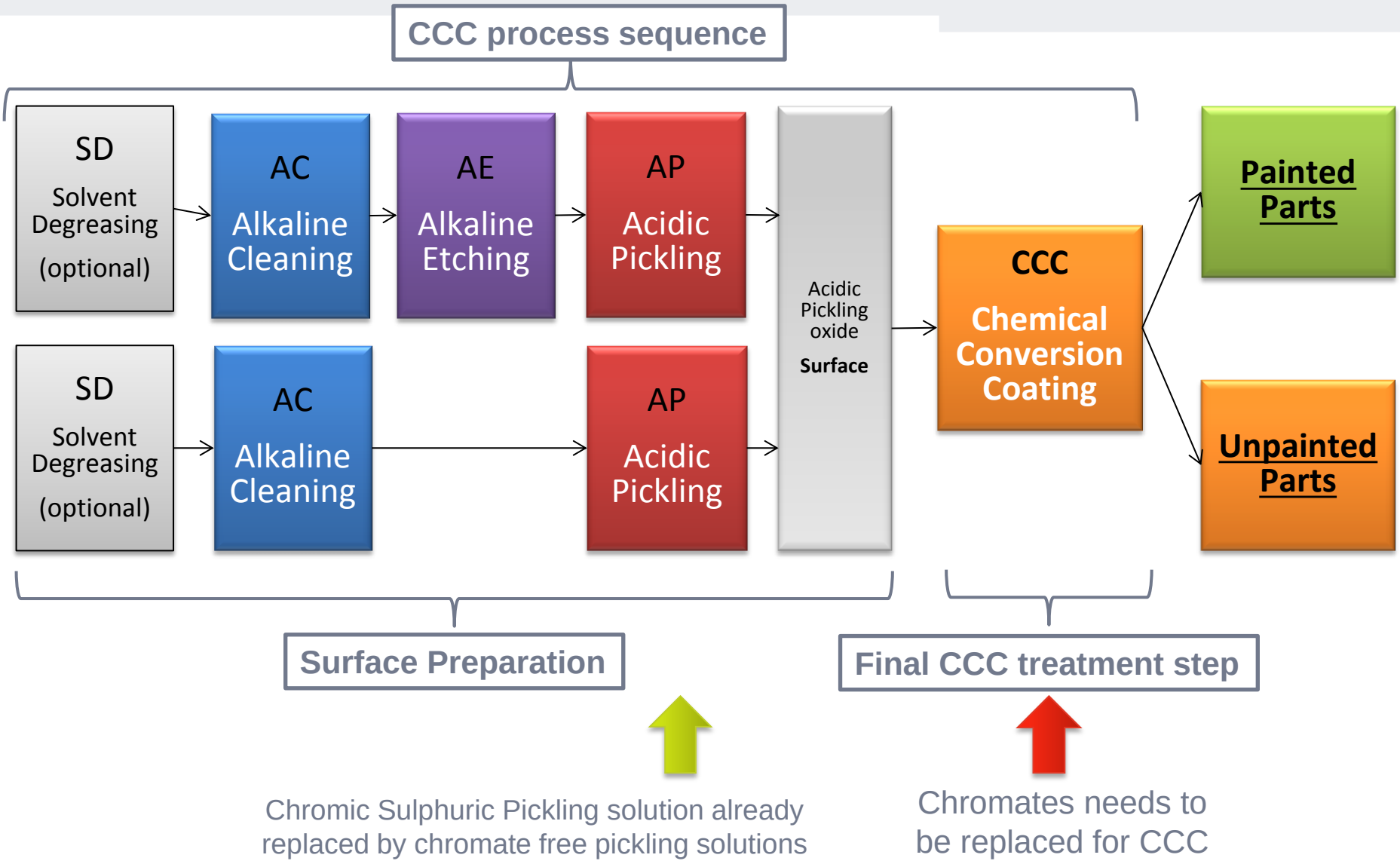
Chemical Conversion Coating Process: Pretreatment options



Chromic Sulphuric Pickling solution already replaced by chromate free pickling solutions

Chromates needs to be replaced for CCC

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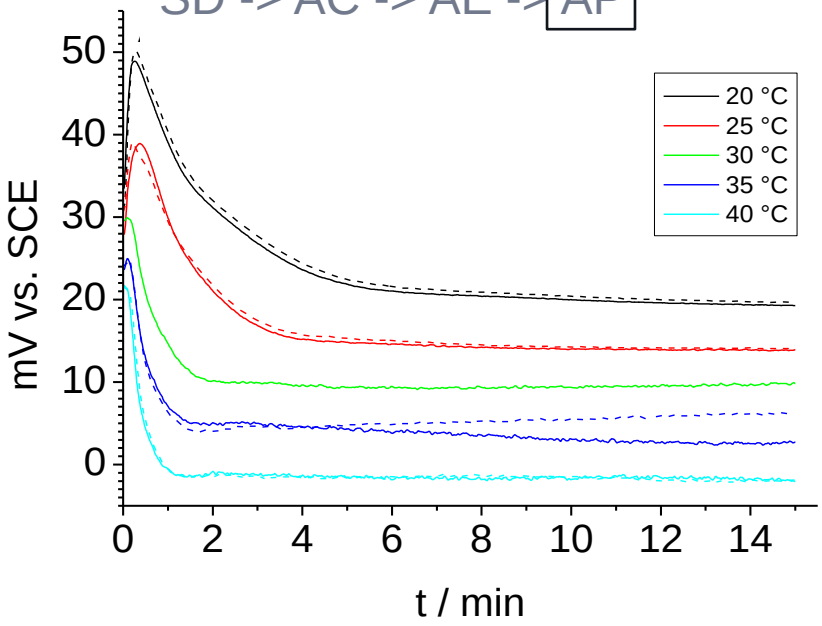
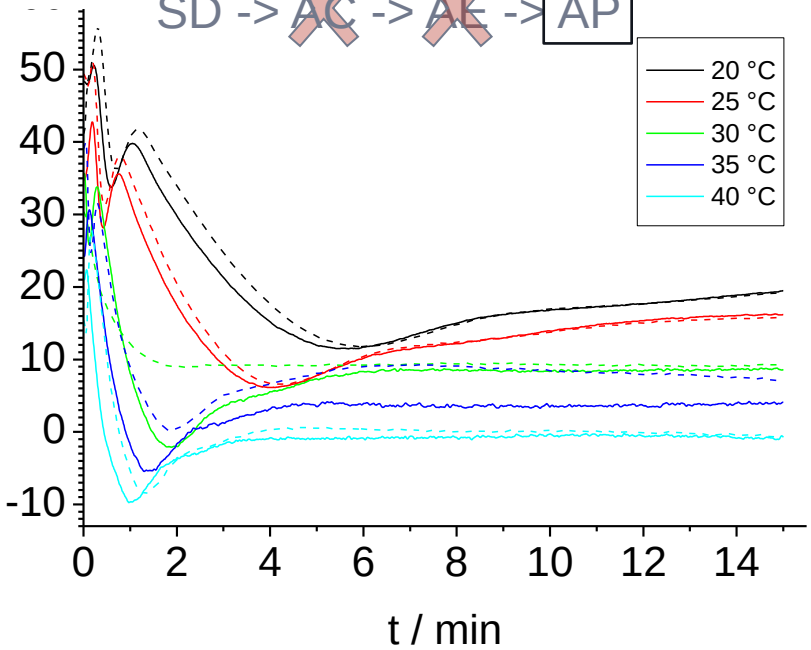
Alloy influence, monitoring of oxide / MDL removal in surface treatment

Open Circuit Potential (OCP) measurements in [F^-, $Fe^{2+/3+}$, HNO_3] based Acidic Pickling solution on 2024 unclad

Applied Process:
SD -> AC -> AE -> AP



Applied Process:
SD -> ~~AC~~ -> ~~AE~~ -> AP



- **For standard pre-treatment with AC and AE, Cu removal correlates with temperature to constant plateau within the specified time limits for pre-treatments**
- **In case of “soft” surface cleaning without alkaline etching, no plateau is reached within 15 minutes at 20° and 25°C in Acidic Pickling solution, indicating that the surface conditions are still dominated by residues of the rolling process**

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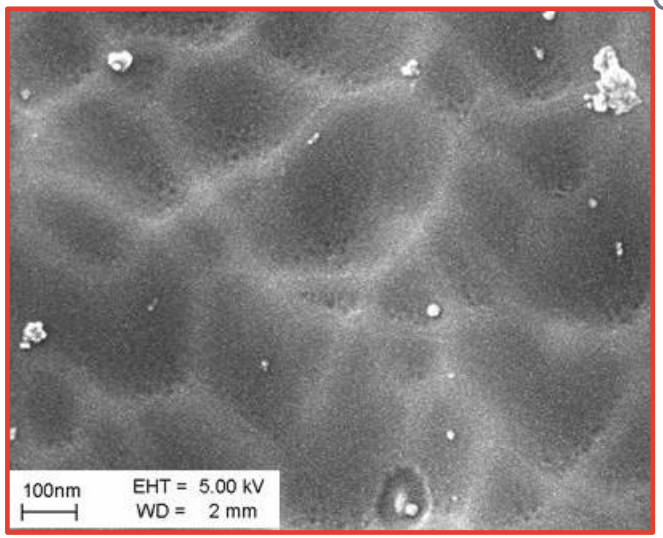
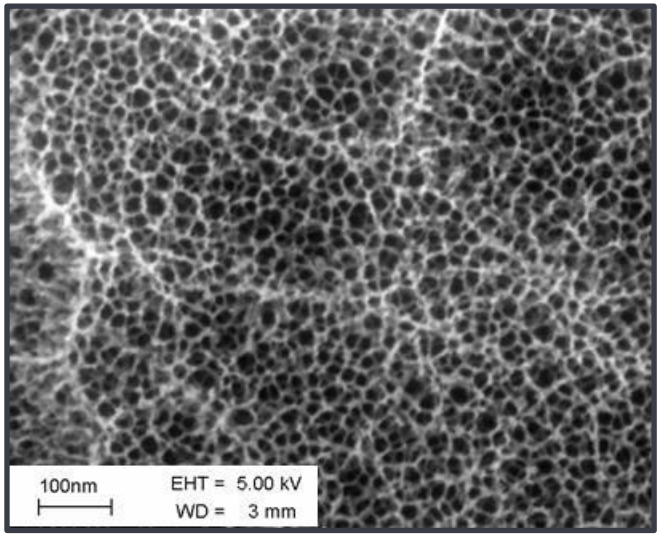
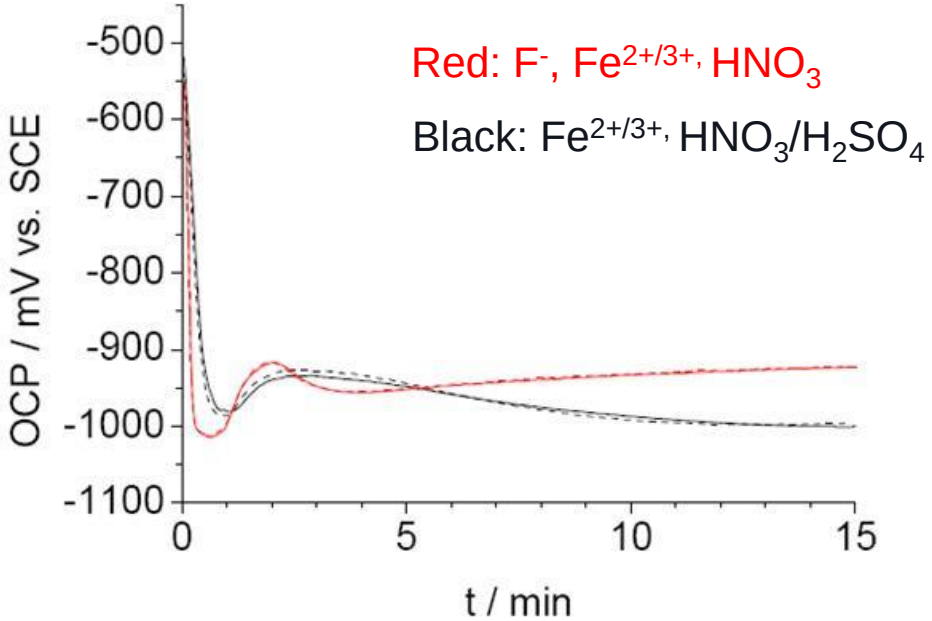
Impact of acidic pickling oxide on the CCC process





OCP of Surtec 650 after 10 min acidic pickling in two solutions



168h SST result after 2 min treatment time

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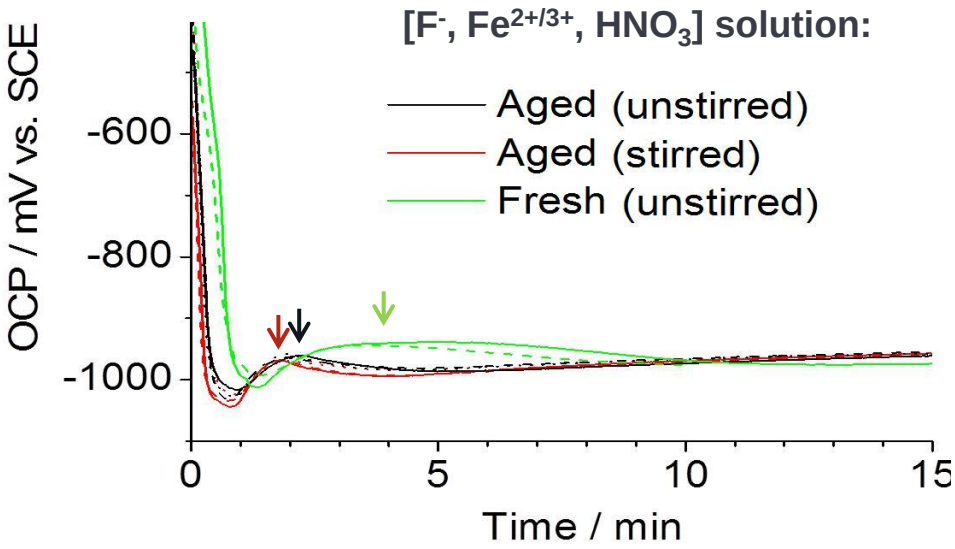
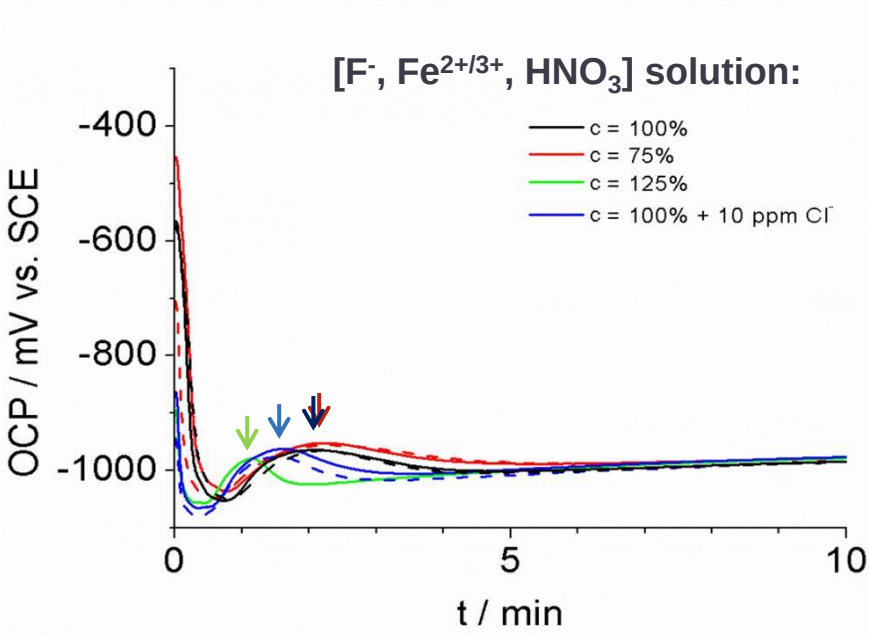
Pickling Oxide: [F^-, $Fe^{2+/3+}$, HNO_3] etching solution

OCP measured in CrIII CCC solution, Surtec ChromitAl 650 after 10 min acidic pickling in different [F^-, $Fe^{2+/3+}$, HNO_3] solutions





- **Conditions of [F^-, $Fe^{2+/3+}$, HNO_3] Acidic Pickling solution are leading to a strong impact on the CCC process.**
- **No stable CCC parameter window**
  - **Difficult to operate the CCC process on its optimum in relation to existing requirements!**

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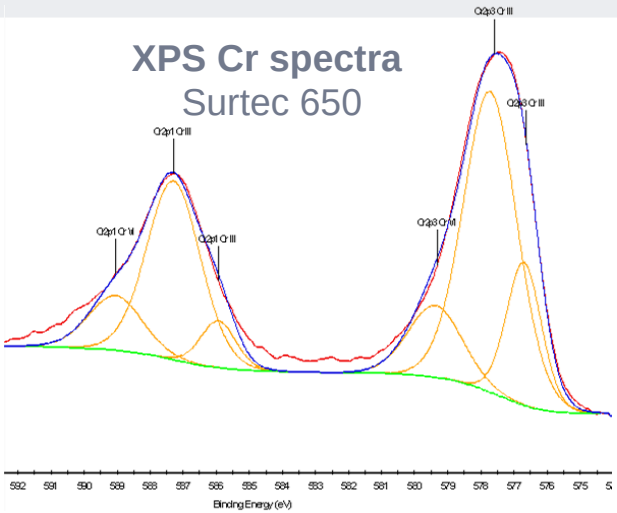
CrIII/Zr plus PACS post treatment for performance improvement

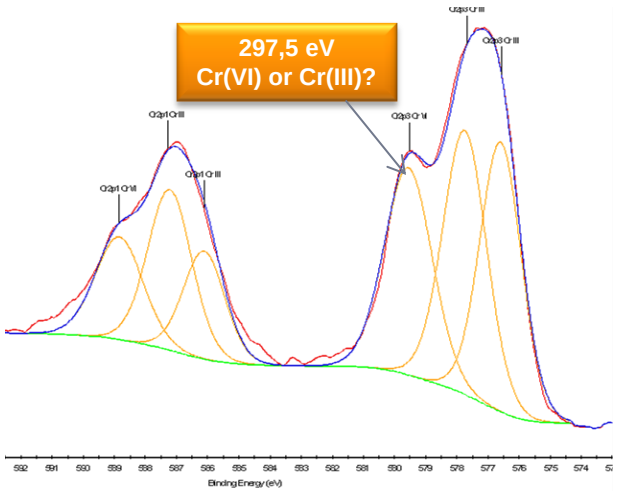
Substrate	Surtec 650		Socomore TCS		Somomore PACS sealing		SST white pits	SST white pits / sample	Average pits per dm^2 per parameter
	Temp.	Time	Temp.	Time	Temp.	Time	48h	168h	168h
2024 uc	23	2					OK	14; 6; 2	6,1
	23	4					OK	13; 21; 22	15,6
	23	6					OK	0; 0; 0	0,0
2024 uc			23	2			OK	9; 15; 18	11,7
			23	4			OK	12; 6; 19	10,3
			23	6			OK	55; 24; 26	29,2
2024 uc			23	2	23	5 min	OK	0; 0; 0	0,0
			23	4	23	5 min	OK	0; 0; 0	0,0
			23	6	23	5 min	OK	0; 0; 0	0,0
2024 uc	23	2			23	5 min	OK	0; 0; 0	0,0
	23	4			23	5 min	OK	1; 0; 0	0,3
	23	6			23	5 min	OK	0; 0; 0	0,0

* „white pit“: start of visible appearance of white corrosion products

XPS Cr spectra
Surtec 650



XPS Cr spectra
Surtec 650 + PACS



- Socomore PACS post treatment is leading to a significant performance improvement in SST
- Generation of potential CrVI species in the coating (location?) and CrVI in the bath / rinsing tank needs to be assessed, in relation to ESH and REACH compliance

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Summary chromate free pre-treatment of aluminium alloys

Chromate containing processes / product

CrVI process replaced

Close to qualification

Degreasing → Alkaline Treatments → Acidic Treatments

- TSA Anodising → Painted / Paint Primer; Sealing, unpainted
- PSA Anodising → Bonding Primer
- Chemical Conversion Coating → Painted / Paint Primer; PT → Un-painted
- Wash Primer → Painted / Paint Primer
- Other processes → DPI Welding: LBW, FSW; Chemical milling

- Replacements for Chromic Sulphuric Acid based pickling processes are qualified and introduced
- In relation to requirements CAA anodising process is replaced by TSA or PSA
- Chromate free treatment solutions are available as CrVI CCC replacement
- Replacements of chromate based paint products are still a hard challenge to meet the technical requirements

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