HARD CHROME: CONVENTIONAL AND TRIVALENT CHROME PLATING

06/08/2021 | Teams | Replacement of hard chrome : panorama of some candidate technologies

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HARD CHROME: CONVENTIONAL AND TRIVALENT CHROME PLATING

- Summary :
  - Brief IRT M2P presentation
  - General context of hard chrome plating
  - Focus on trivalent chromium developments
  - Conclusions

IRT M2P Presentation

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- Missions
  - Accelerating innovation and growth for industrial companies
  - Developing key technologies, shared amongst major industrial sectors
  - Providing technological platforms to industries
    - ➔ R&D Services
    - ➔ Multi-partners projects with Public-Private co-funding
    - ➔ Training

- Specificities
  - Technological offers driven by Industry
  - Public funds (*PIA*) dedicated to private/public partnership with balanced co-funding
  - Partners involved in project completion (staff provision, sub-contracting)

Key markets

Technology Readiness Level

Ideas ➔ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | ➔ Products

ACADEMICS	IRT M2P	INDUSTRIES
Upstream Research	Facilitate and speed up technological transfer	Experimental development

IRT M2P Innovation gateway

IRT M2P : LOCALIZATIONS AND SURFACE TREATMENT

IRT M2P PRESENTATION

- 4 sites (in Lorraine and Alsace, in the East of France) :
  - Metz (Life Cycle Assessment, Elaboration, Heat treatments, Forge, Mechanical ST, Thermochemical ST, Superficial HT, joining)
  - Uckange (Fusion and recycling, powders atomisation)
  - Porcelette (Composites)
  - Duppigheim (Electrolytic ST)

- Electrolytic Surface Treatments :
  - Anodization (Al, Ti)
  - Micro-arc oxidation (Al, Ti, Mg)
  - Chemical conversion (Al, Ti, Mg)
  - Chemical and electrochemical coatings (Hard Cr, Ni, Zn/Ni, Zn/Fe
  - Chemical and electrochemical polishing (for additive manufacturing parts)
  - Painting application
  - Anaphorese and electrophorese coatings

General context of hard chrome plating

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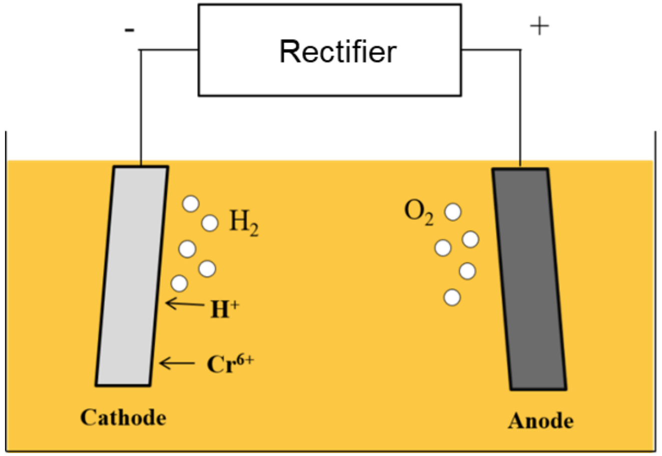
HARD CHROME PLATING: GENERALITIES

GENERAL CONTEXT OF HARD CHROME PLATING

- Hard chrome plating is today made from hexavalent chromium and use for the functional aspects of these coatings :
  - High hardness of the coatings (about 800 to 1200 Hv)
  - Wear and impact resistance
  - A low friction coefficient with good tribological properties
  - Corrosion resistance

- Hard chrome is an electrolytic process, chromium coatings are obtained by Cr salts reduction :



<u>Cathodic reactions :</u>

$Cr^{6+} + 6\ e^{-} \longrightarrow Cr^{0}$

$2H^{+} + 2\ e^{-} \longrightarrow H_{2(g)}$

<u>Anodic reactions :</u>

$2\ H_2O \longrightarrow O_{2(g)} + 4H^{+} + 4\ e^{-}$

$Cr^{3+} \longrightarrow Cr^{6+} + 3\ e^{-}$

HARD CHROME PLATING: APPLICATIONS

GENERAL CONTEXT OF HARD CHROME PLATING

- Those coatings are used in several industrials sectors, such as :
  - Automotive (shock absorber rods, brake pistons…)
  - Aeronautics (landing gear, aircraft door hook, brake discs…)
  - Defence (gun tube interior…)
  - Railway industry (TGV tripod,
  - General industry (print cylinders, piston rods, roll milling…)

HARD CHROME PLATING: RESTRICTIONS

GENERAL CONTEXT OF HARD CHROME PLATING

- Main issue : hexavalent chromium salts used in industry are CMR (Carcinogenic, Mutagenic and Reprotoxic)

- With REACh regulation : the use of hexavalent chromium is forbidden, without authorization, in the European Union since September 2017 :

  - The current authorizations have been delivered to CTACsub consortium, which overflows chemicals suppliers (such as Atotech or MacDermid for chromic acid, compound used in chrome plating process)

  - The current authorizations have been delivered for a duration of 7 years and the use of hex chrome will be forbidden in 2024 in the EU

- Strong need to find alternatives, that led to research projects conducted at IRT M2P in order to develop a hard chrome process based on CrIII electrolytes (which are not CMR and not impacted by REACh regulations)

Focus on trivalent chromium developments

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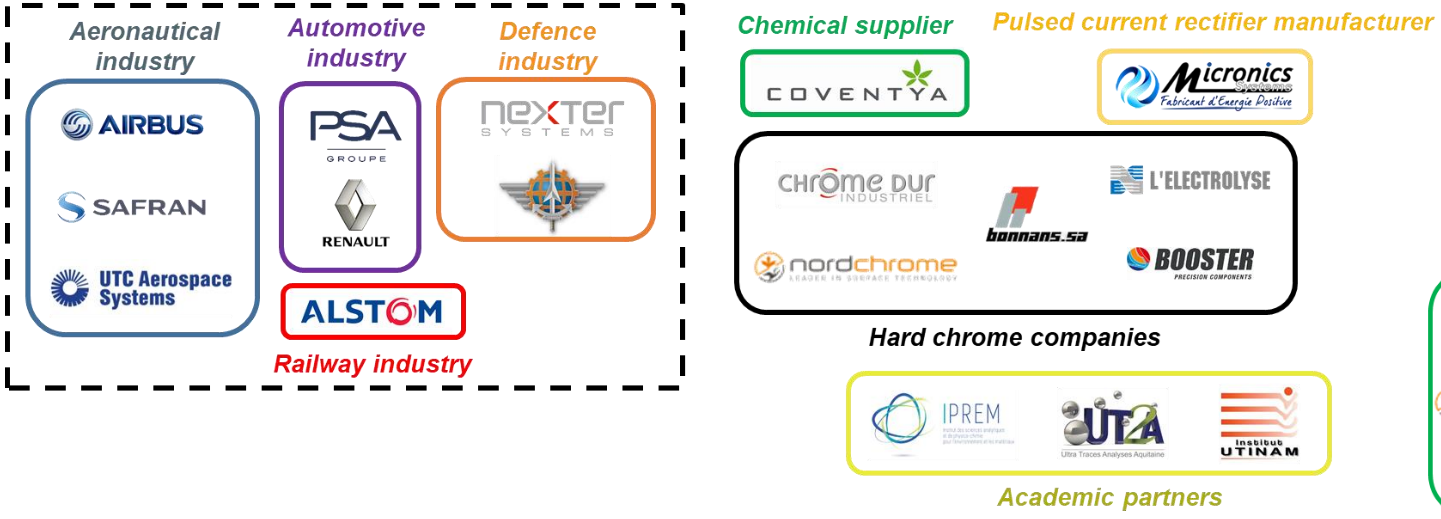
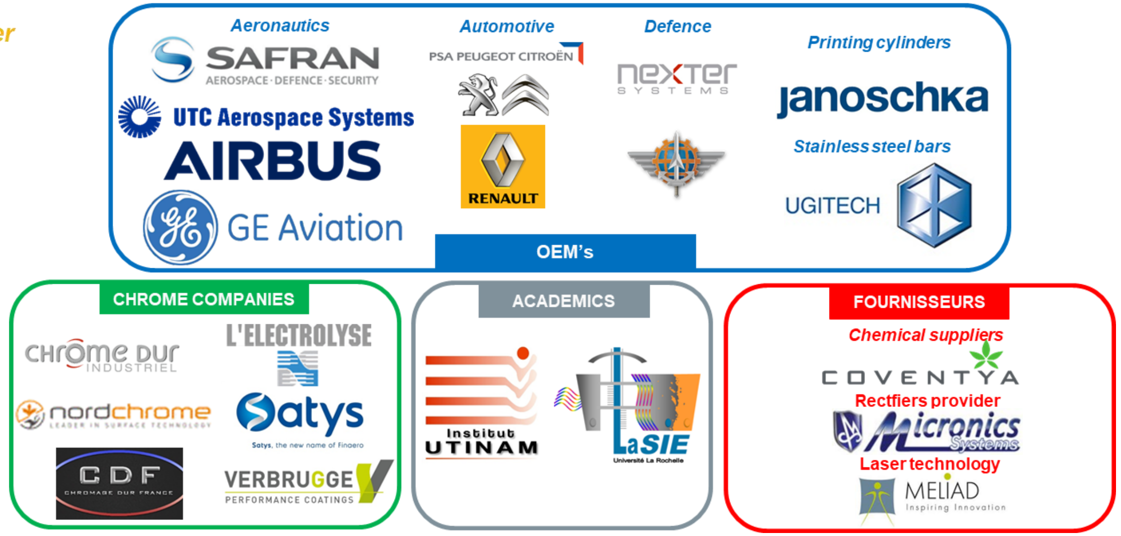
HCTC AND CRONOS PROJECTS

FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

- Two research projects are managed by IRT M2P : HCTC (2014-2018) followed by CRONOS (2018-2022) :
  - Overall budget of 7 M€ for the two projects for 8 years
  - 25 partners involved (with 21 industrial partners, OEM's, SME and academics)
  - 4 PhDs conducted, two for each project
  - Development of the trivalent chromium electrolyte patented by Coventya : DURATRI 240



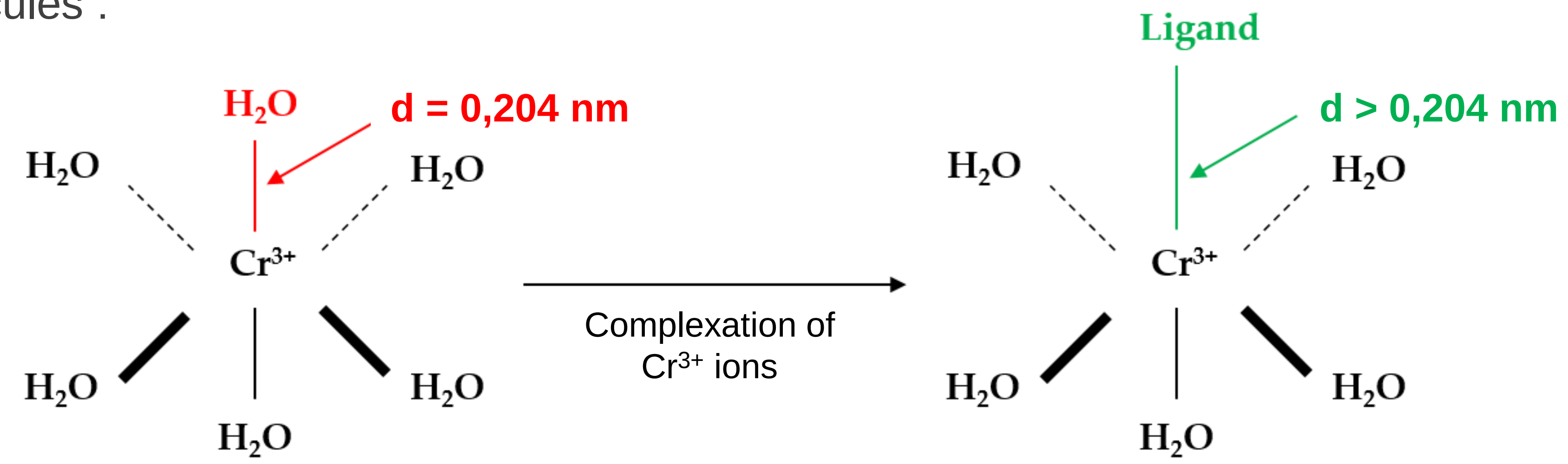
HCTC consortium



CRONOS consortium

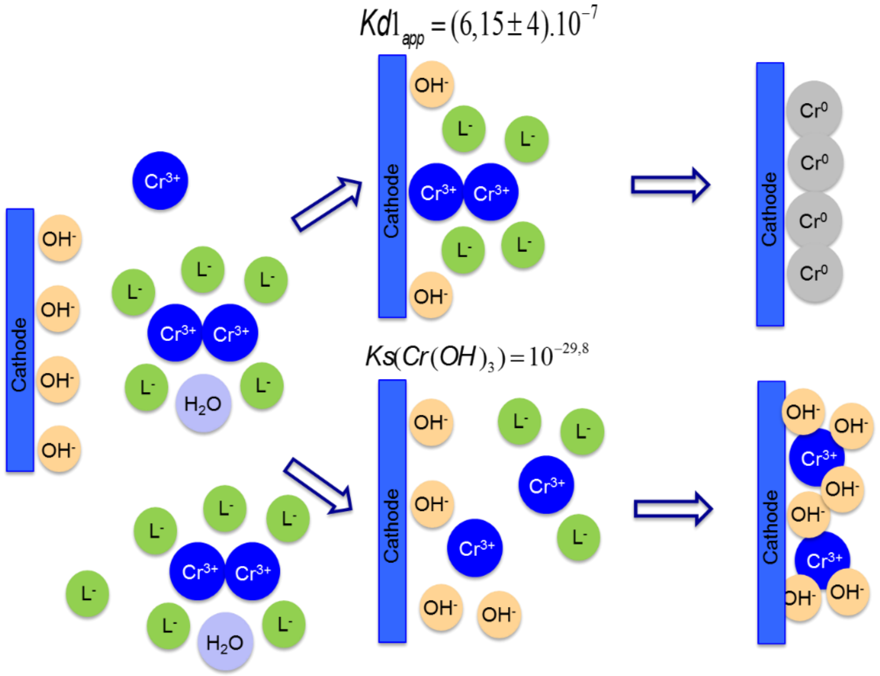
TRIVALENT CHROMIUM REDUCTION
FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

- Trivalent chromium in very stable in aqueous solution :
  - Necessary to complex trivalent chromium ions in order to obtain a chromium coating
  - This chromium complexation is generally made with organic compounds which will replace one or several H_2O molecules :



- The complexation of the Cr^{3+} ions by organic ligand leads also to the co-deposition of carbon in the coatings made from trivalent chromium electrolytes
- This is a major difference compared to hex chromium based coatings

- Due to the characteristics of the chemistry of the bath, two different scenario occur near the cathode interface during the reduction process :



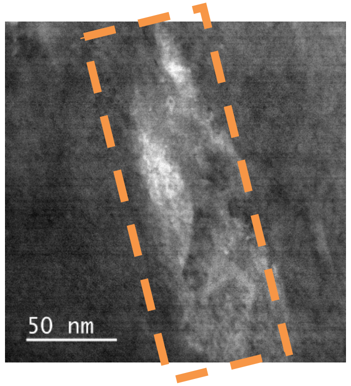
Competition between the steps of **decomplexation** et de **precipitation** of Cr III ions.

→ This competition is necessary in order to obtain metallic chromium coating.

- The Cr coating will contain carbon and oxygen in addition to chromium. These elements will have an impact on the properties of the obtained coatings

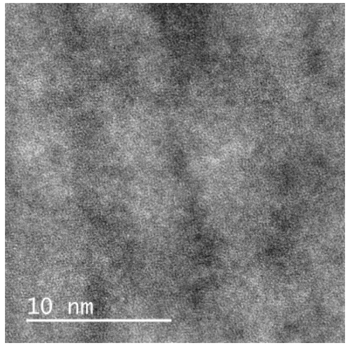
- The presence of carbon in the coatings play a role on the crystalline structure

CrVI coating (**< 0.5 %wt.)**



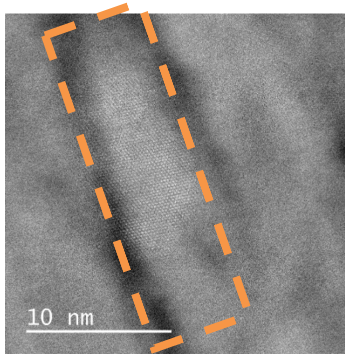
Crystallites size :
50 x 150nm

CrIII coating **(10 %wt.)**

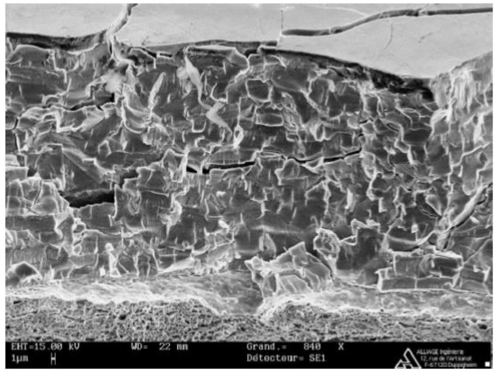


No chromium crystallites observed
→ Amorphous structure

CrIII coating **(3-4 %wt.)**

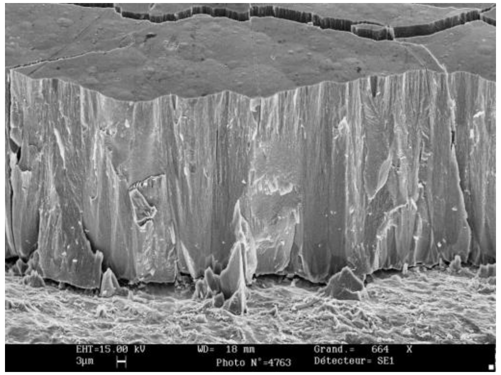


Crystallites size :
10 x 30nm



Ductile structure of reference chromium coatings

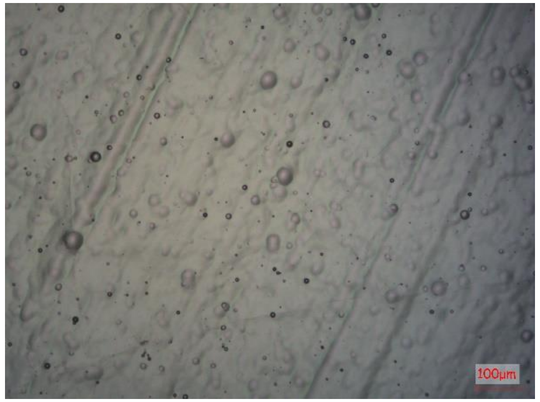
Carbon content seems to be responsible for the brittle structure of the CrIII coatings compared to hex chromium coatings



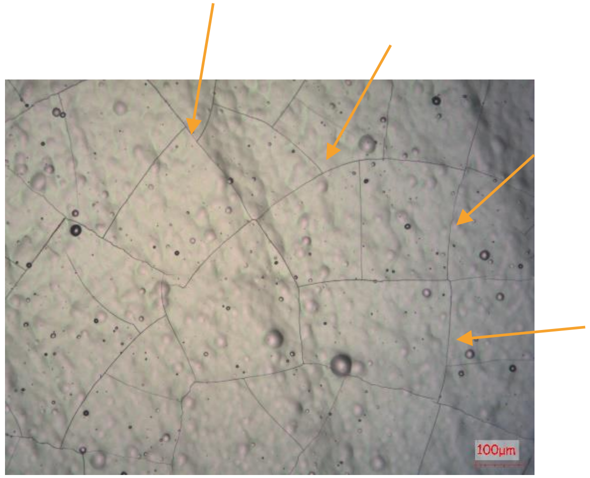
Brittle structure of CrIII coatings

INFLUENCE OF OXYGEN
FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

- The presence of oxygen in the coatings influence the coating cracks



As plated deposit: no crack observed



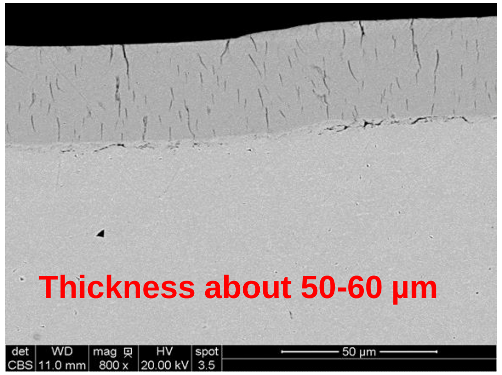
Emergence of cracks after few days out of the bath

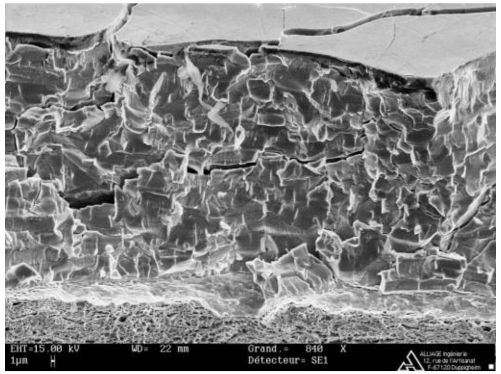
  - Oxygen, which is present as hydrated oxides and/or hydroxides, goes to dehydration phenomenon and will create some mechanical stresses in the coating

  - The brittle structure of CrIII-based coatings, compared to hex-chromium reference coatings, with the dehydration of the chromium hydroxides is probably responsible of the through cracks observed

COMPARISON OF CHROMIUM COATINGS PROPERTIES
FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

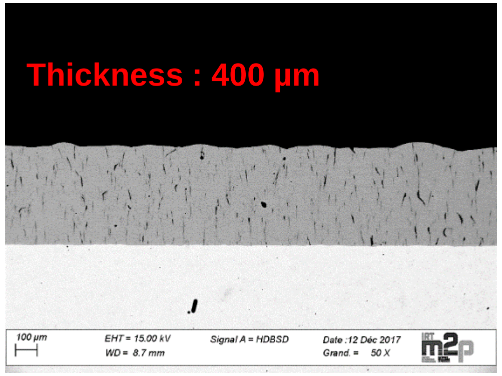
- Deposits obtained from hex chromium salts :

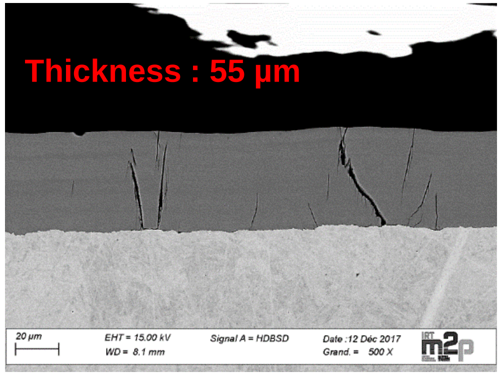


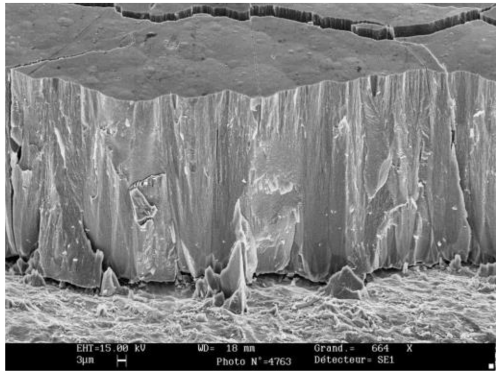


- ➢ Coatings are more « ductile »
- ➢ Microcracks networks
- ➢ Almost only chromium in the coating, no impurities

- Coatings obtained from trivalent chromium electrolytes :







- ➢ Coatings are more « brittle »
- ➢ Through cracks in the coatings
- ➢ Carbon and oxygen are trapped in the coatings

COMPARISON OF CHROMIUM COATINGS PROPERTIES

FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

Properties	CrVI based coatings	CrIII based coatings	Comments
Plating rates	10 to 60 µm/h	5 to 70 µm/h	*Depending on geometry of the parts and current density*
Hardness	800 - 1200 Hv	750 - 1050 Hv	
Appearance	Bright	Bright or dull	
Chemical composition	Few traces of carbon and oxygen (< 1%$_{wt.}$)	About 2%$_{wt.}$ of oxygen et 2%$_{wt.}$ of carbon	
Morphology	Microcracks coatings	Through cracks and also microcracks. The cracks are wider	
Crystalline structure	Crystallized, centered cubic structure	Amorphous or nano-crystallized	
Temperature effect	Decrease the coating hardness	Increasing of the hardness, cracks become wider	
Fatigue resistance	Endurance limit of about 400 MPa at 10^7 cycles	Endurance limit similar or superior to CrVI	*Made by rotary bending*
Taber Wear resistance	WI between 1 et 2	Similar to CrVI	
Adhesion (on steel)	Excellent	Inferior to CrVI, but same with an underlayer (Ni, Cu…). Depend on also on the performed tests	*Adhesion is similar on stainless steels, coppers or nickel alloys*
Corrosion resistance	Low as plated	Very low without an underlayer	*Evaluated by NSST*
Hydrogen embrittlement	About 0,25%$_{wt.}$ as plated, 85% is removed after heating	About 1%$_{wt.}$ as plated, 85% removed after heating	*Traction tests have to be performed according to ASTM F519*

COMPARISON OF CHROMIUM COATINGS PROPERTIES
FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

- Comparison of process parameters

Parameters	Current Cr VI Electrolyte	DURATRI 240 electrolyte (Cr III)
Chromium concentration	125 g/L	20 g/L
Complexing agent	-	400 - 700 g/L
Wetting agent	According to the baths	Not necessary
pH	< 1	4.5 – 5.5
Bath temperature	40 - 65°C	30 - 60°C
Current density	20 - 90 A/dm^2	20 - 70 A/dm^2
Anodes	Lead - Steel	Graphite - Stainless steel - Ti+ MMO
Agitation of bath	Venturi - air	Venturi
Health, Safety and Environment		 No CMR compounds

EXAMPLE OF INDUSTRIAL APPLICATIONS: AIRPLANE DOOR HOOKS

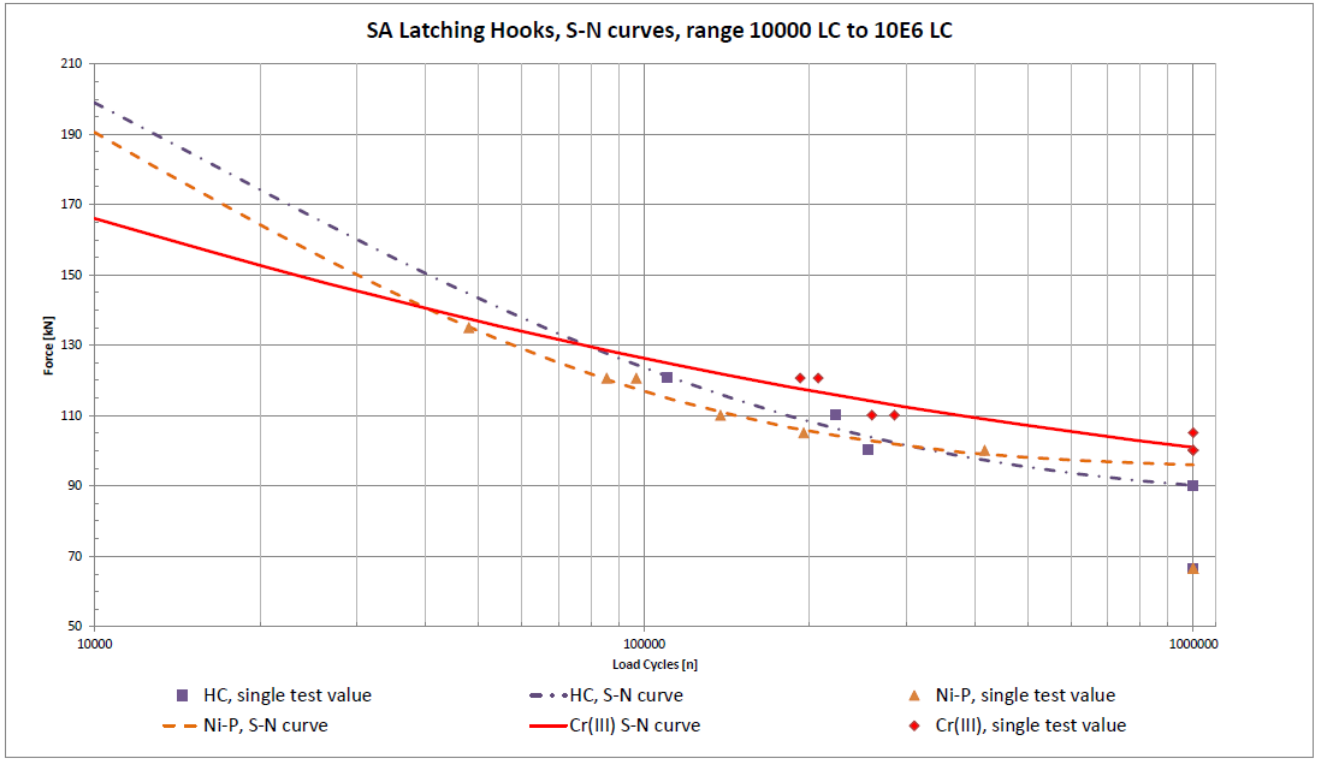
FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

- In the project, an important work related to the treatment of airplane door hooks was performed
- Those hooks (in 15-5 PH stainless steel) with coating requirements :
  - Thickness of 30 µm
  - Surface preparation with a nickel strike underlayer
  - Heating of the coating after plating of 23 hours at 190°C

EXAMPLE OF INDUSTRIAL APPLICATIONS : AIRPLANE DOOR HOOKS

FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

- All the plated hooks were tested on specific fatigue bench by Airbus :
  - Four different loads were applied from 66 to 120 kN
  - The tests were performed until the break of the hook or 10^6 cycles

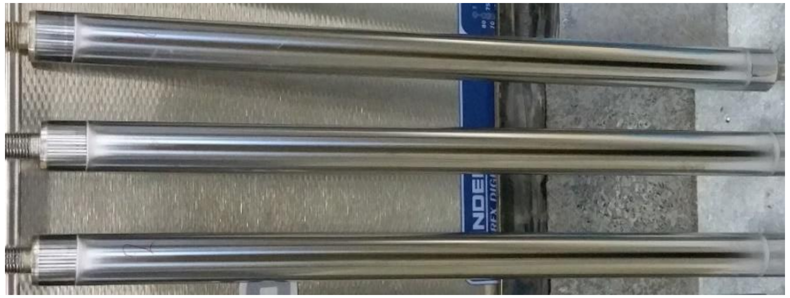


  - The fatigue resistance of the hooks is better with trivalent chromium compared to hex chrome reference of chemical Ni

EXAMPLE OF INDUSTRIAL APPLICATIONS : SHOCK ABSORBER RODS

FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

- Many test campaigns were performed (with different suppliers of automotive OEM's of the project) on shock absorber rods :



- Thickness of 15 à 20 µm
- With or without nickel underlayer

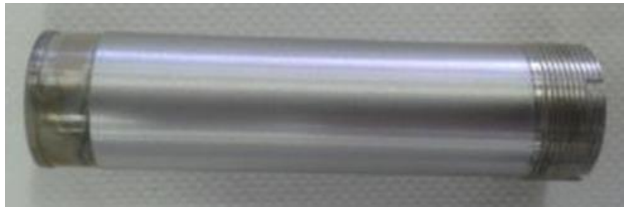
Properties	Requirements conformity
Hardness	**Compliant**
Adhesion	**Compliant**
Kinetic	**Compliant**
Corrosion	**Compliant with and without nickel underlayer**
Cracks	**Low limit of compliancy**
Roughness	**Low limit of no compliance (R_z)**
Oil leakage	First campaign wasn't successful due to roughness values. Second campaign planned in second semester of 2021 with a conform roughness after plating.
Endurance tests	

EXAMPLE OF INDUSTRIAL APPLICATIONS : OTHER PARTS
FOCUS ON TRIVALENT CHROMIUM DEVELOPMENTS

- Many other parts have been plated in the project. Some of the characterization results are still under progress, with some delays due to Covid crisis

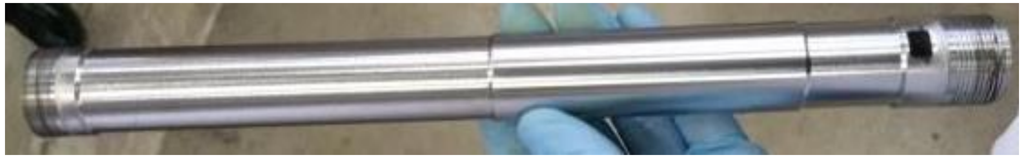
Printing cylinders

Valve body



Shears blade

Piston



Piston rings

- Plated materials in the projects:

Material	Alloys
Steels	**15CDV6**, 32CDV13, 35NCD16, 20MnV6, 55NCDV7, 18MnV6, 25CD4, 34NCD6 XC42, XC48, **C40**, X13VD 300M, 4340
Stainless steels	15-5-PH, **316L**, 1.4057, 1.4462, 1.4307, Z12CDNV12
Others	Brass, copper, Inconel 718, Cast iron

Conclusions

CONCLUSIONS AND FUTURE WORKS

- The trivalent chromium process is still under industrialization in order to evaluate the robustness of the process.

- Today, in the project, there are 5 industrial tanks (250 to 800 liters) which produce plated parts and important results to better understand this new process.

- Some characterizations on test bench are ongoing and some other will be performed in the next months on other parts.

- The research and development works are still ongoing, especially on the chemistry of the bath and some process parameters (pulsed currents, anodes…) in order to increase the properties of the coatings, to be closer of the reference coating performances

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9 EXPERTISES MATÉRIAUX & PROCÉDÉS

- POUDRES MÉTALLIQUES
- FONDERIE AVANCÉE
- ANALYSE DU CYCLE DE VIE & RECYCLAGE
- TRAITEMENTS DE SURFACE MÉCANIQUES
- TRAITEMENTS & REVÊTEMENTS DE SURFACE
- TRAITEMENTS THERMIQUES & THERMOCHIMIQUES
- MATÉRIAUX COMPOSITES
- ASSEMBLAGES MULTI-MATÉRIAUX
- ANALYSES & CARACTÉRISATION

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