

Chrome Plating from Cr(III) in Ionic Liquids

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OUTLINE

I - Generalities on Hard Chromium Plating (CrVI)

Alternative processes: Market, Processes, Programmes

II – RESULTS during IONMET programme

1 - Objectives

2 - Experimentations

3 - Results

- Adhesion : Pretreatment, Increasing adhesion :
Nickel, Organic additives

- Hardness, Structure

4 - Composite deposits :

- Experimentations, structure

III - Conclusions

HARD CHROMIUM PLATING

- Aqueous solutions of Cr(VI) compounds :
 - CrO_3 : 250 à 350 g/L
 - Catalyseurs : Sulphate, SiF_6 , Organo-sulfonates
 - Temperature : 50 à 60°C
- Characteristics of the Cr deposit :
 - μ hardness: 1000HV/100g
 - μ fissuration
 - Excellent adhesion to the substrate



ADVANTAGES and DRAWBACKS

HARD HEXAVALENT CHROMIUM PLATING

ADVANTAGES :

- **HARDNESS**
- **WEAR and ABRASION RESISTANCE**
- **CORROSION RESISTANCE**
- **FRICTION COEFFICIENT**
- **EASILY APPLIED**
- **ECONOMICALLY INTERESTING...**

ADVANTAGES and DRAWBACKS

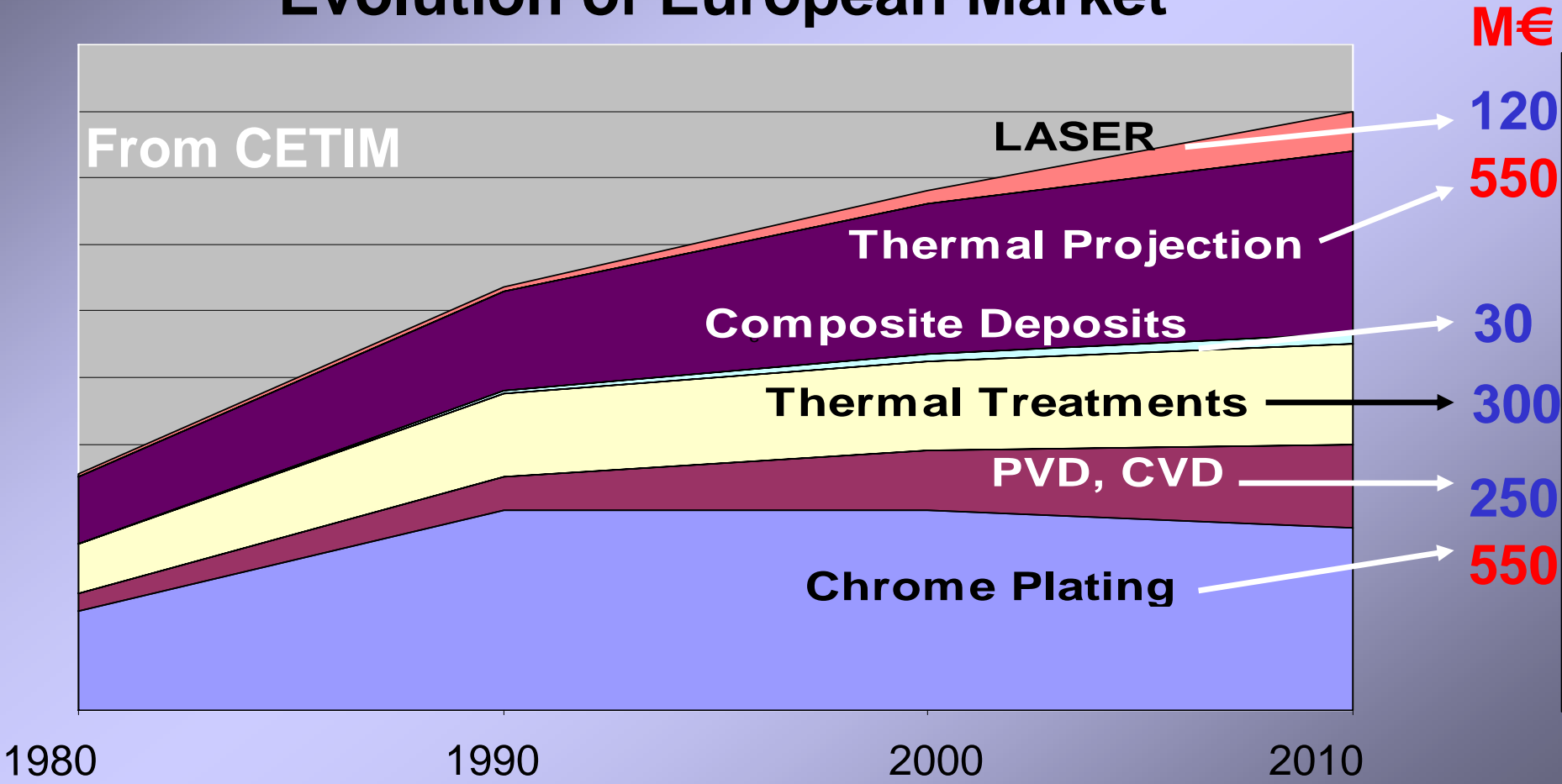
HARD HEXAVALENT CHROMIUM PLATING

DRAWBACKS :

- **IMPACT on ENVIRONMENT**
- **THROWING and COVERING POWER**
- **TECHNICAL CONSTRAINTS (gaz evolution, risk of Contamination...)**
- **CHEMICAL RISKS**
- **PROCESS SOMEWHERE HAZARDOUS**
- **REGULATION MORE and MORE DRASTIC**

ALTERNATIVE PROCESSES

Evolution of European Market



ALTERNATIVE PROCESSES

PHYSICAL PROCESSES :

- PVD-CVD,
- THERMAL PROJECTION, HVOF
- THERMAL TREATMENTS
- LASER....

CHEMICAL PROCESSES (Aqueous solution)

- ELECTROLESS,
- ELECTROCHEMICAL

PROGRAMMES

Large Programmes :

- HCAT



Hard Chromium Alternative Team

- Programme CTC



*"Providing World-Class Services for
World-Class Competitiveness"*

US Navy - Concurrent Technology Corporation (Ni, Co, particles)

- ECOCHROM : IMS (EU, USA, JAPAN, KOREA)



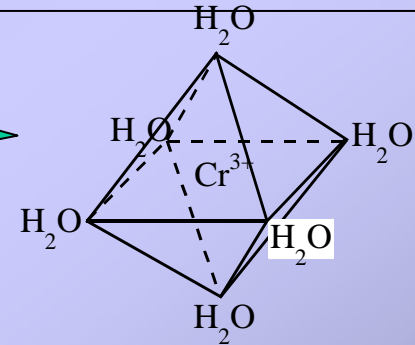
- IONMET : EU (33 partners)



ECOCHROM

PROBLEMATICS :

- High stability of $\text{Cr}^{3+}(\text{H}_2\text{O})_6$ complex
- High reduction potential ($\text{Cr}^{3+} \rightleftharpoons \text{Cr}^0 \Rightarrow \text{H}_2 \nearrow \Rightarrow \text{pH} \nearrow$)
- $\text{pH} \nearrow \Rightarrow$ formation of non-reducible compounds :
 olation, oxolation, polymerisation, hydroxides...
- Numerous compounds able to be created (>1000 – Recoura)



PROCESSES DEVELOPED in ECOCHROM

- Using trivalent chromium complex compounds
- Using trivalent chromium obtained by reduction

MAIN CHARACTERISTICS of RESULTS

- (+) Environmental
- (+) Rate, Hardness increasing with HT
- (+) Wear resistance
- (-) Chemical control of the bath
- (-) Cracks through deposits

RESULTS in IONMET

OBJECTIVE : Development of processes using IONIC LIQUIDS in Metal Finishing Industry :

Electroplating, Electropolishing, Electrorefining...

INTERESTS

- **Modification of the anodic and cathodic reaction**
- **Elimination of water reaction**
- **Green solvents and green chemistry**
- **Deposition of special metals and alloys**
- **IONIC LIQUIDS are well known**

RESULTS on HARD CHROMIUM DEPOSITION

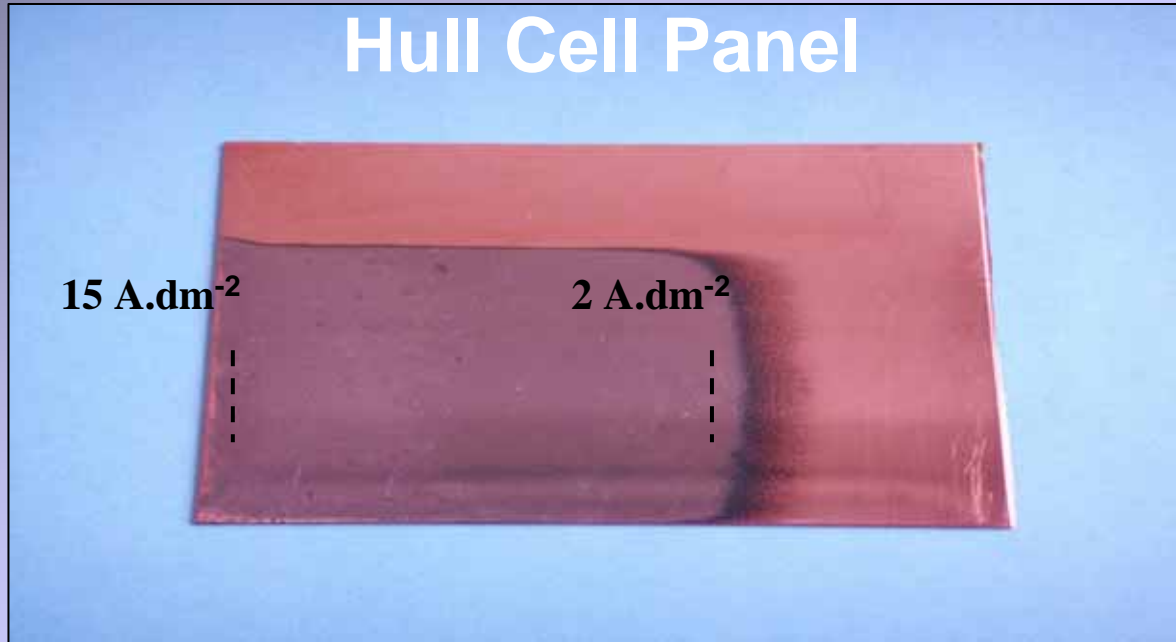
RESULTS in IONMET

Experimental conditions : thick deposits

- Composition : 1/2,5 (molar ratio)
CrCl₃,6H₂O / Choline chloride
- Substrate : cylinder XC38 steel (C35)
(7cm long, Ø1cm, S=0,2 dm²)
- T=40°C
- Conductivity : ~ 20mS.cm⁻¹ at 40°C
- Cathodic Current Density : 15 A.dm⁻²
-
- Anode : cylindrical anode in platinised titanium
grill or metal oxydes (Ir₂O₃)
- 5 L beaker with double jacket to operate
thermostatically



RESULTS in IONMET



RESULTS :

- metallic and bright homogeneous aspect
- good reproducibility
- efficiency ~ 30 – 40 %
- deposition rate ~ 0,7 μ m.min⁻¹ (15 A/dm²)
- Hardness ~ 600Hv

RESULTS in IONMET

Pre-treatment conditions

Process in 2 phases

1 - Typical pre-treatment in aqueous media :

- alkaline degreasing
- electrolytic degreasing
- anodic etching (H_2SO_4)

2 - Immersion in plating bath :

- wet, directly after phase 1
- after drying
- after sample preparation in IL

RESULTS in IONMET

Samples : Cr deposition



RESULTS in IONMET

Increasing adhesion : Pre-Nickel Deposition

XC38 with nickel under-layer

Experimental conditions for Ni under-layer :

- Ni aqueous sulfamate bath
- 2,3 A.dm⁻², T=50°C, pH=4,4
- 25 min for ~ 10µm

RESULTS in IONMET

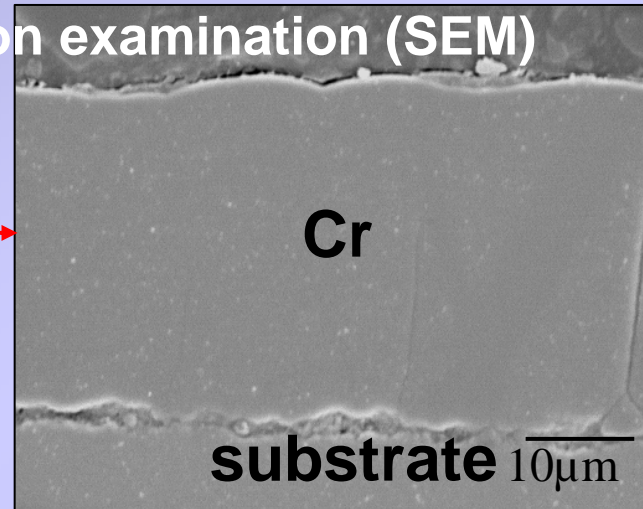
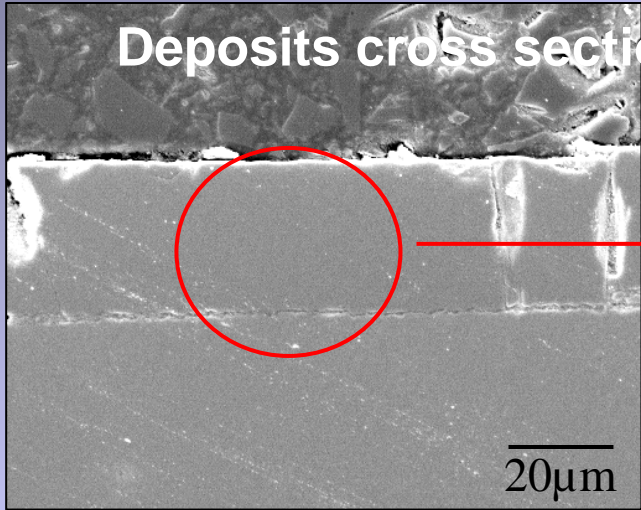
Samples (Ni + Cr)



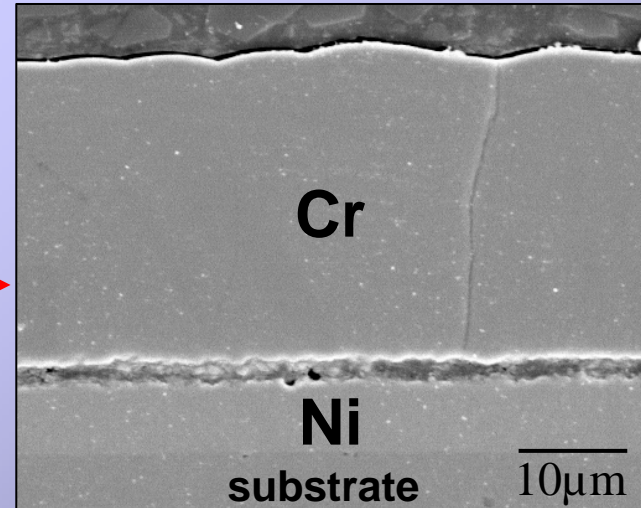
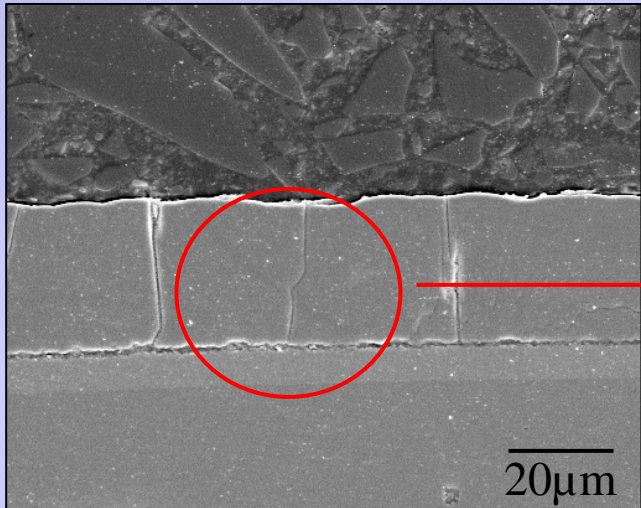
RESULTS in IONMET

Deposits cross section examination (SEM)

Without Ni



With Ni



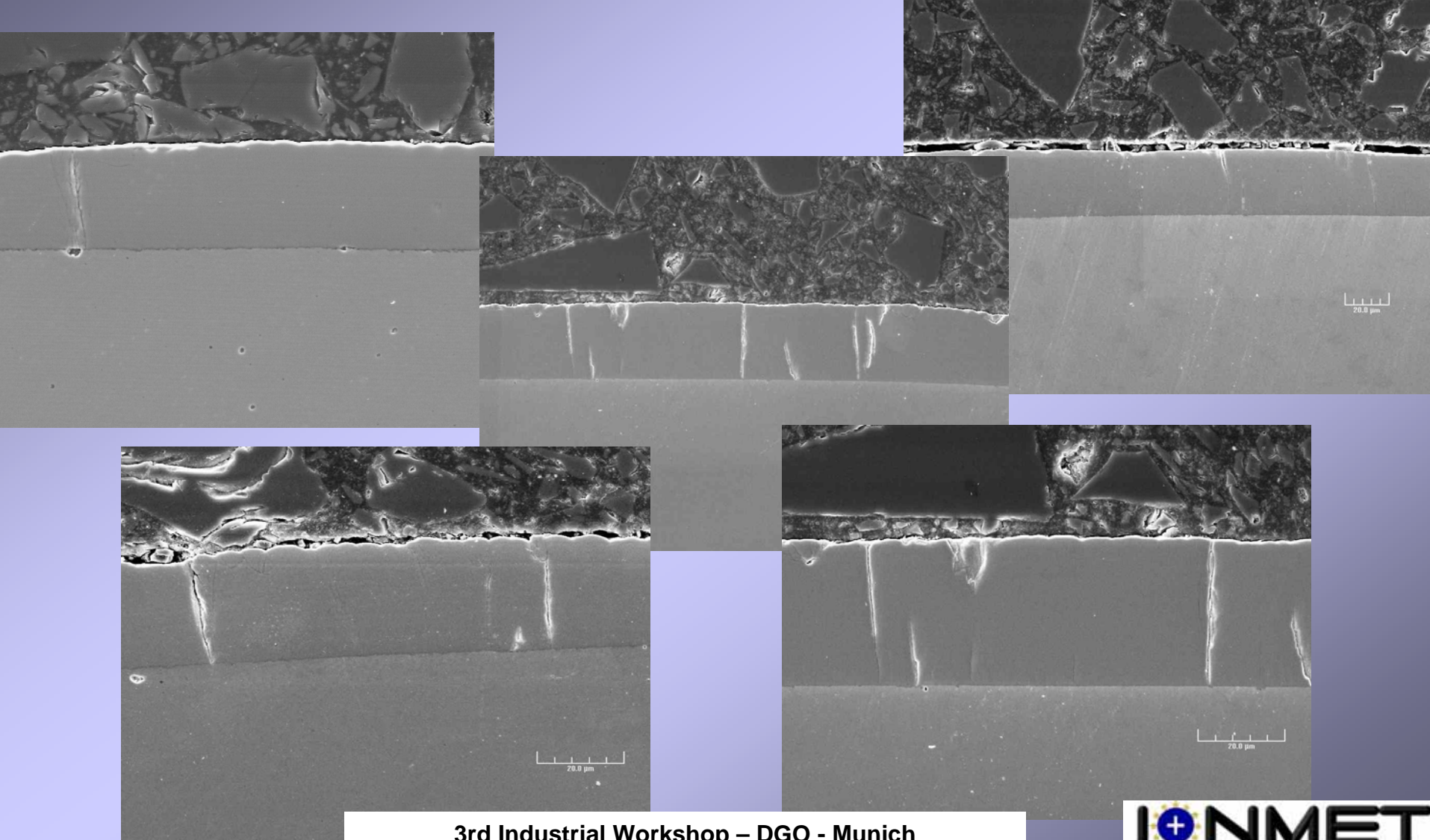
RESULTS in IONMET



Influence of organic additive

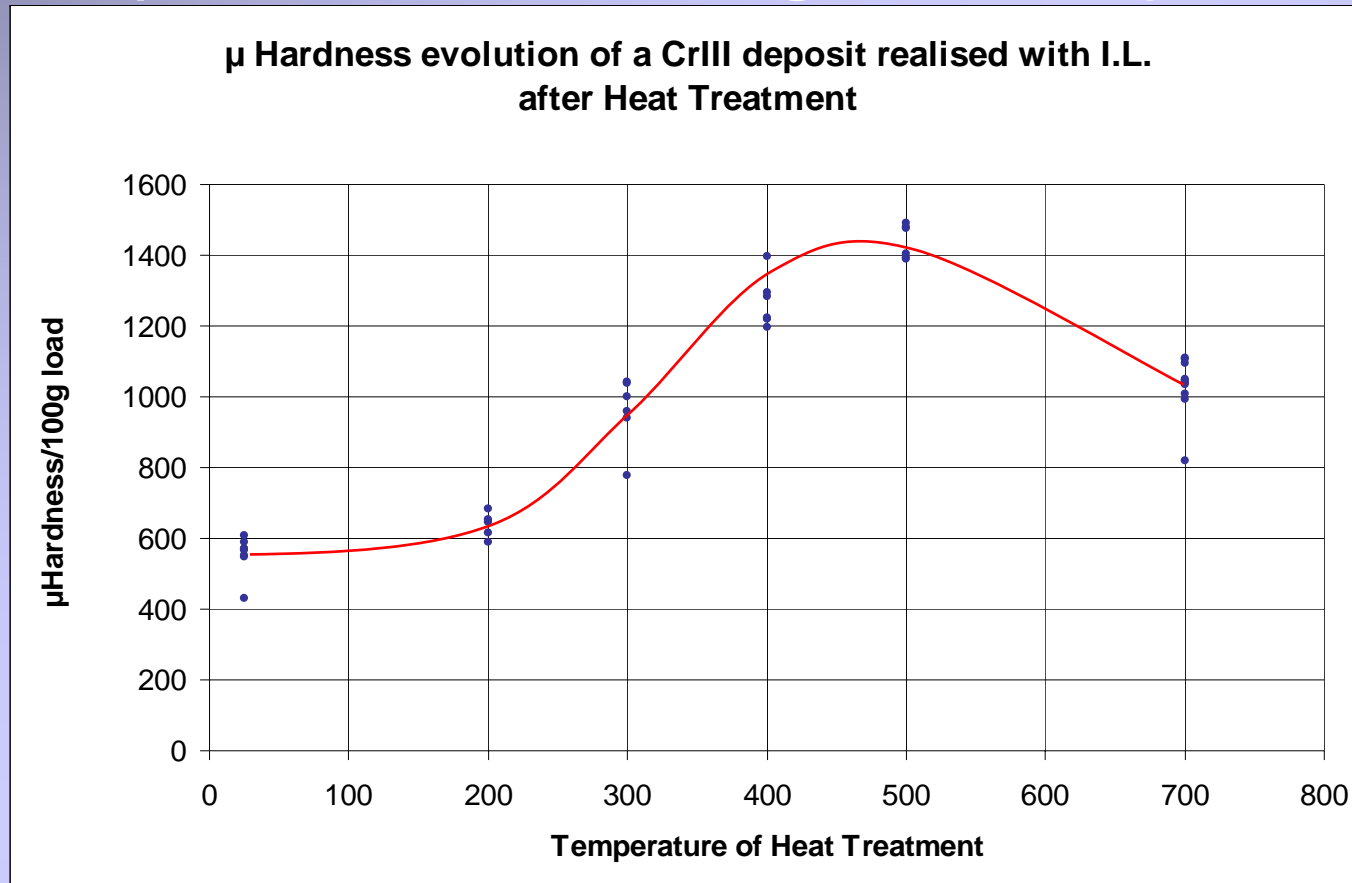
[C] Organic additive	J (A/dm ²)	T (°C)	t (min)	Cond. (mS/cm)	Thickn.	Rate of depos.	Rc
10	20	50	25	25	26	1.04	35
	25		20	23	32	1.60	43
20	20	50	25	23	27	1.1	36
	25		15	23	21	1.43	38
	25	60	40	29	28	0.71	19
40	20	50	25	23	11	0.45	15

RESULTS in IONMET

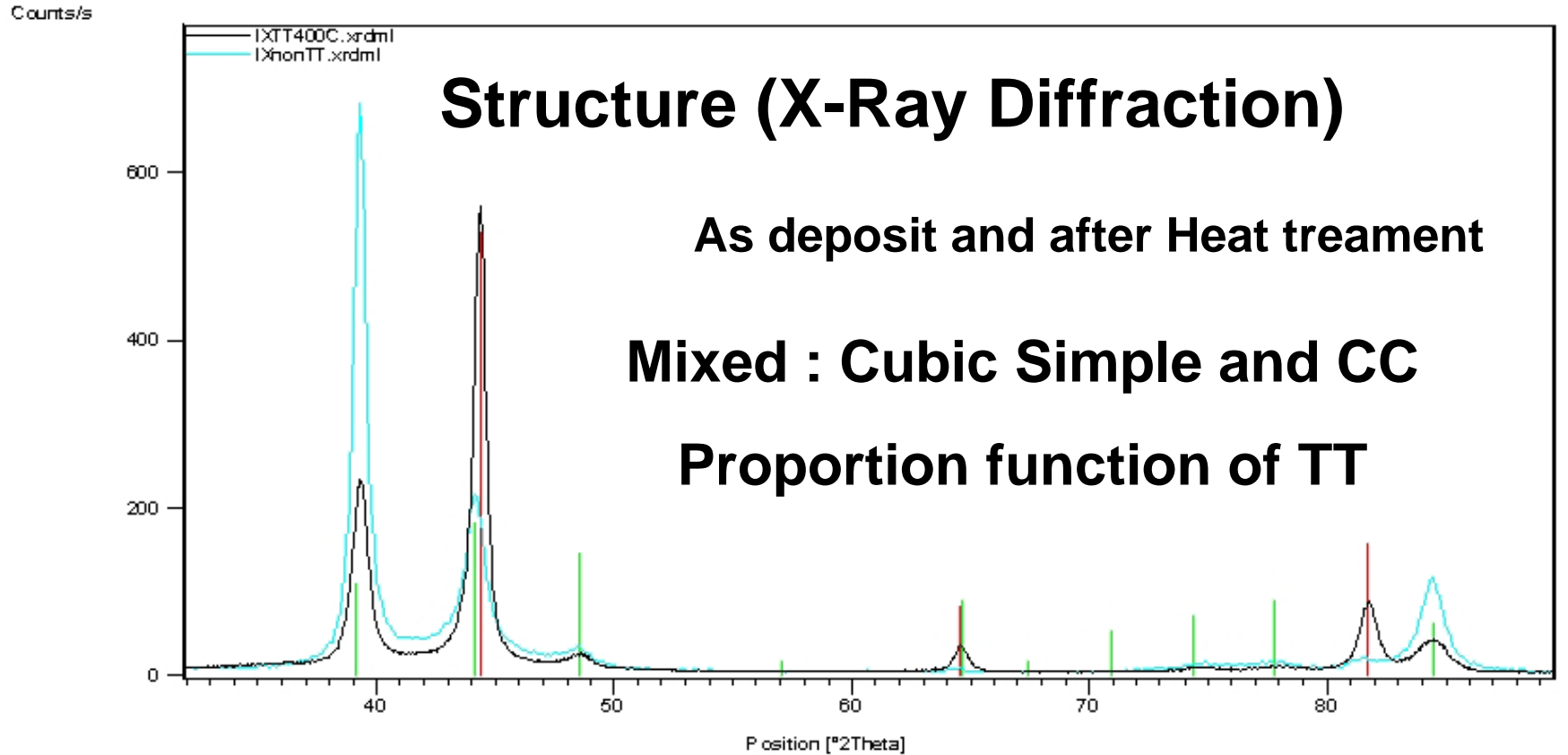


RESULTS in IONMET

Evolution of μ -hardness as a function of thermal treatment (duration 1h under Argon – 350°C)



RESULTS in IONMET



Peak List

00-006-0694; Cr

00-019-0323; Cr

RESULTS in IONMET

COMPOSITE DEPOSITS :

**Chromium + SiC or Alumina particles
(or PTFE)**

RESULTS in IONMET

Cr Composite deposit



XC 38 steel with Cr composite deposit :
Thickness of deposit : 50 - 60 μm

RESULTS in IONMET

Cr Composite deposit

- **Composition of solution, surface preparation : same as in previous experiments**
- **Nature of particles = 10 & 20 g/L, Size : 0.3 and 1 μm**
- **T= 40°C**
- **Dc : 15 A/dm²**
- **Rate of deposition : 1.2 à 1.7 $\mu\text{m}/\text{mn}$**
- **Efficiency : 35 - 40%**
- **Magnetic stirring**

RESULTS in IONMET

Cross-section of the Cr deposit with particles (SEM)

10µm



20µm



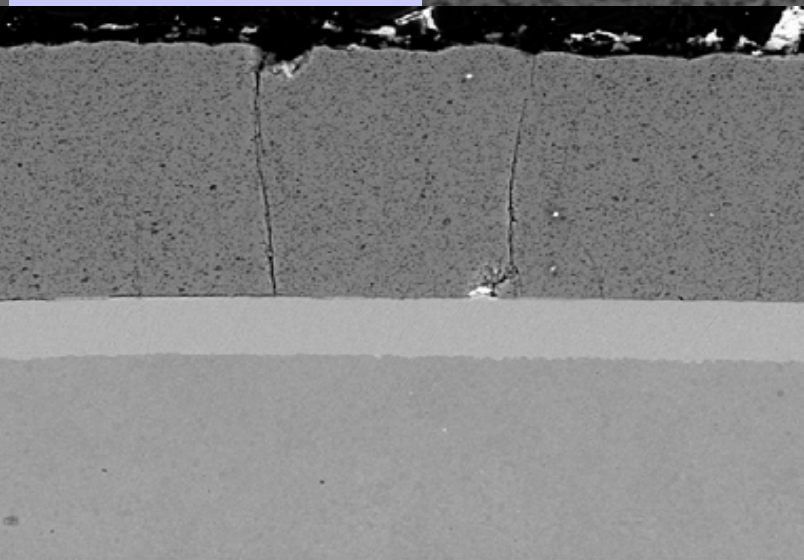
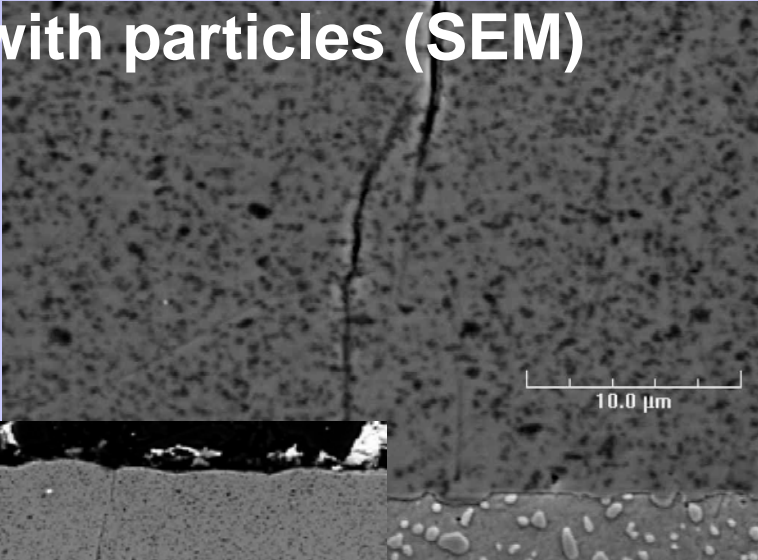
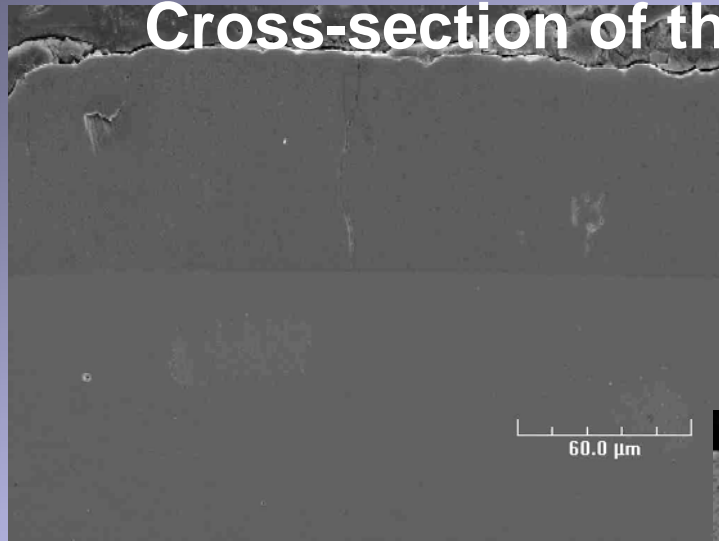
10µm



10 g/L
particles

RESULTS in IONMET

Cross-section of the Cr deposit with particles (SEM)

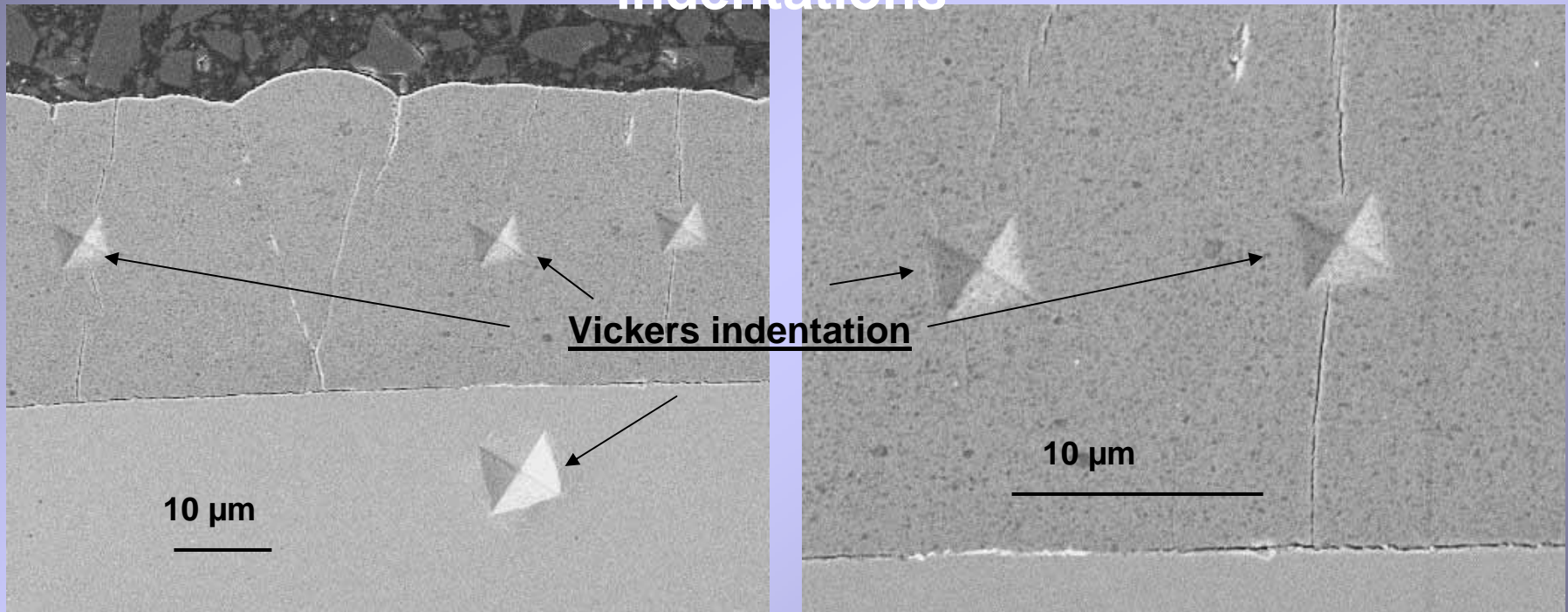


CrNi0009
non métallisé
L x1,0k 100 μm

20 g/L
particles

RESULTS in IONMET

Cross-section of Cr Composite deposit: Vickers indentations



Vickers indentations - μ -hardness : about 700 HV/100g

CONCLUSIONS

- **IONIC LIQUIDS** allow hard chromium deposition in friendly and environmentally conditions
- Hardness increases with H.T. and modification of the microstructure
- **Some characteristics have to be improved :**
 - Adhesion, but seems sufficient in some industrial applications
 - Corrosion resistance due to cracks through the deposit
- **IONIC LIQUIDS** allow deposition of Cr Composite deposit:
Hard and lubricant particles

