

Apport de la Microscopie
Electronique à la
Compréhension de la
Construction de Dépôt par
Projection.

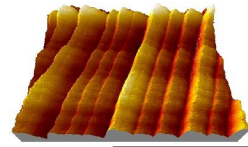
Alain DENOIRJEAN
alain.denoirjean@unilim.fr



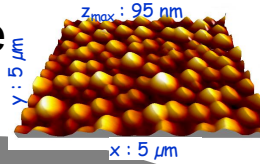
UMR 7315

European Ceramic Center : CEC (14 000 m²) for research and teaching





Procédé
sol gel

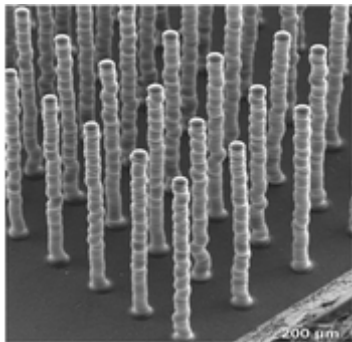


Organisation structurale
multiéchelle des matériaux

Resp. : philippe.thomas@unilim.fr

SPCTS

Procédé
Injection
jet d'encre
céramique



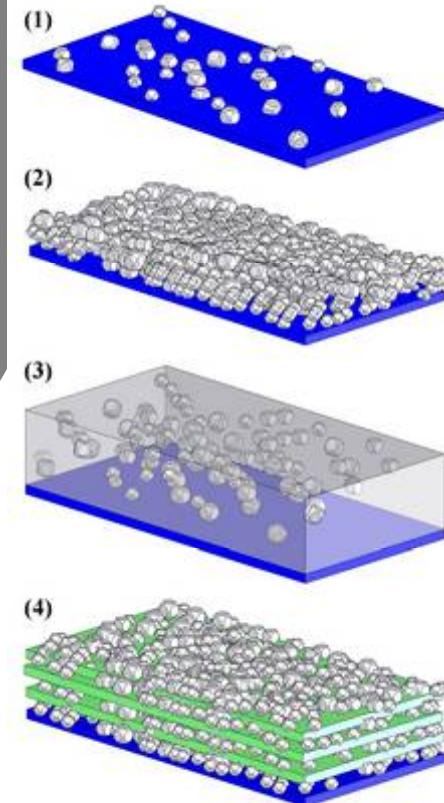
Procédés
Céramiques

Resp. : fabrice.rosignol@unilim.fr

Procédés de
traitements
de surface

Resp. : alain.de-noirjean@unilim.fr

Procédé
LECBD



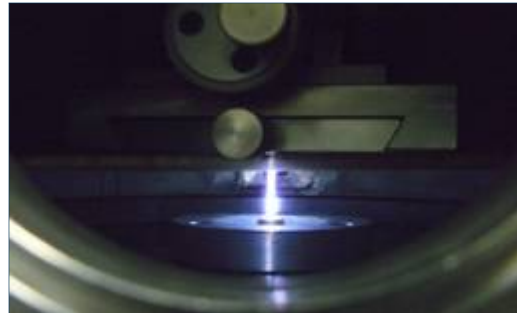
Épaisseurs de couches et Procédés

10 nm to 1 μm



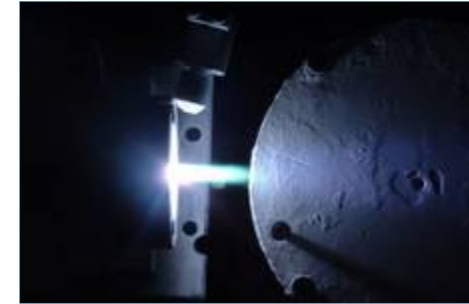
Ablation laser

1 to 20 μm

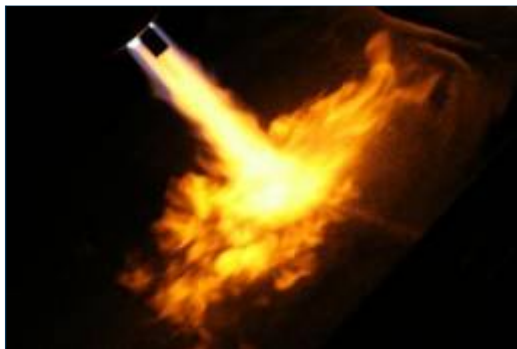


PECVD / PVD

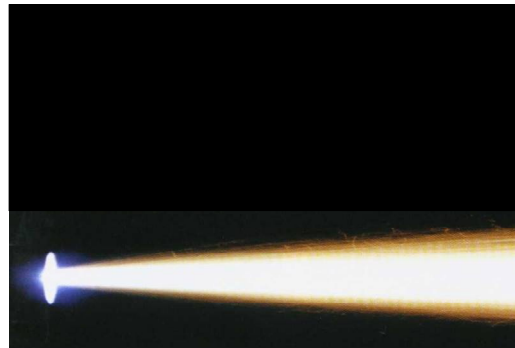
10 to 1000 μm



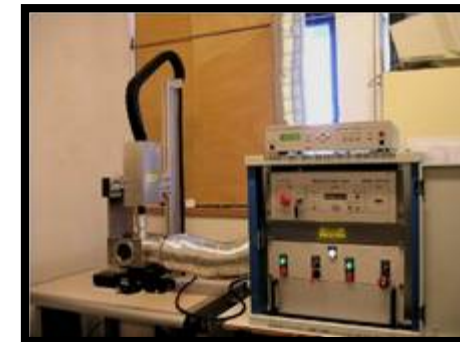
Plasma thermique
SPS / APS



Flamme

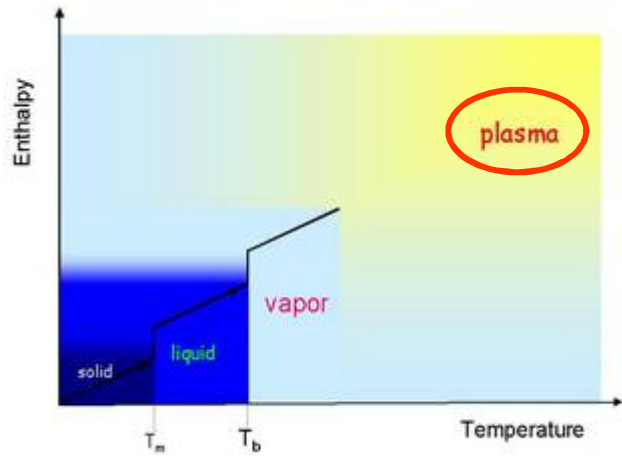


Arc électrique

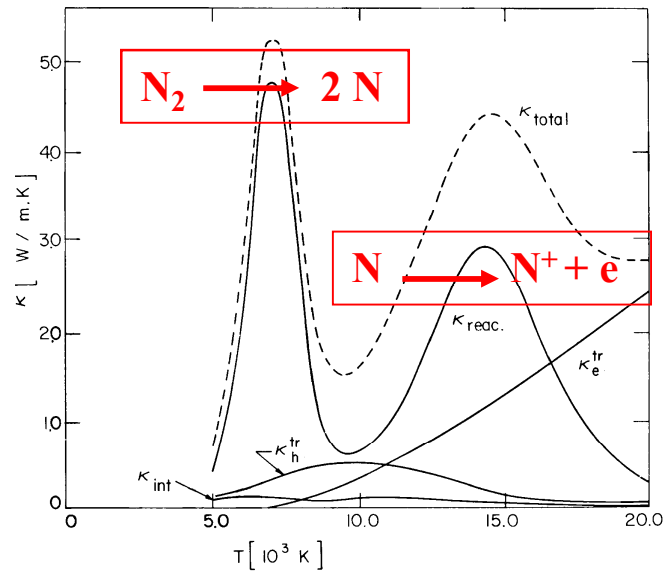


Traitement laser

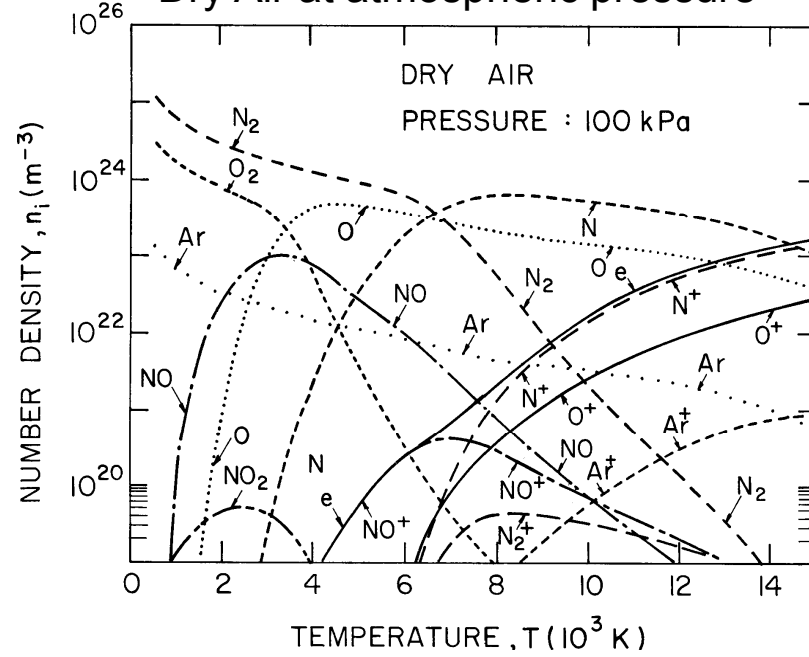
Plasmas the 4th state of matter



Thermal conductivity for Nitrogen at atmospheric pressure



Dry Air at atmospheric pressure





9

Quand la tension électrique entre les charges est très importante...

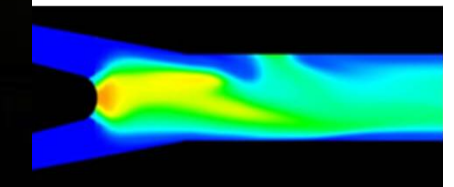
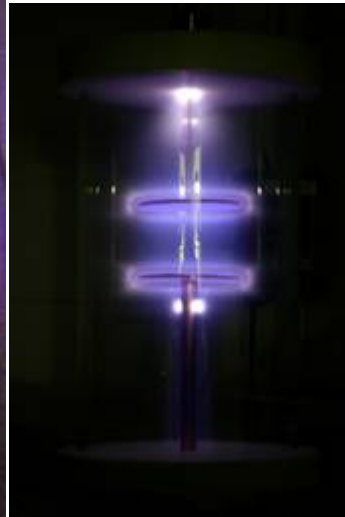
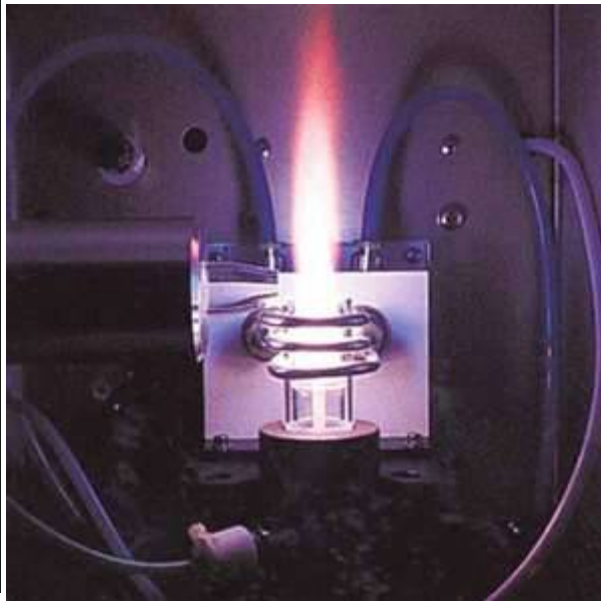
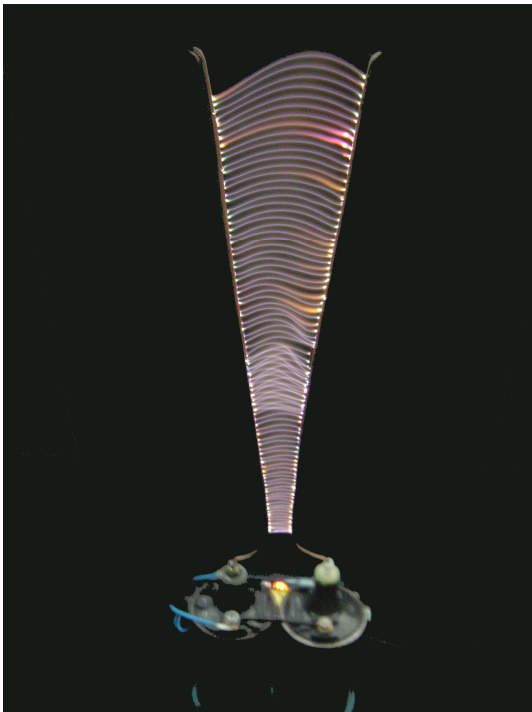


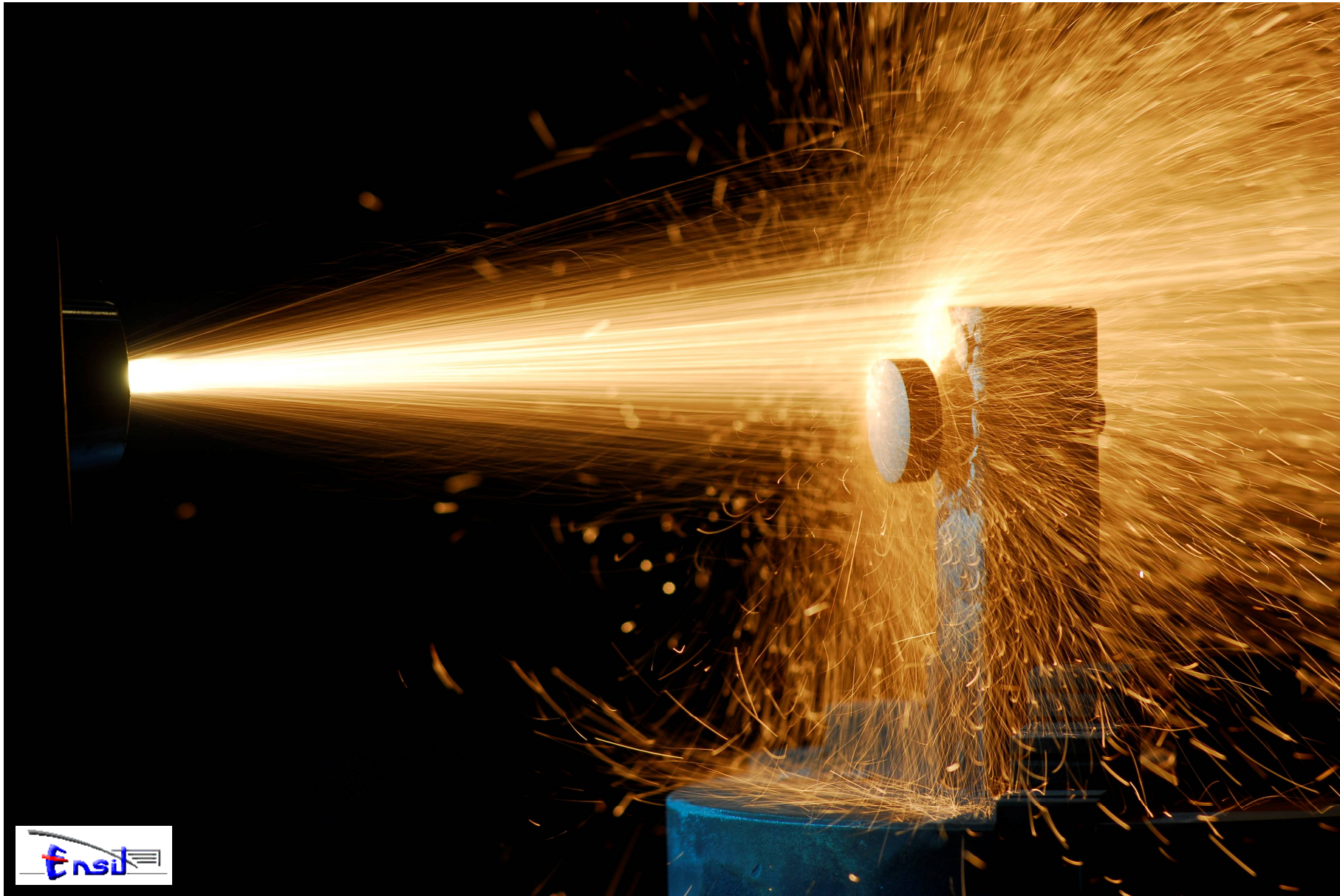
10

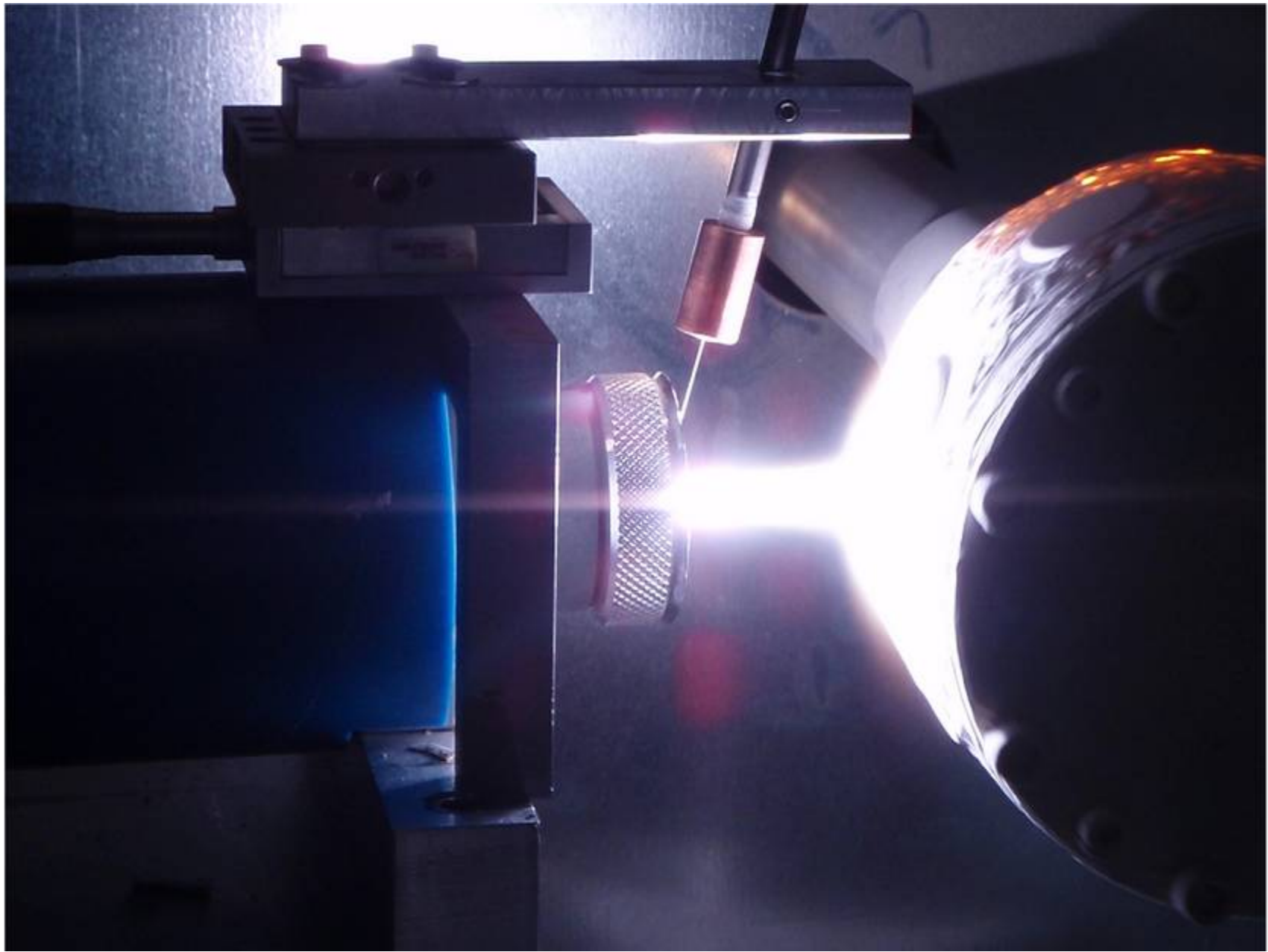




Westinghouse Plasma Corporation plasma torches that burn at over 12,000° F are used in plasma gas

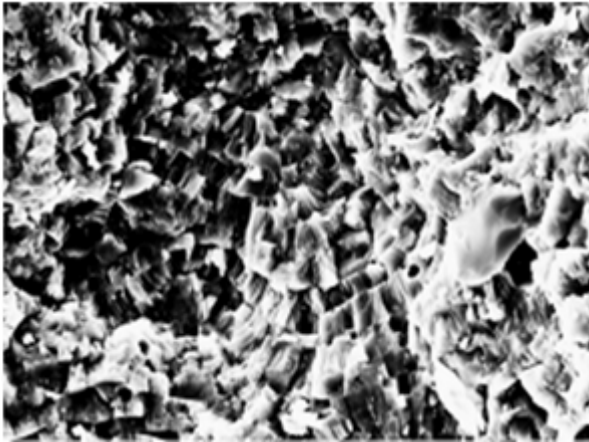




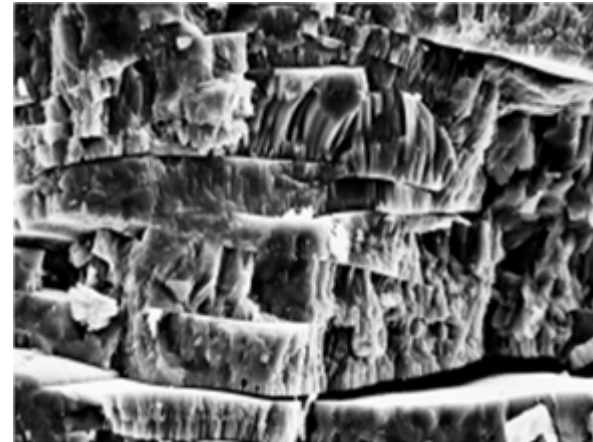


Exemple de dépôts

Dépôt conventionnel



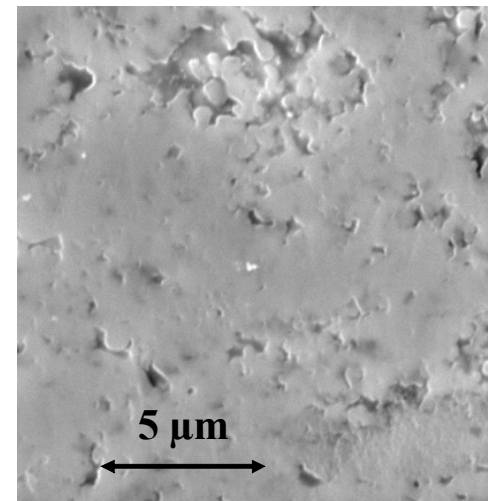
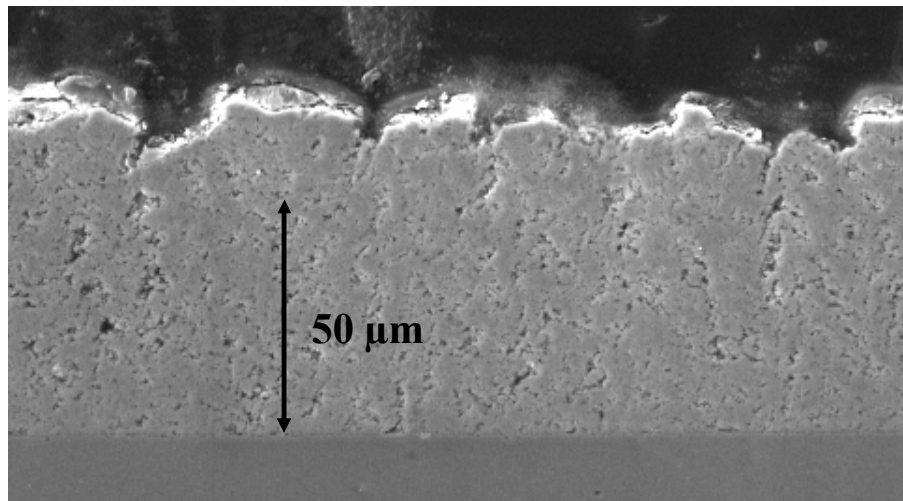
TiO₂



D.C. plasma spraying 10 μm

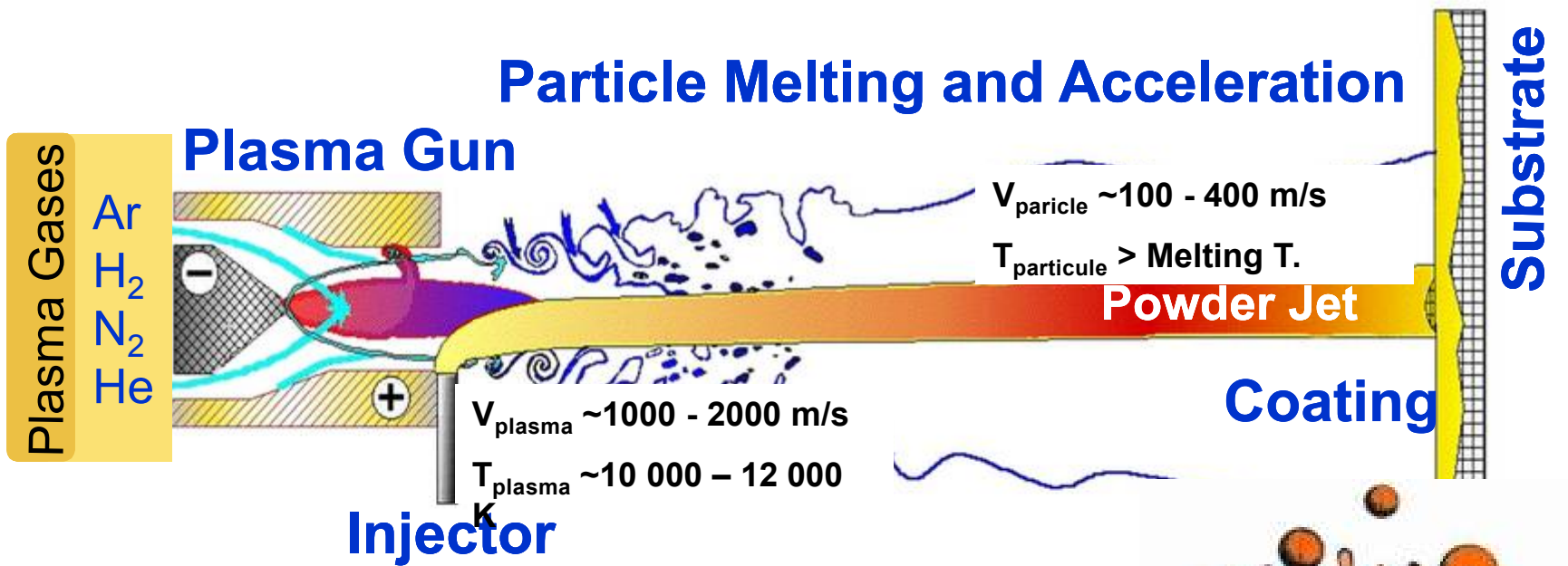
R.F. plasma spraying

Dépôt Nanostructuré

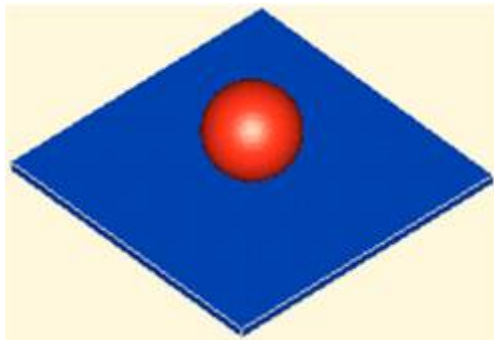


ZrO₂

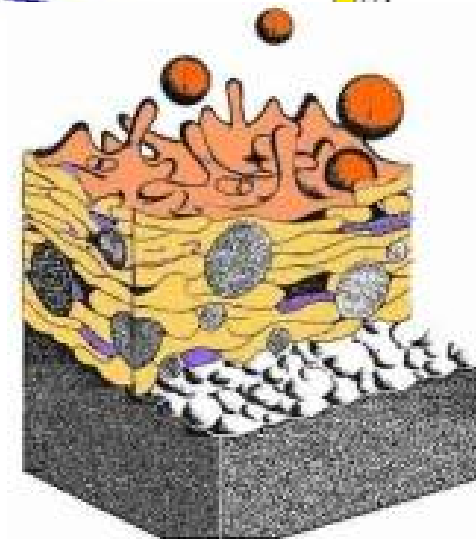
Introduction – Thermal Plasma Process



Particle Impingement

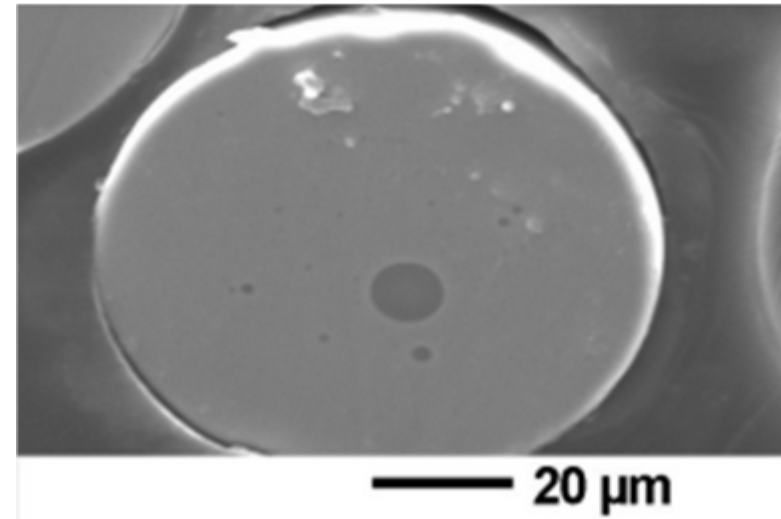
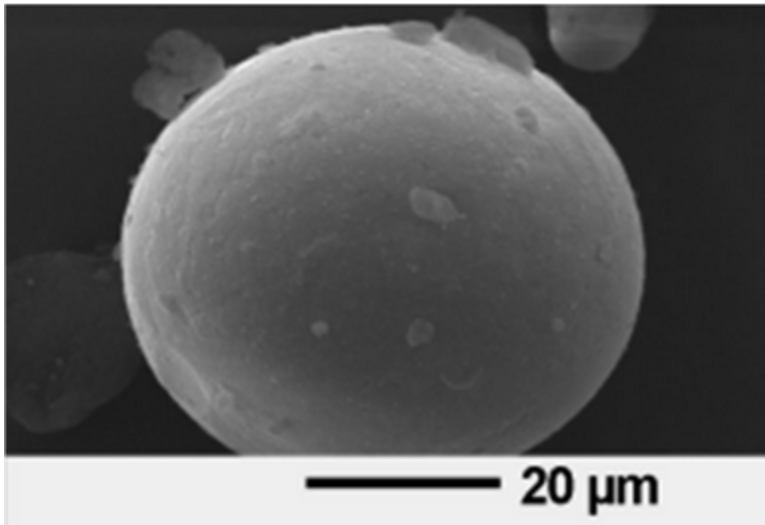


Splat Layering



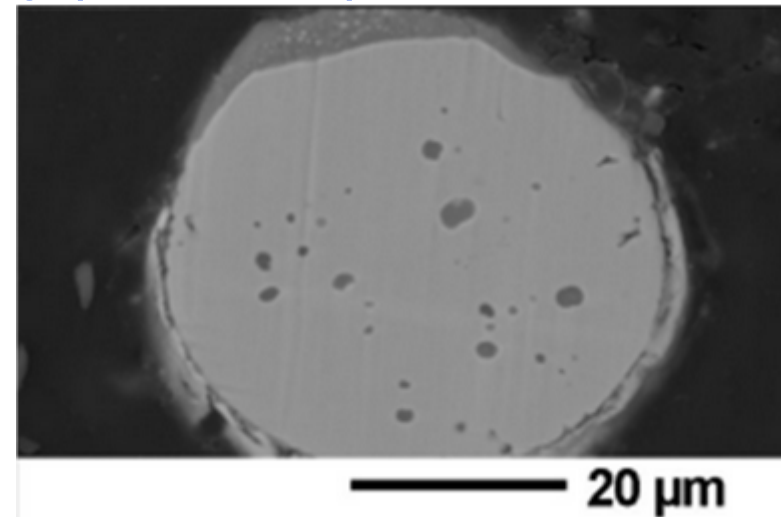
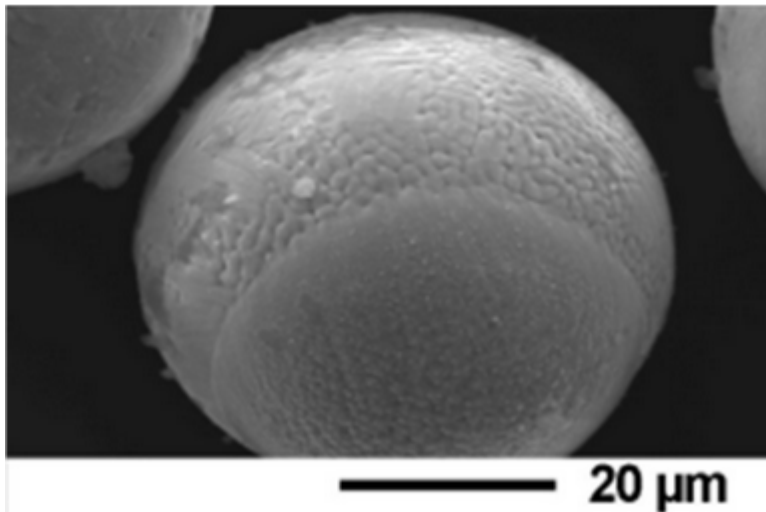
Microscopy & EDS

Standard Spray Parameters



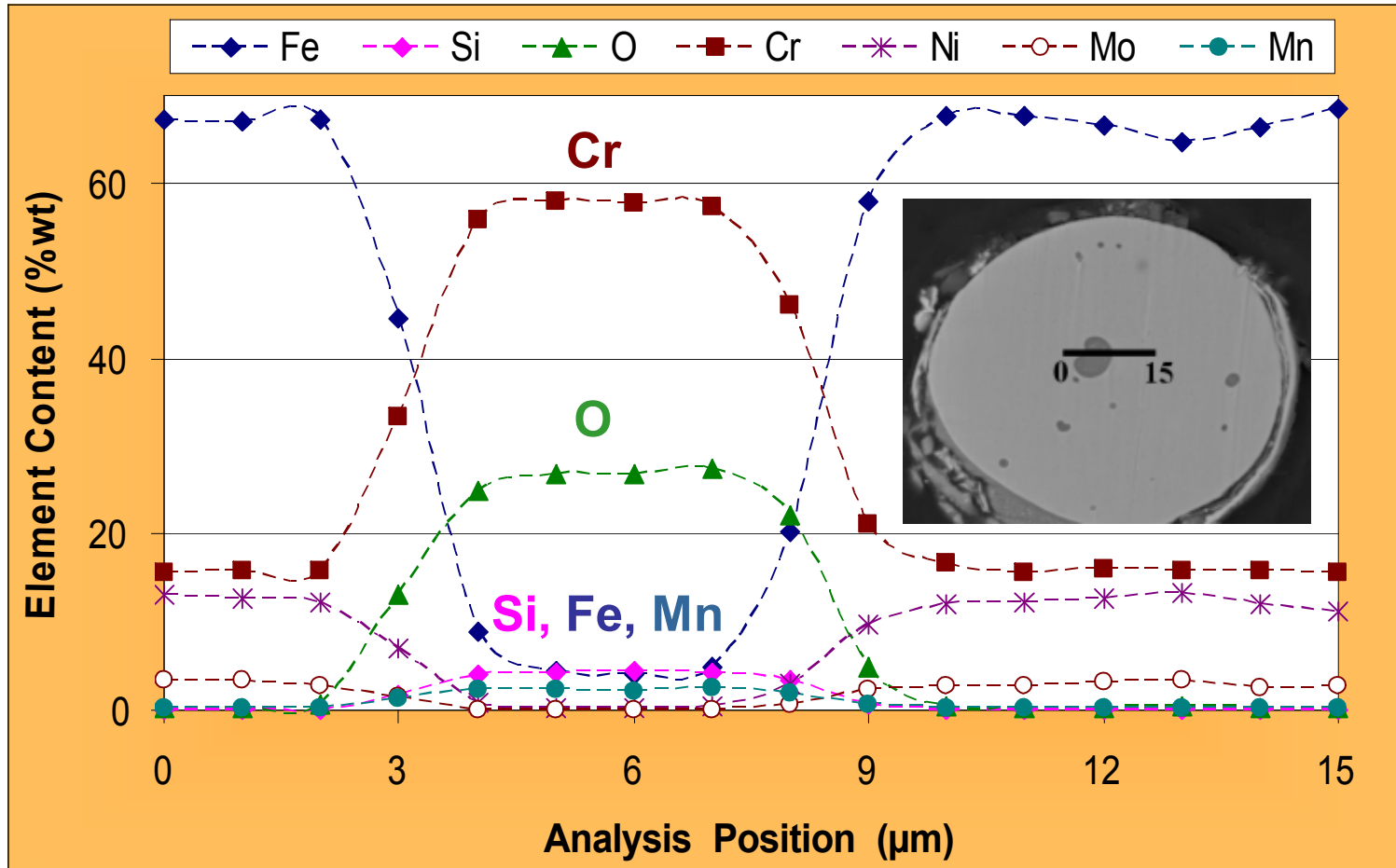
Collected Metco (-106+45 μm)

Collected Techphy (-63+50 μm)



Electron Micro-Probe Analysis (EMPA)

Standard Spray Parameters



In Nodule
 O, Cr, Si, Mn ↗
 Fe ↘
 Ni, Mo ~ 0

Cap / Nodules
 Almost similar composition

Objectifs : Définition matériau / Dépôt

- ▲ Dépôt à gradient de fonction : Céramique / NiCr

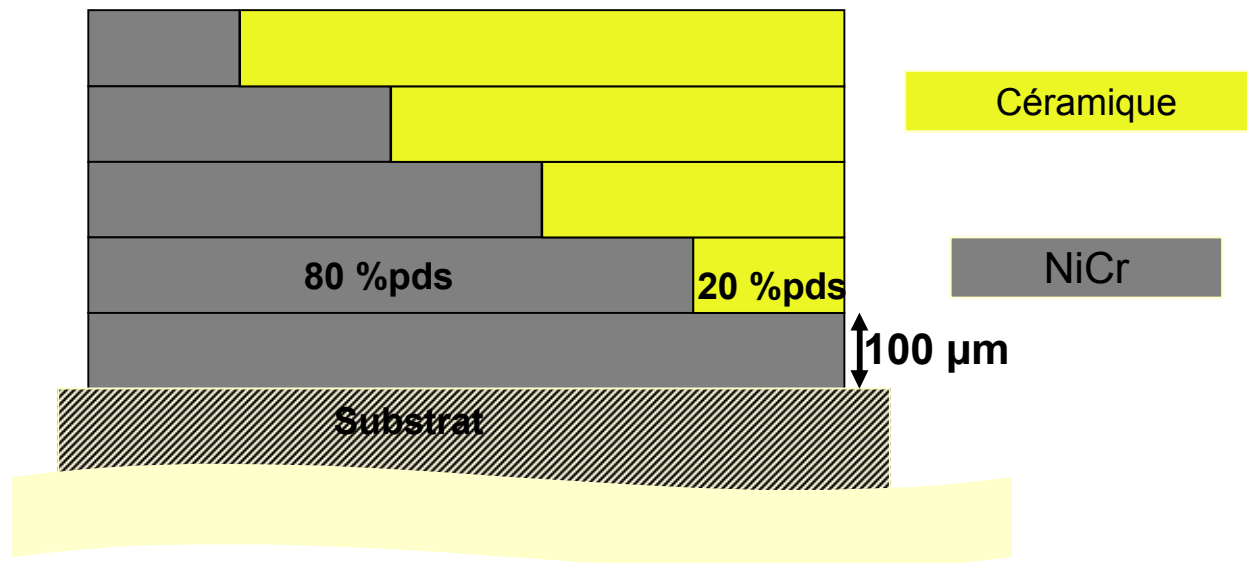
Evaluation de la nature de la phase céramique :

Zircone, yttriée

Zircone, cériée

Alumine titane

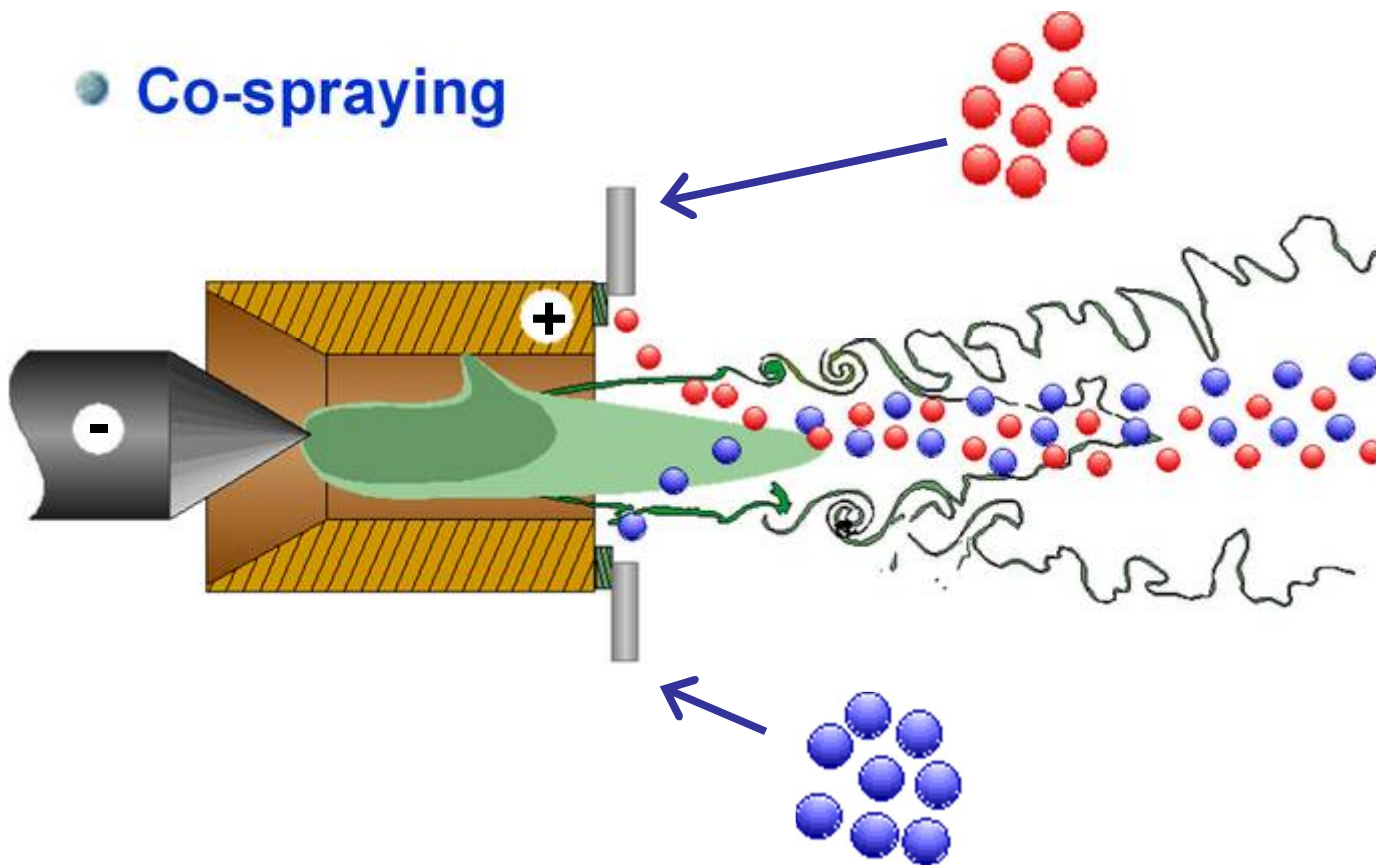
- ▲ Réalisation d'un dépôt à gradient de composition sur 5 couches



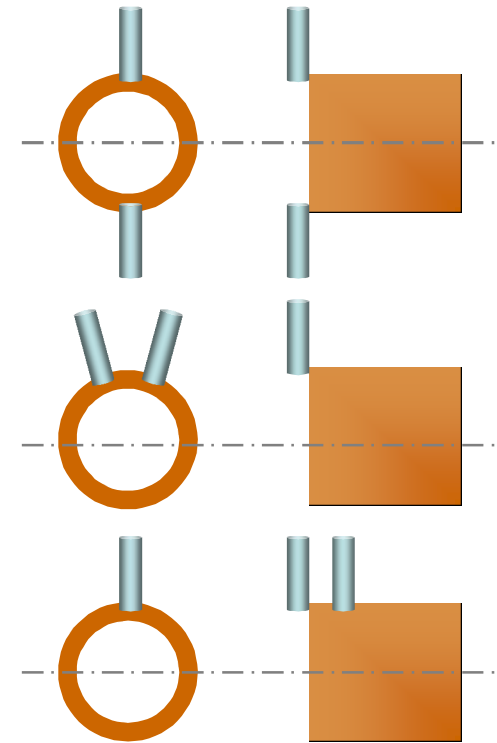
Introduction – Quo Vadis Cermet Deposits?

Cermet Fabrication Techniques

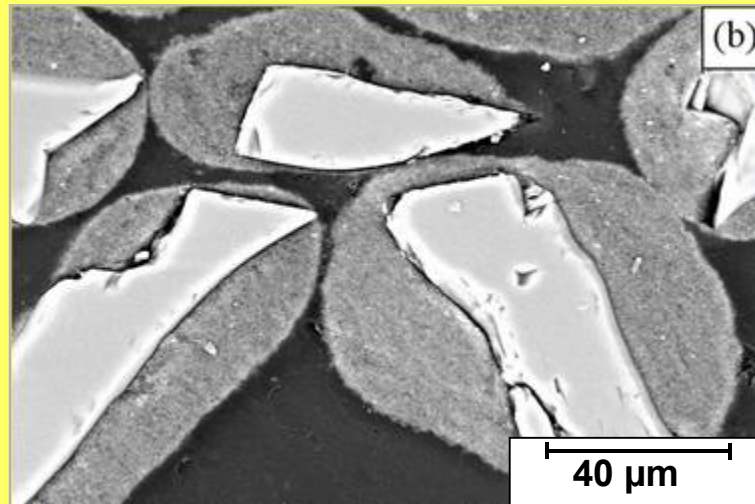
- Pre-mixed Powder
- Co-spraying



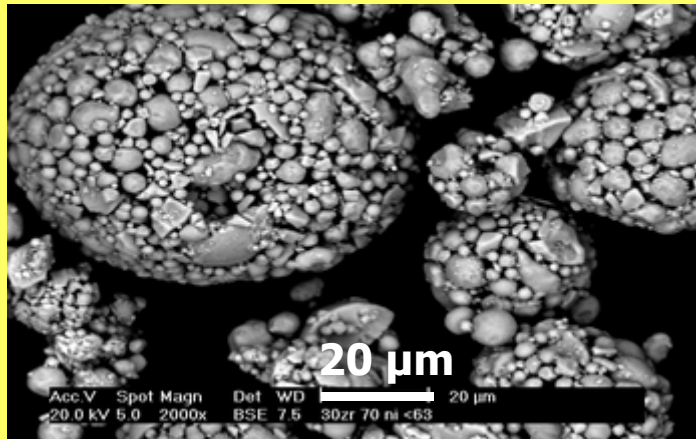
Multi-injector Configurations



SiC - Al₂O₃



H. Ageorges, SPCTS



Poudre agglomérée

A. Denoirjean, SPCTS

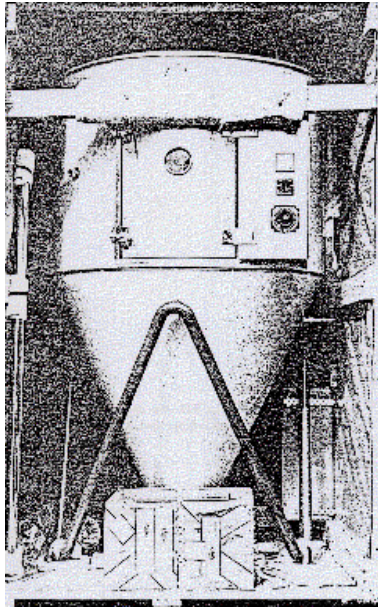
10 μm

**Poudre agglomérée frittée
(frittage sous air T<1000°C)**

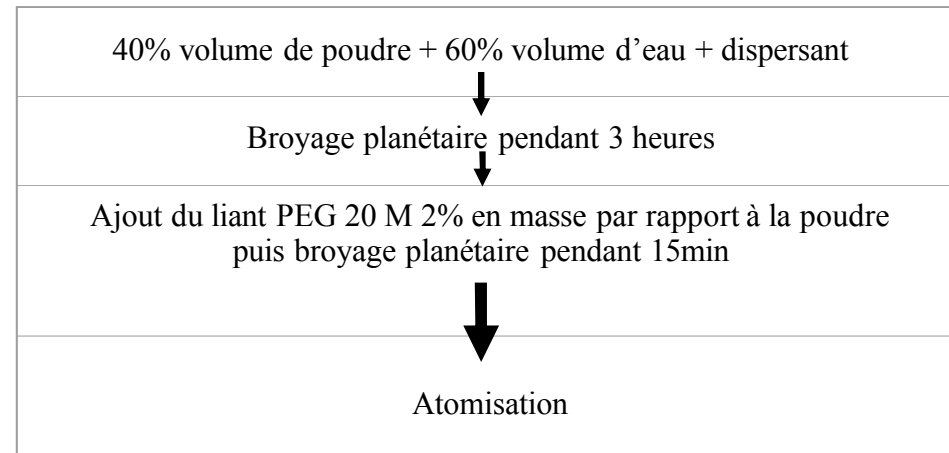
Introduction – Production de poudres cermets

Agglomération

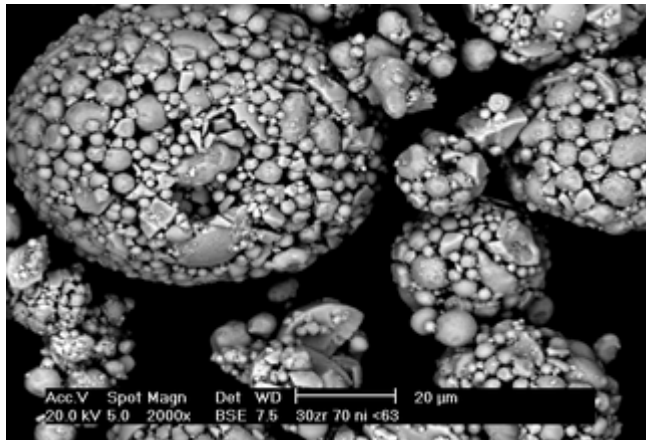
En collaboration avec T. Chartier, D. Tetard, S. Chaulange



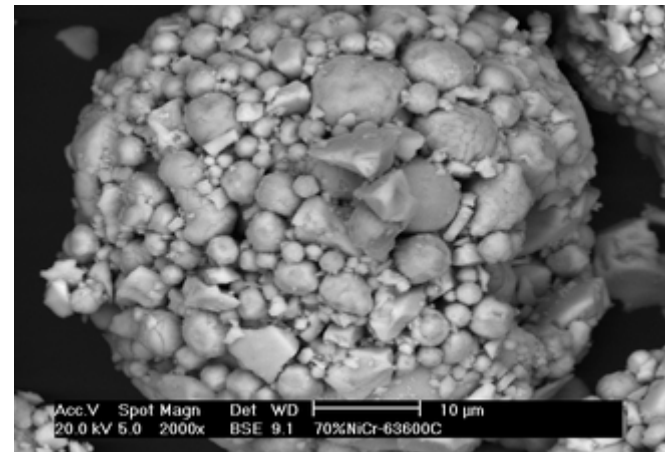
Les différentes étapes pour l'agglomération



Rendement massique de 15 à 40 %

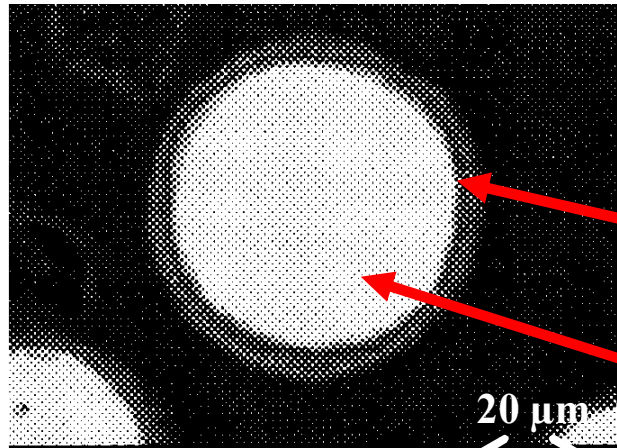


Poudre agglomérée, vue en surface



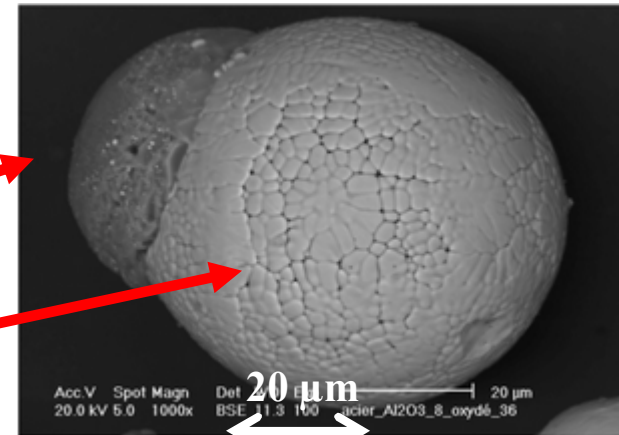
Poudre frittée, vue en surface

Reinforcement of metallic coatings by ceramic inclusions



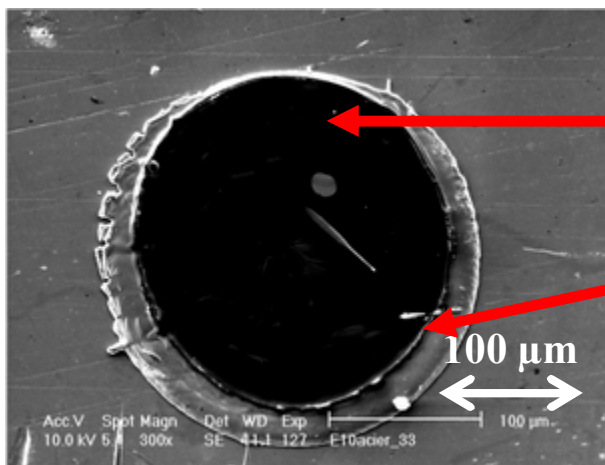
alumina

steel



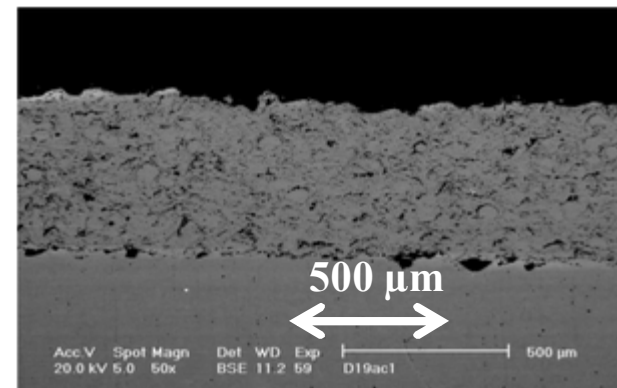
**Coated particle
Made by mechanofusion**

**Particle collected in
flight**



alumina

steel

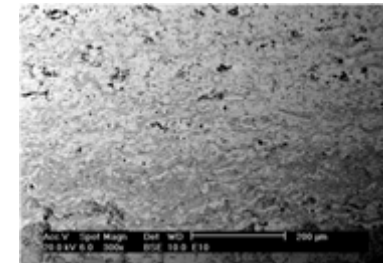
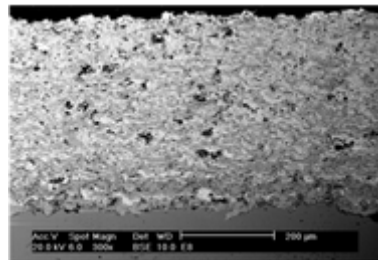
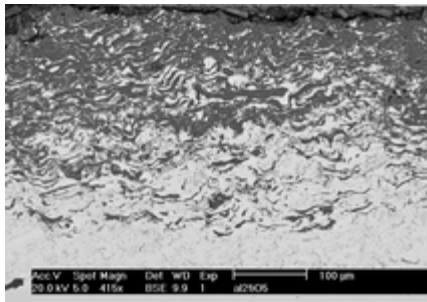


Splat

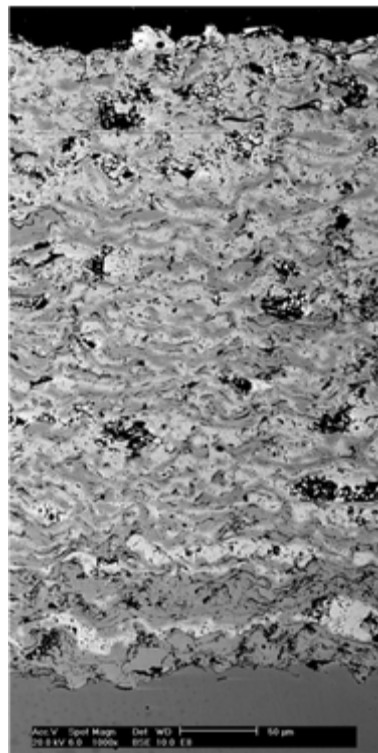
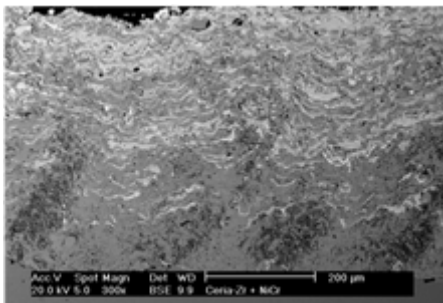
Coating

Analyse des dépôts : Micrographie des dépôts

Cermet Al_2TiO_5 / NiCr



Cermet $\text{ZrO}_2, \text{CeO}_2$ / NiCr

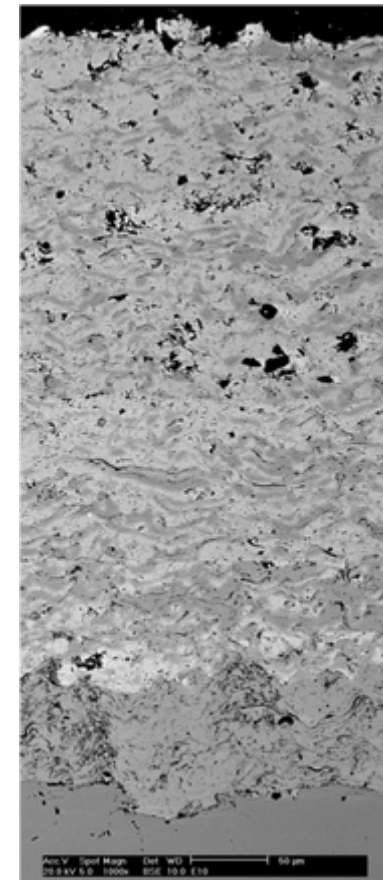


73 %_{cal}
NiCr

55 %_{cal}
NiCr

80 %_{cal}
NiCr

20 %_{cal}
NiCr



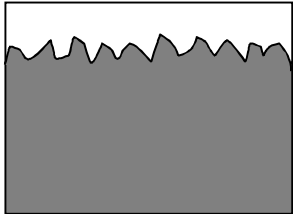
Cermet $\text{ZrO}_2, \text{Y}_2\text{O}_3$ / NiCr

Which coating adhesion mechanism ?



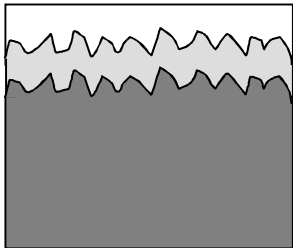
Ra ~ 0,06 μm 0 MPa

T < 100°C



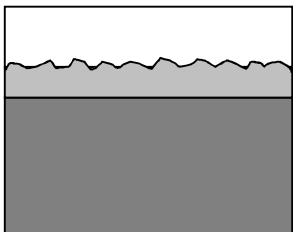
Ra ~ 5 μm (RT ~ 50) 20 MPa Mechanical

T < 100°C



Ra ~ 5 μm 55 MPa Mechanical + Interfacial ?

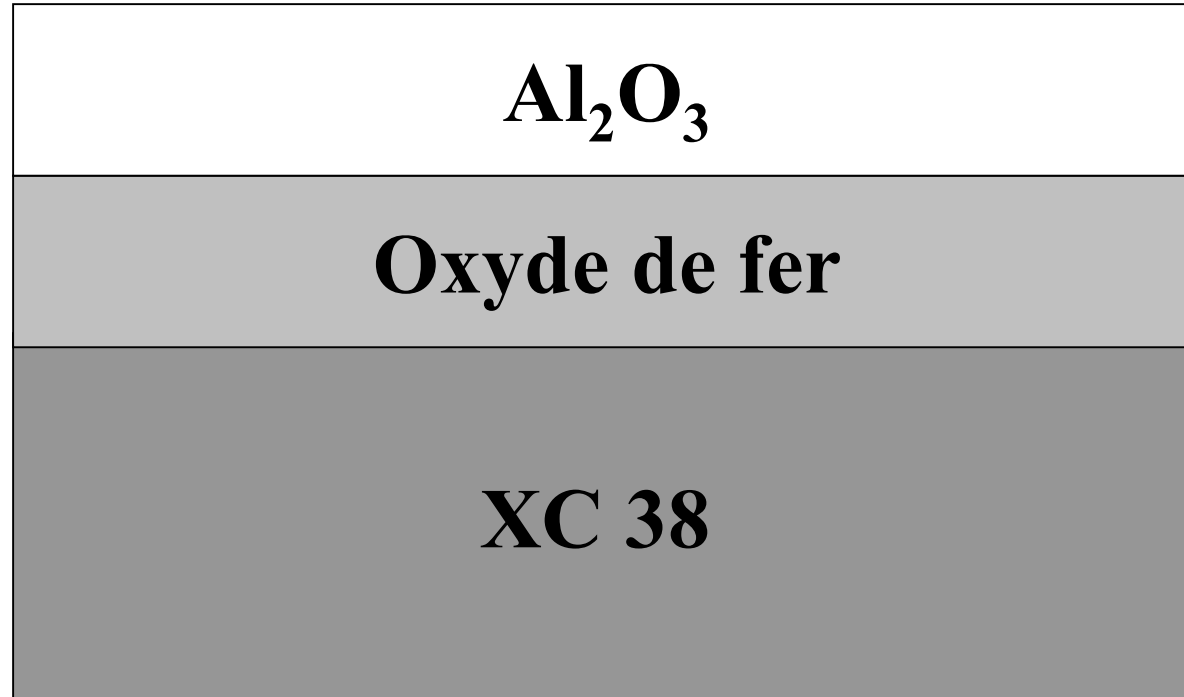
T = 350°C



Ra < 1 μm > 55 MPa Interfacial – Mechanical ?

T = 350°C

Positionnement de l'étude



Points clés

cohésion de la couche d'oxyde

interface XC 38 / oxyde de fer

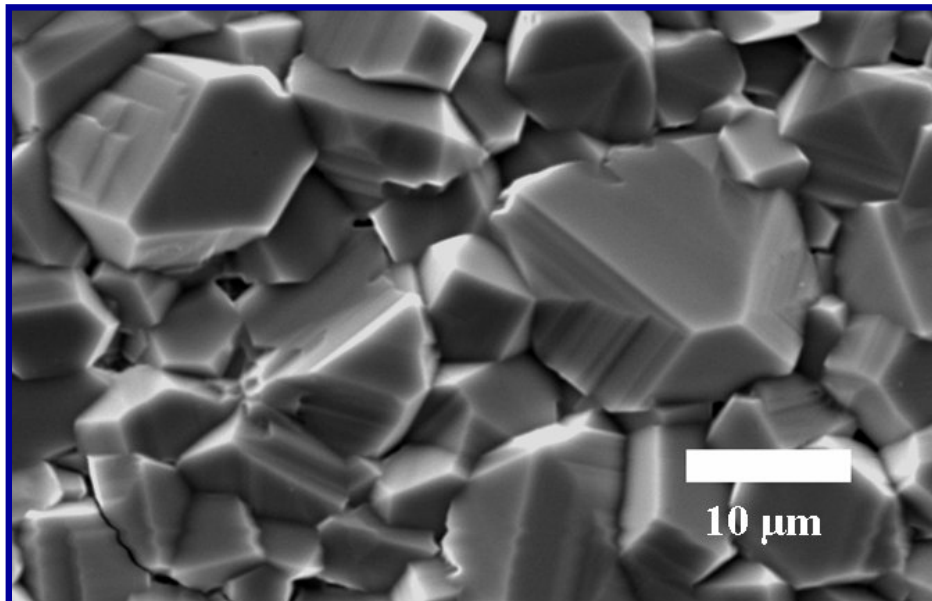
interface oxyde de fer / Alumine

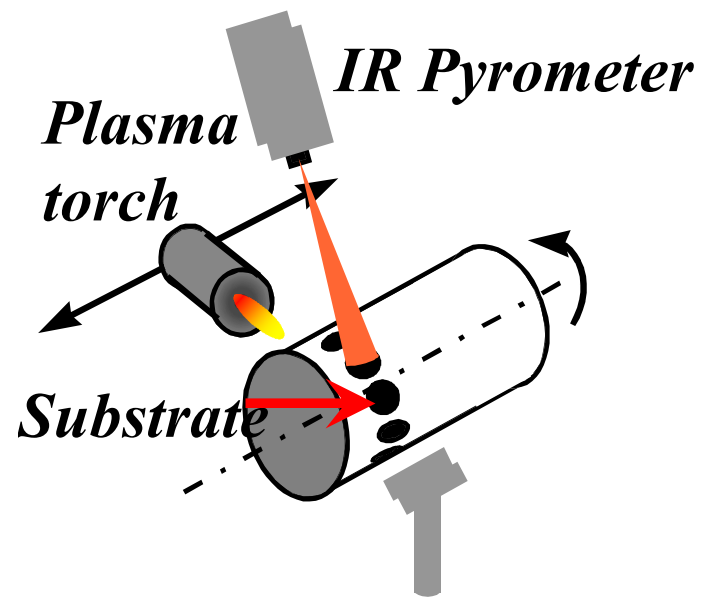
Optimum preoxidation treatment

High pressure: $P_{\text{CO}_2} = 10^5 \text{ Pa}$

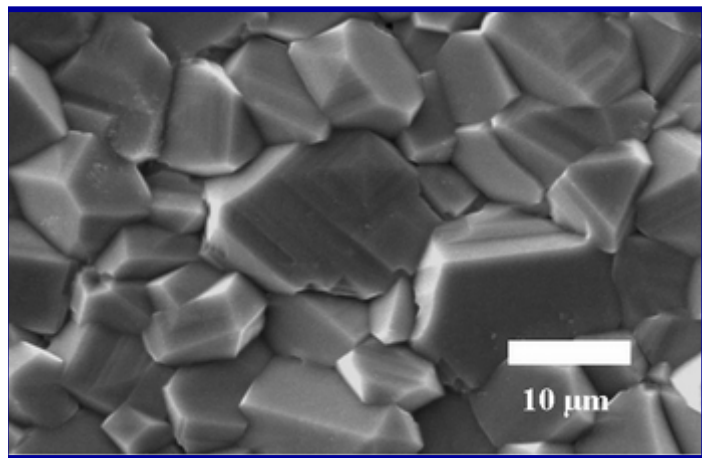
Short exposition time: $t < 15 \text{ min}$

High Temperature: $T = 1000^\circ\text{C}$

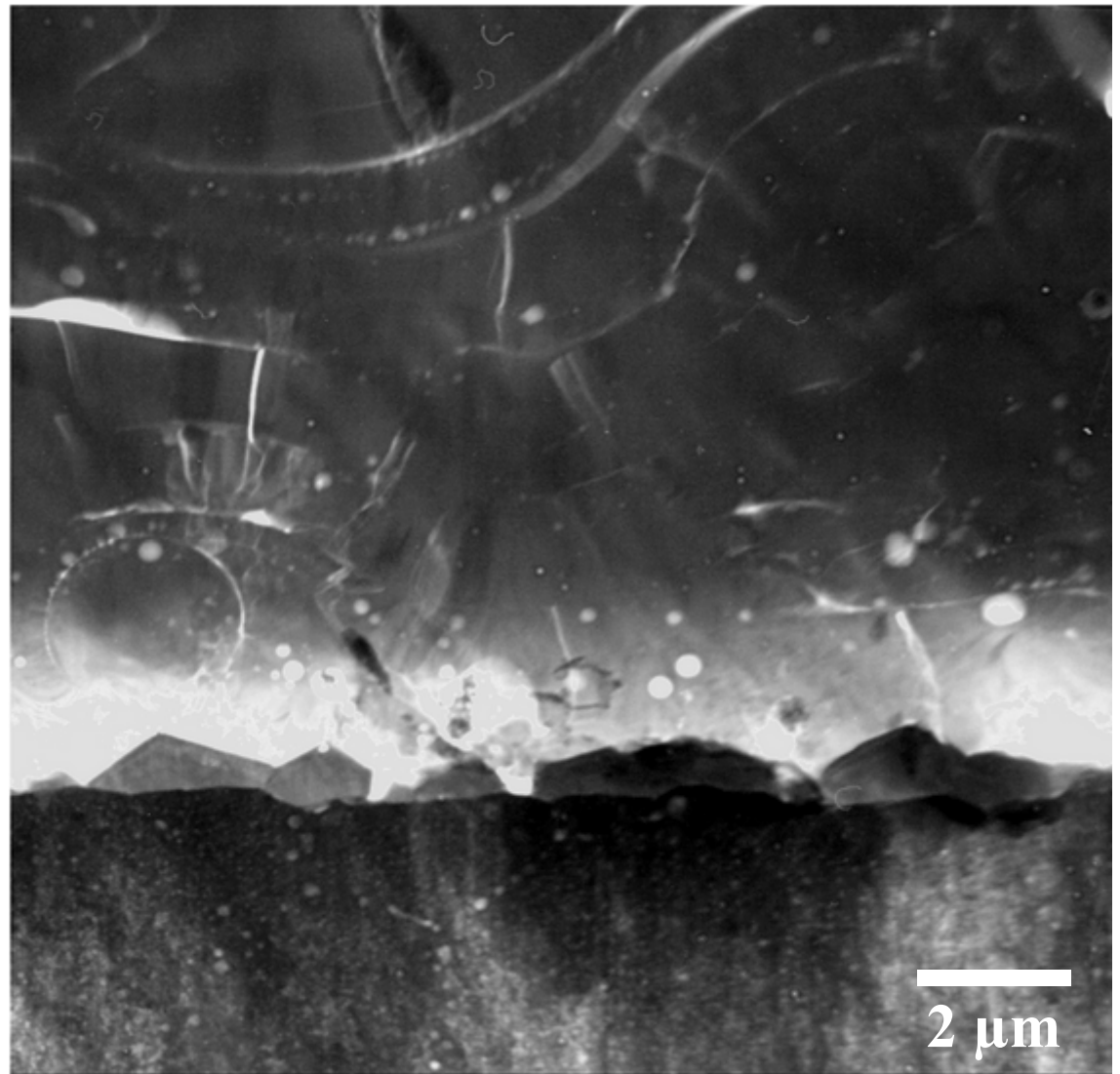


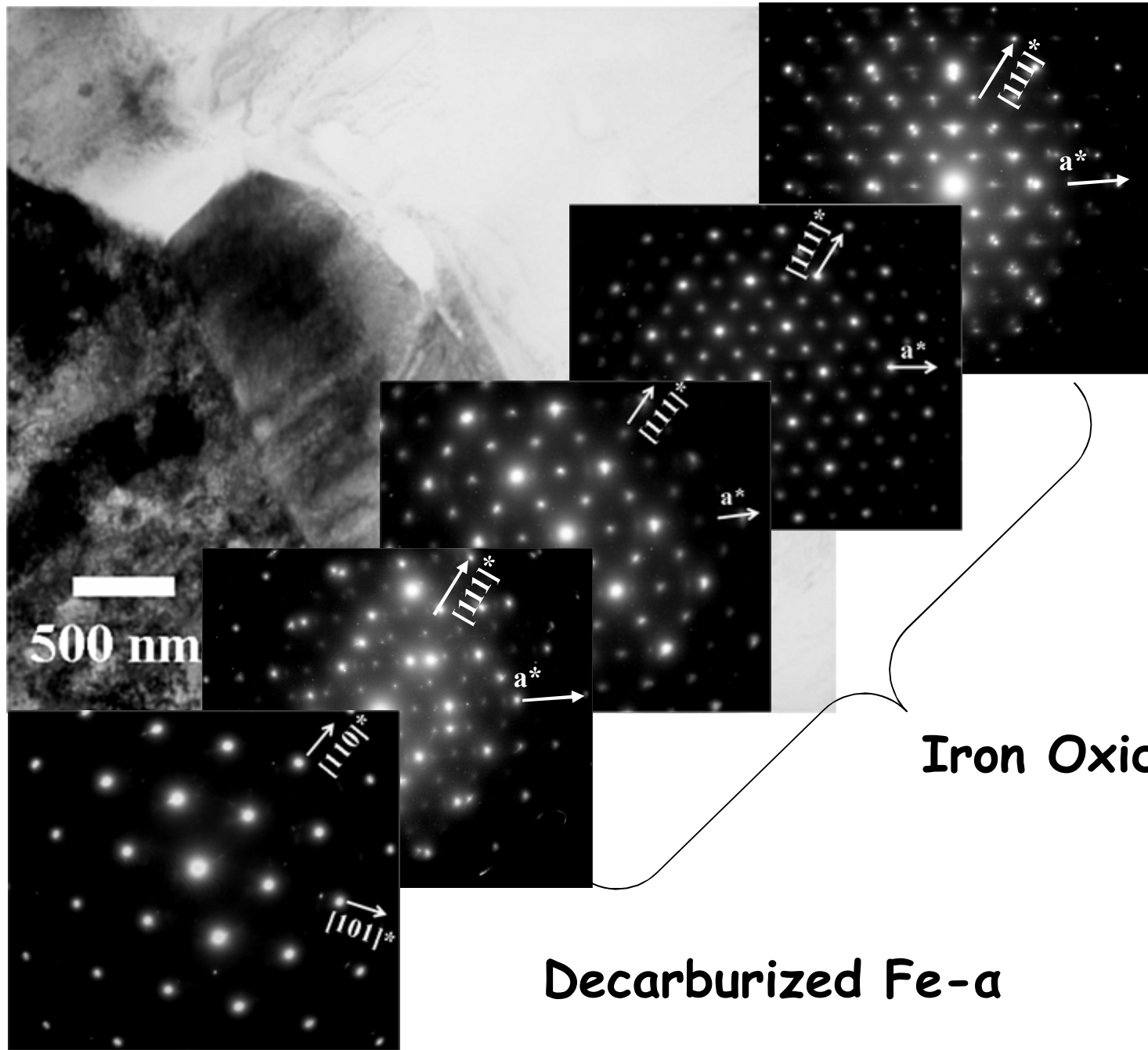


Preheating 1min 30 – 350 °C



Alumina coating





Cristal plat

γ Alumina

Iron Oxides

Decarburized Fe-a

500 nm

$[111]^*$

a^*

$[111]^*$

a^*

$[111]^*$

a^*

$[111]^*$

a^*

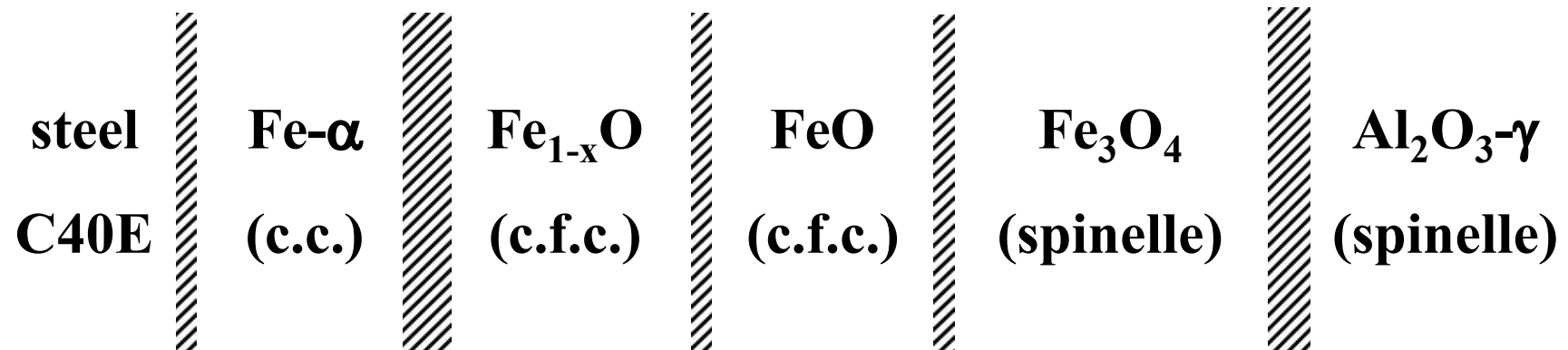
$[110]^*$

$[101]^*$

Interface role between alumina coating and oxidized substrate with wüstite layer bondcoat

Continuity of the cristal network

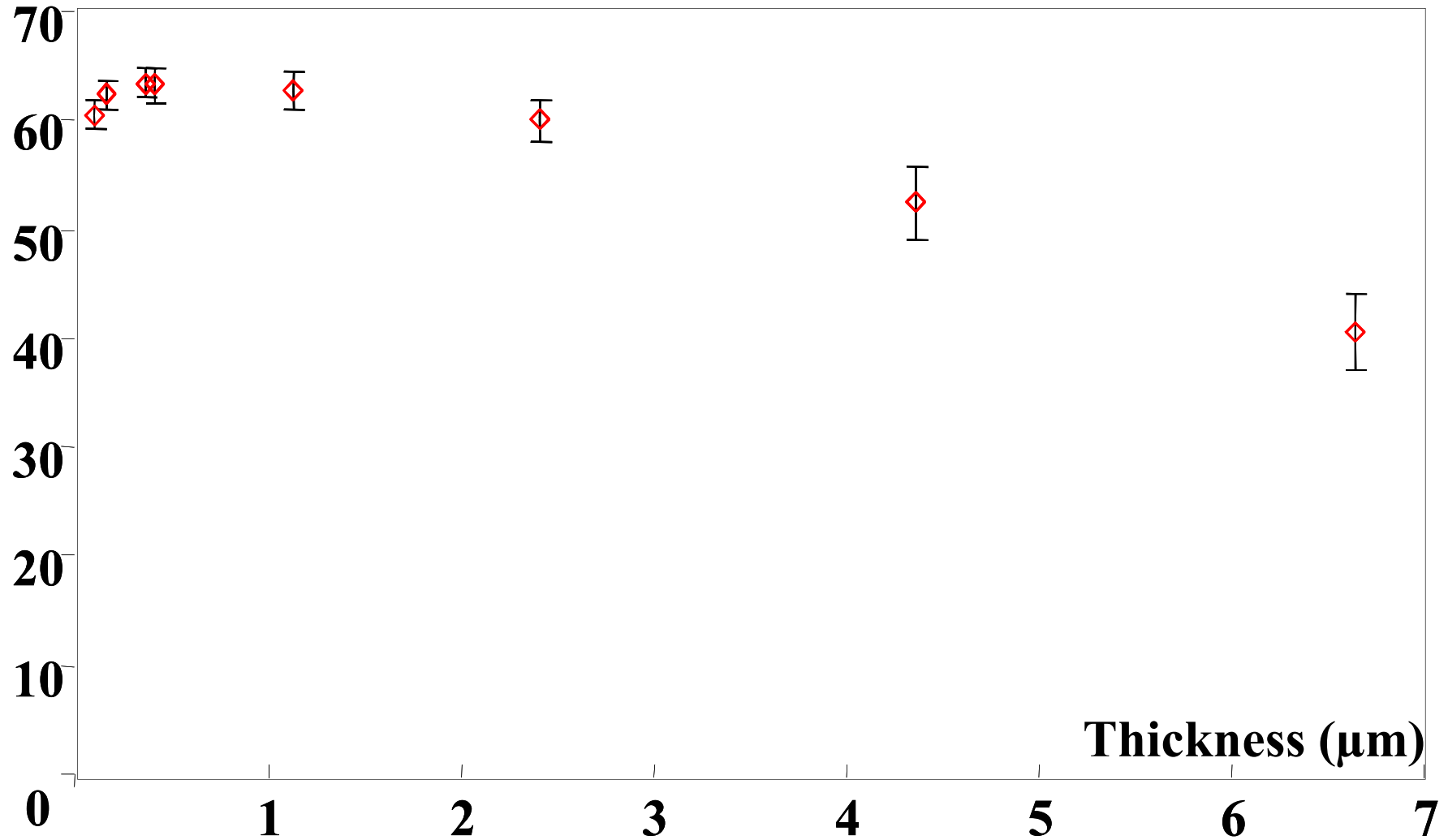
→ physical-chemical adhesion



homoaxial Heteroepitaxy

Preheating in furnace under CO₂ atmosphere

Adhesion (MPa)

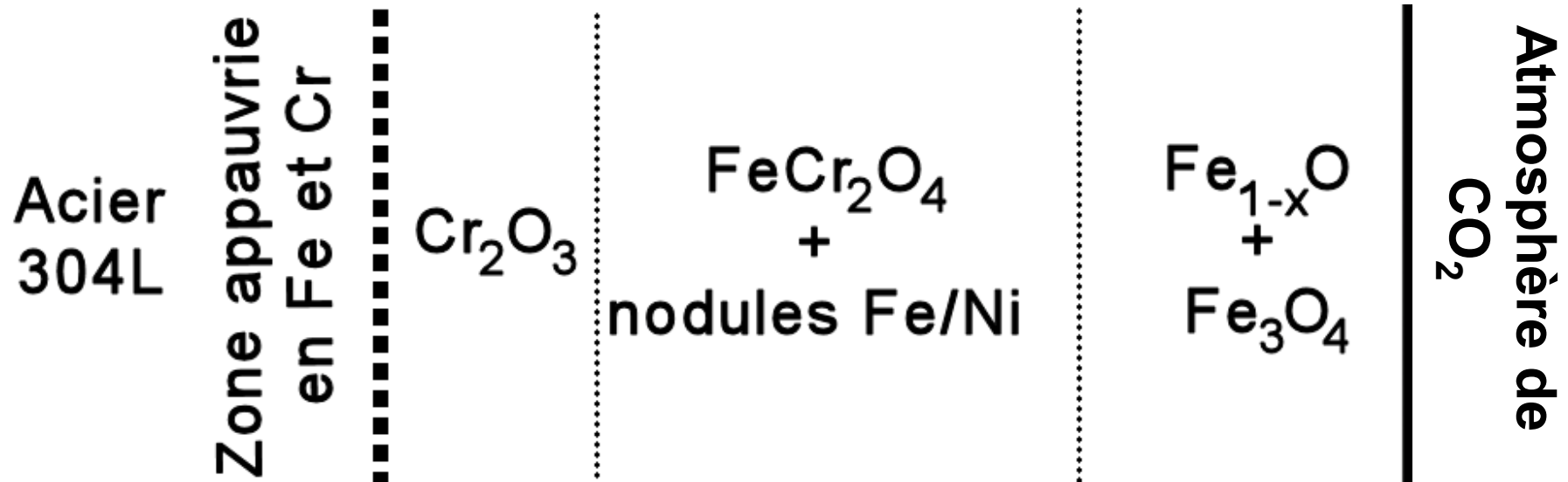


Revêtements céramique sur métaux

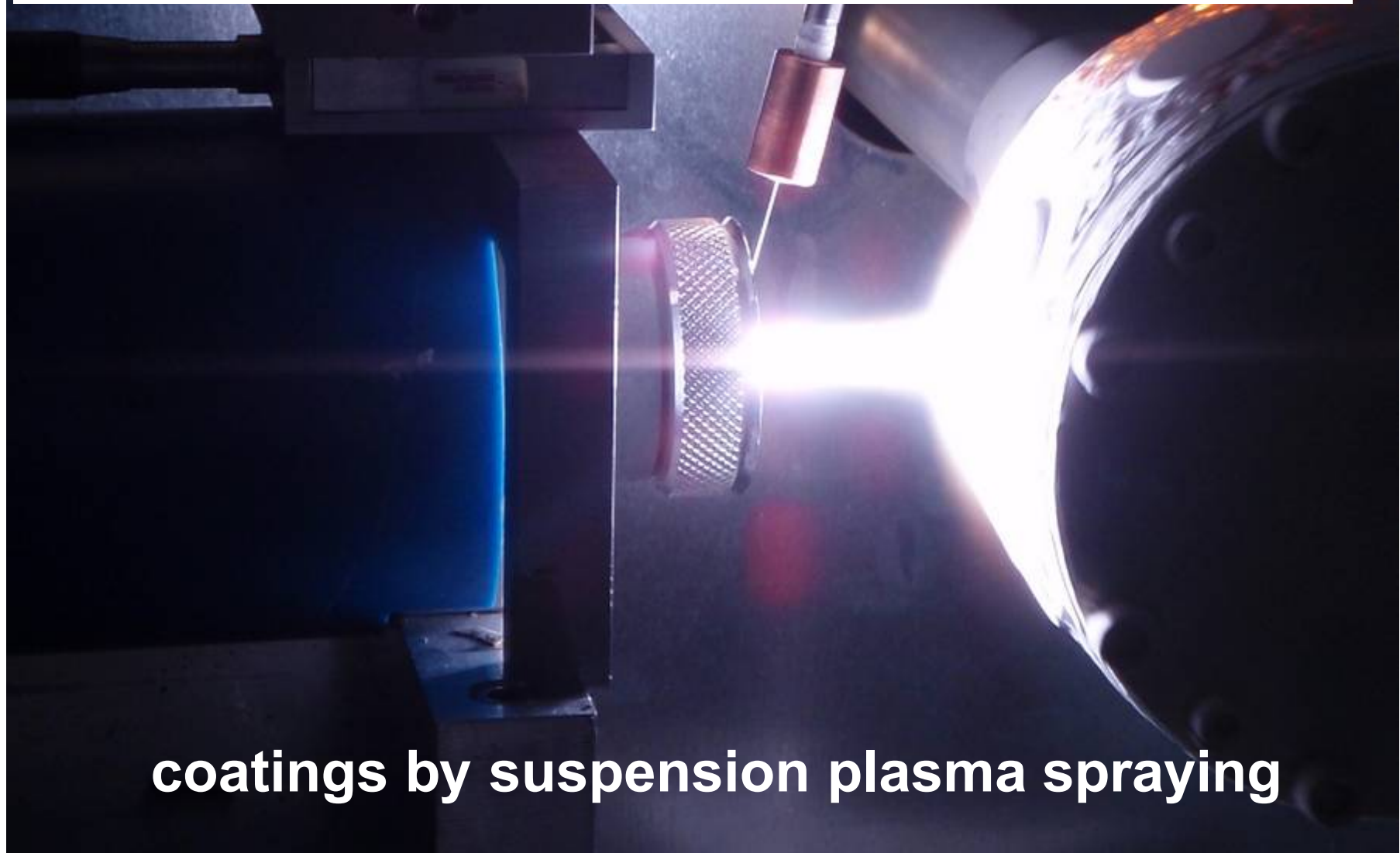
« La liaison cristallographique »

Formation contrôlée en four de wüstite (Fe_{1-x}O)

→ Etude cinétique



process development

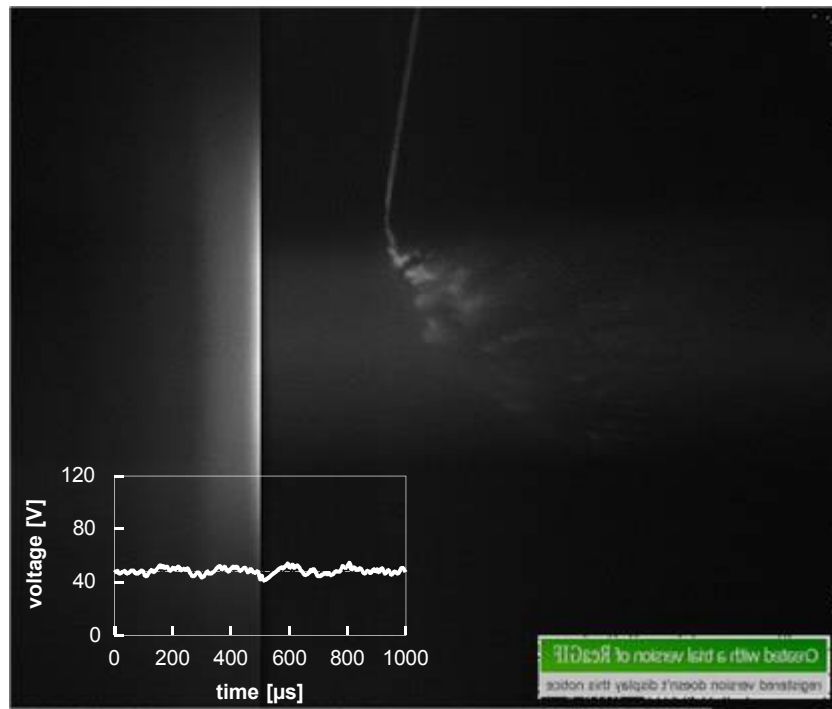


coatings by suspension plasma spraying

effect of arc root fluctuations

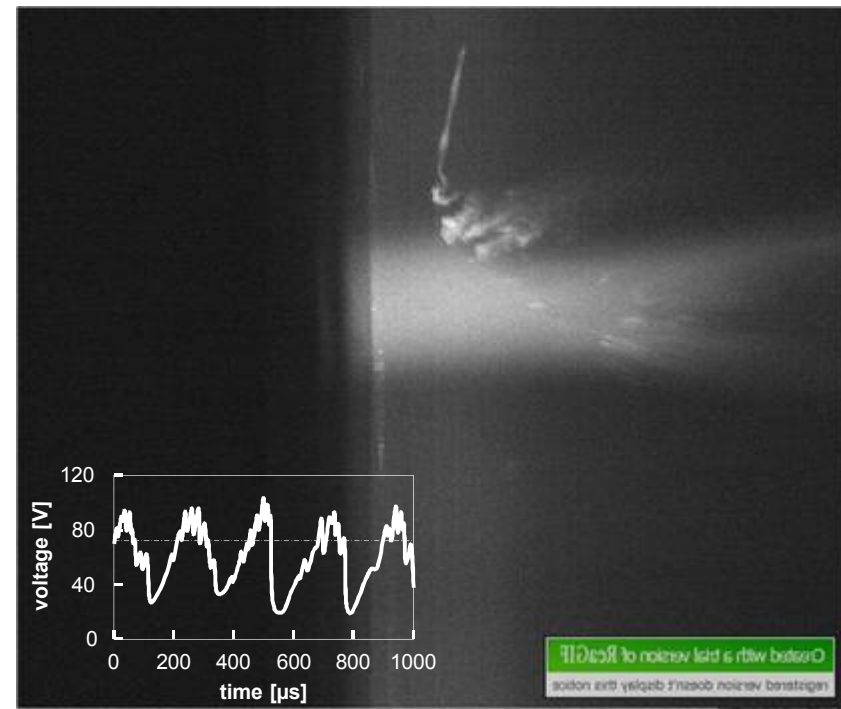
Ar-He (30-30) – I = 700A

0.6 MPa



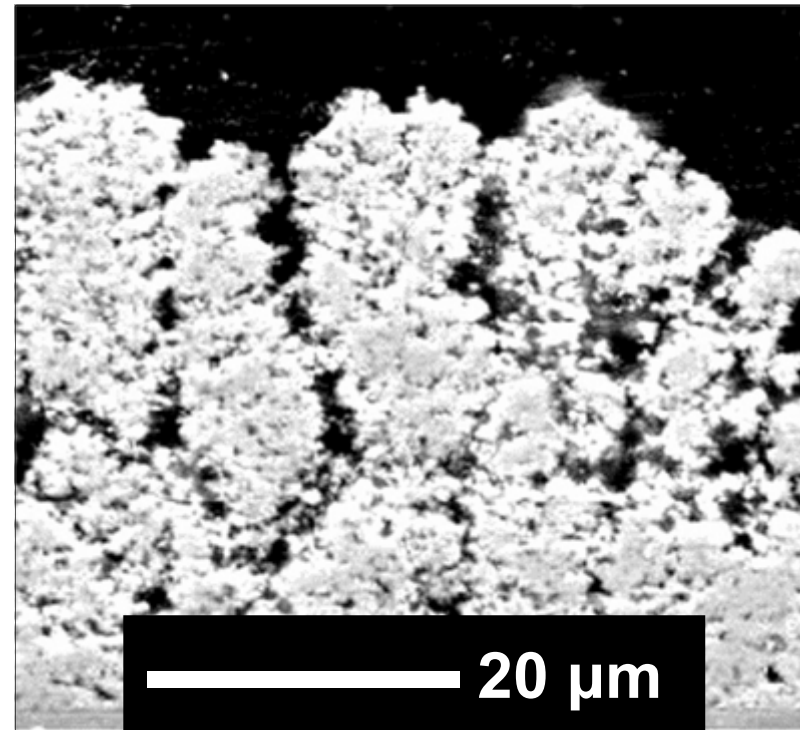
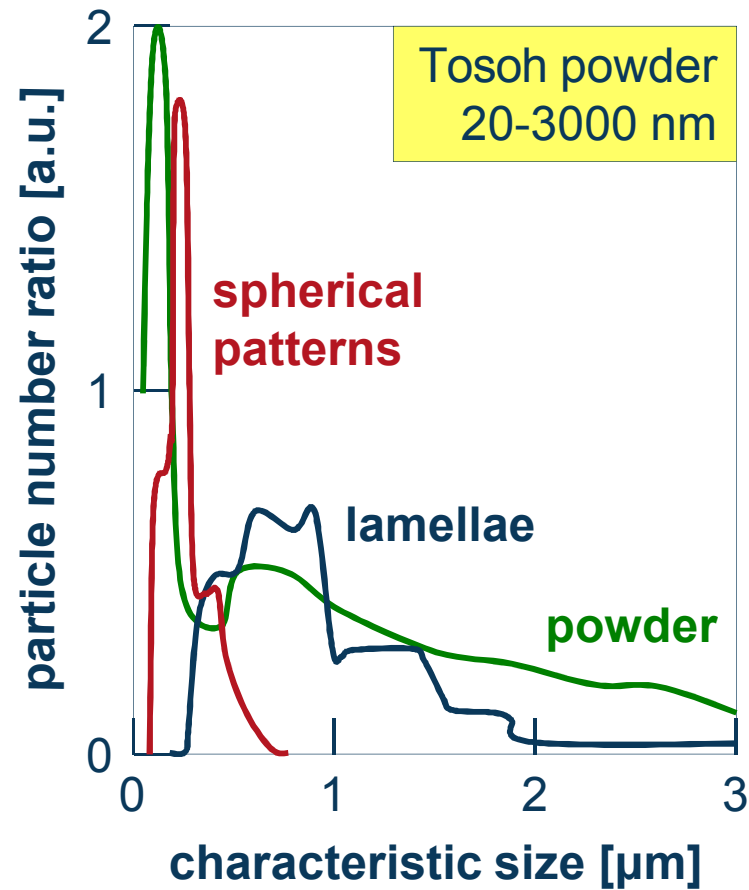
Ar-H₂ (45-15) – I = 500A

0.4 MPa



effect of particle size distribution

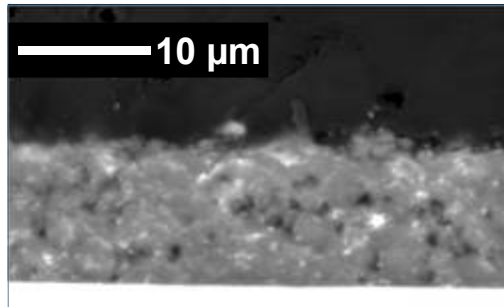
nano-sized particles with agglomerates and aggregates



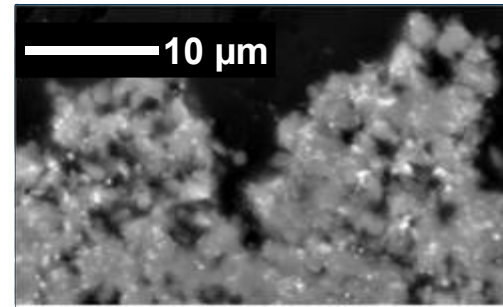
plasma: Ar-H₂ (25 vol.%)

Al₂O₃-ZrO₂ composite coatings by SPS

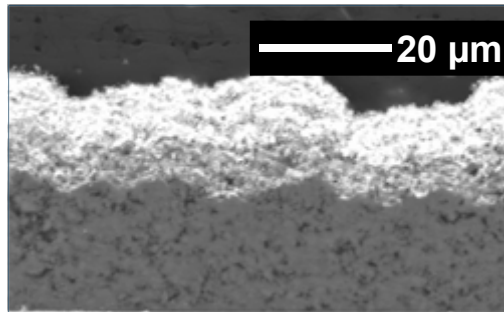
Ar-He (30-30)
h = 12 MJ.kg⁻¹
SD = 30 mm
d₉₀-d₁₀ = 420 nm



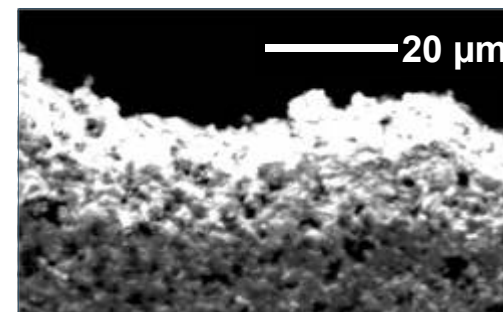
Ar-He (30-30)
h = 14 MJ.kg⁻¹
SD = 40 mm
d₉₀-d₁₀ = 420 nm



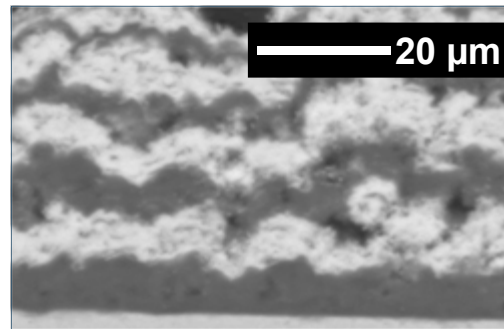
Ar-He (30-30)
h = 12 MJ.kg⁻¹
SD = 30 mm
d₉₀-d₁₀ = 420 nm



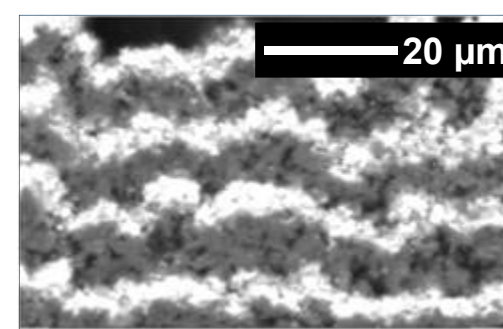
Ar-He (30-30)
h = 12 MJ.kg⁻¹
SD = 30 mm
d₉₀-d₁₀ = 1270 nm



Ar-He (30-30)
h = 14 MJ.kg⁻¹
SD = 30 mm
d₉₀-d₁₀ = 420 nm



Ar-He (30-30)
h = 12 MJ.kg⁻¹
SD = 30 mm
d₉₀-d₁₀ = 420 nm



coating architecture

8YSZ
mono-crystalline
 $d_{10} \sim 30 \text{ nm}$
 $d_{50} \sim 50 \text{ nm}$
 $d_{90} \sim 120 \text{ nm}$

**coating / substrate
interface**

Ar-He (30-30) 600 A
11,5 MJ.kg⁻¹
SPCTS torch
12 MW.m⁻²

1 μm

granular structure

- large variation in grain diameters
- d_{90} particle size distribution?
- coalescence of particles? (in-flight or on the substrate?)

columnar structure

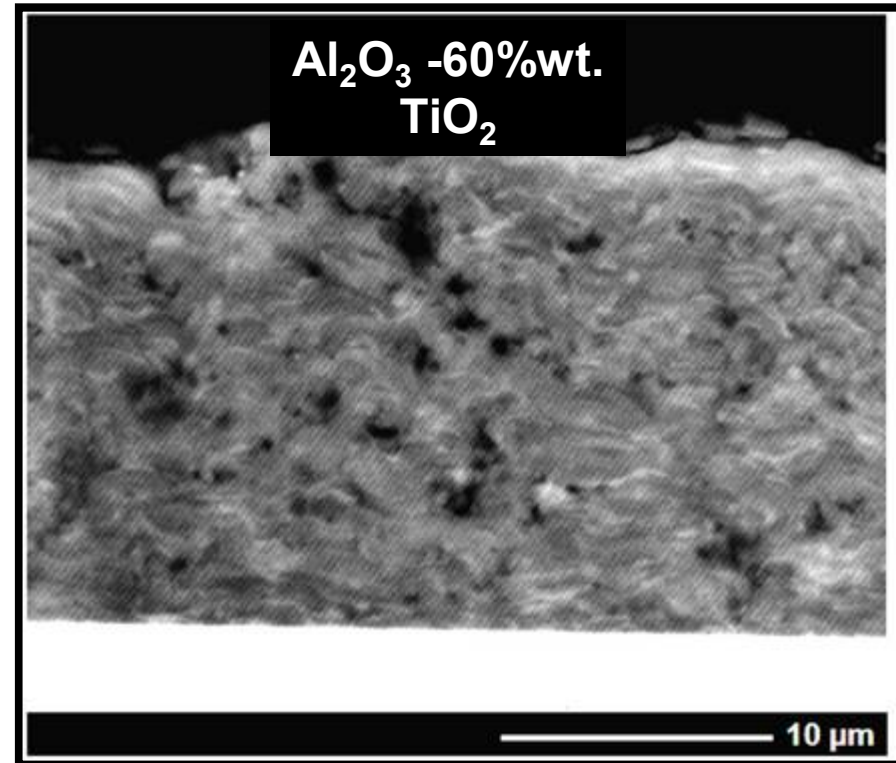
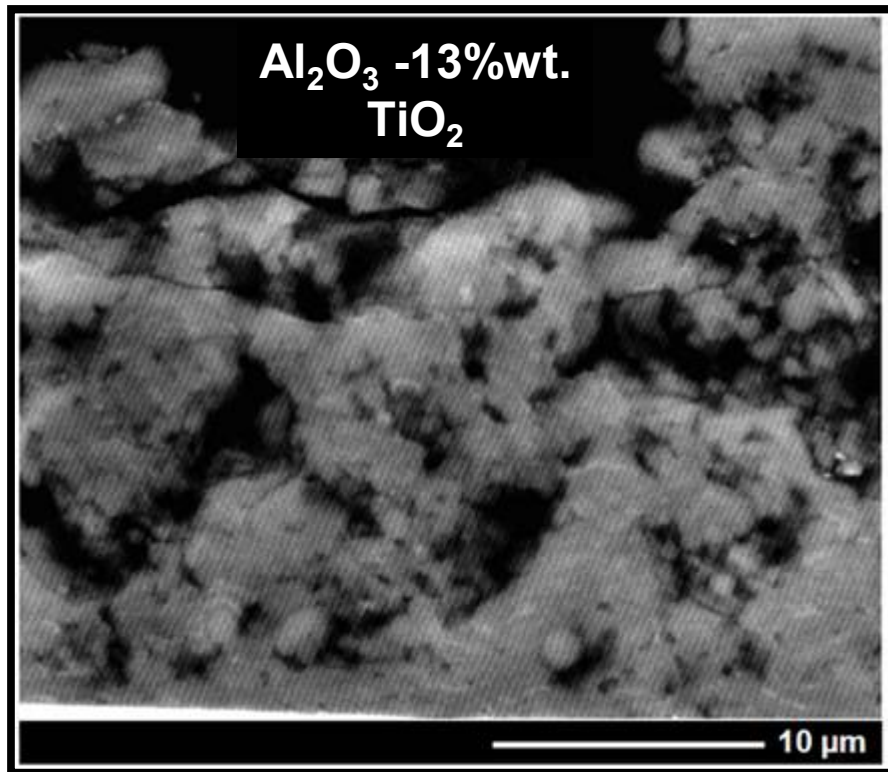
- a few hundreds of nanometers thick
- several particles stacked on top of each other
- continuous columns through lamellae

$\text{Al}_2\text{O}_3/\text{TiO}_2$ coatings

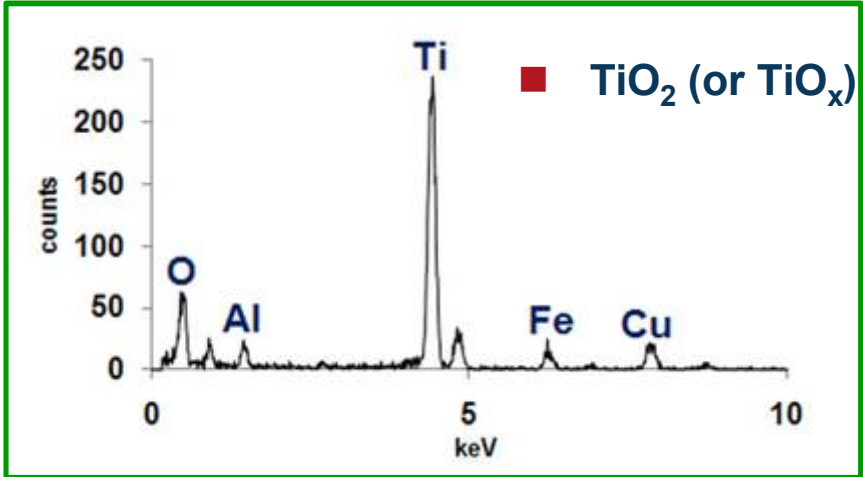
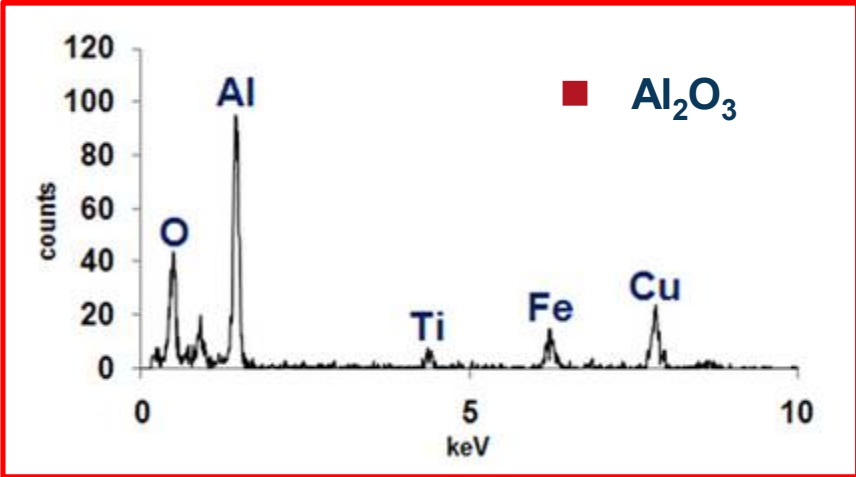
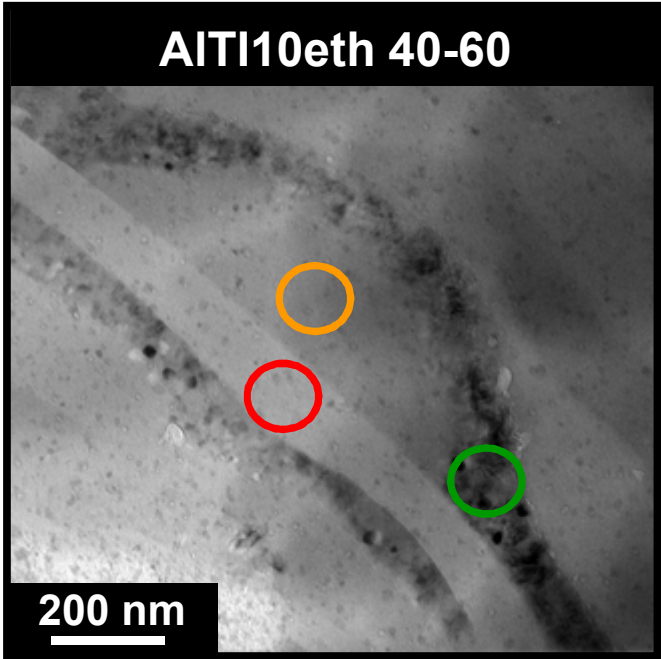
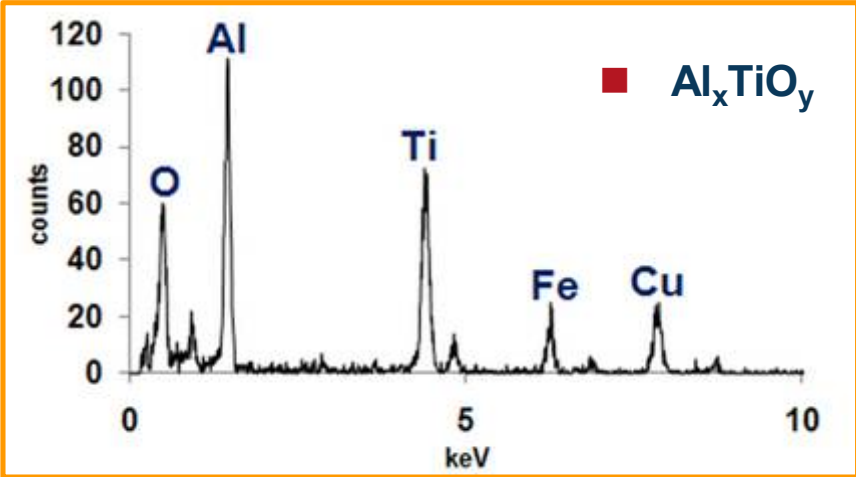
**BSE
microscopy**

- 20 kV
- WD = 10 mm

- grey: Al element
- white: Ti element

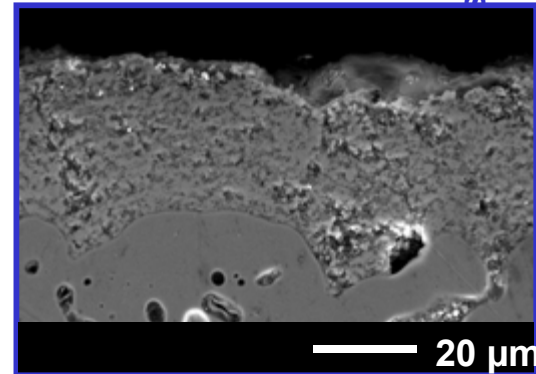
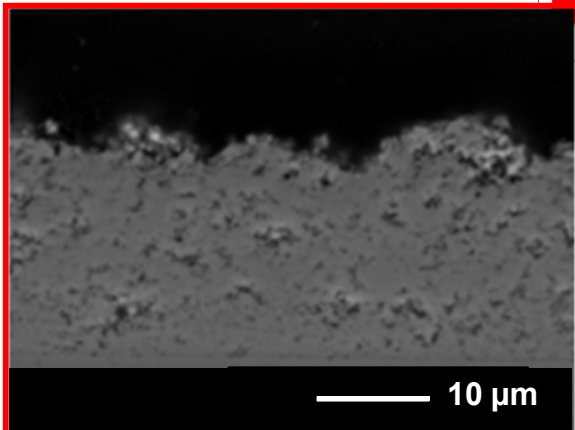
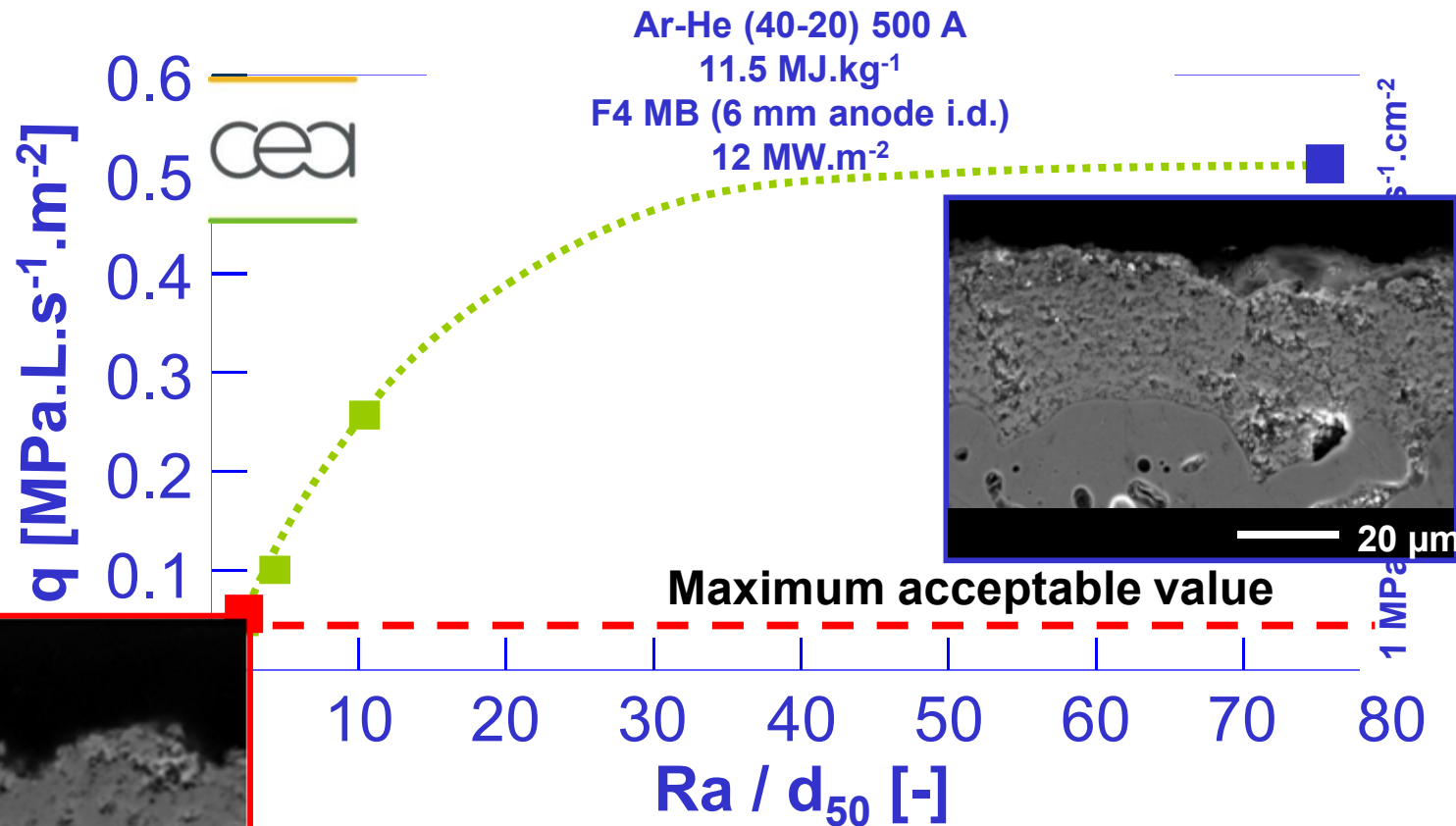


EDS analyses

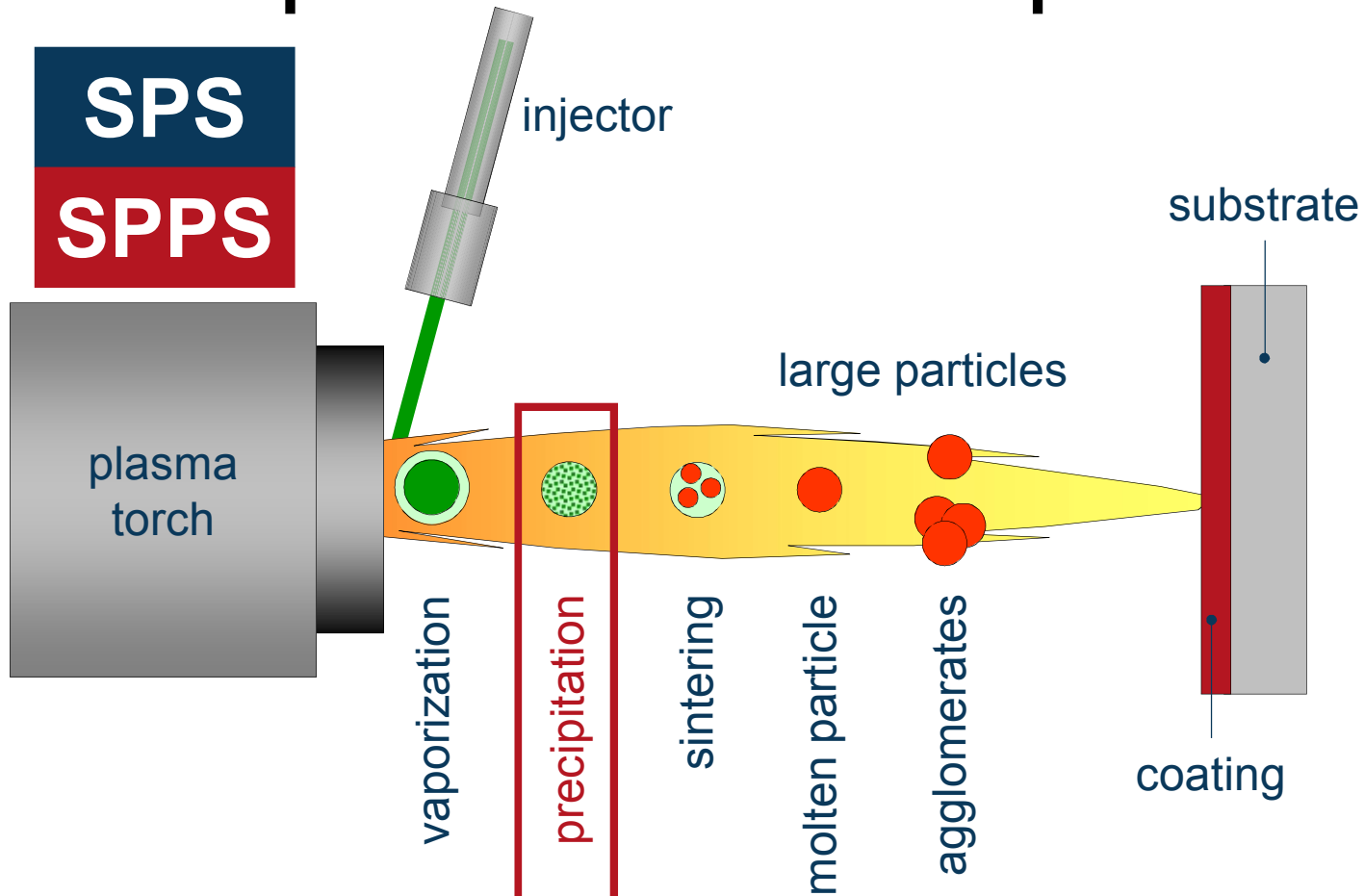


Gas permeability

Sulzer PTF4 plasma torch

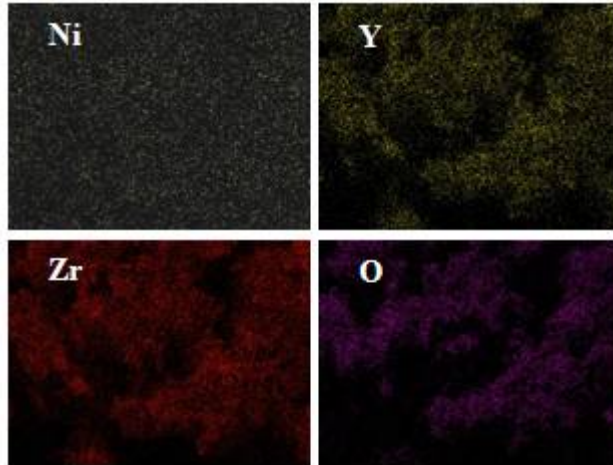
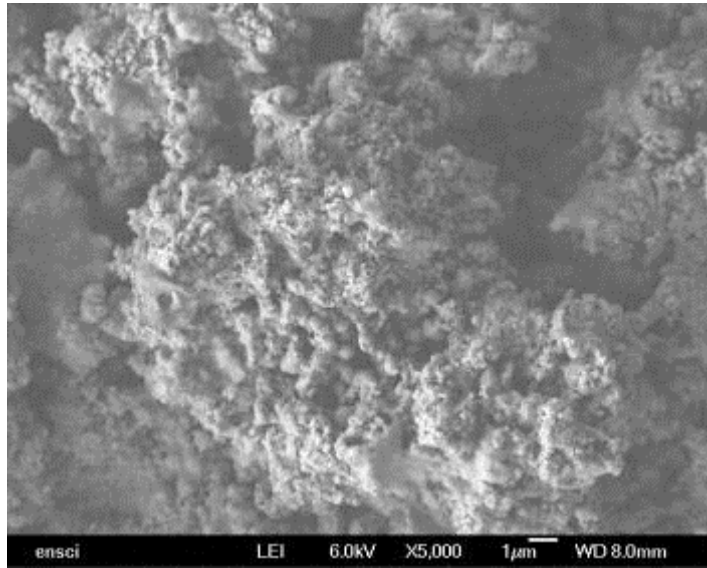


SPPS process / SPS process

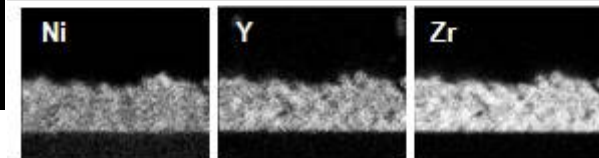
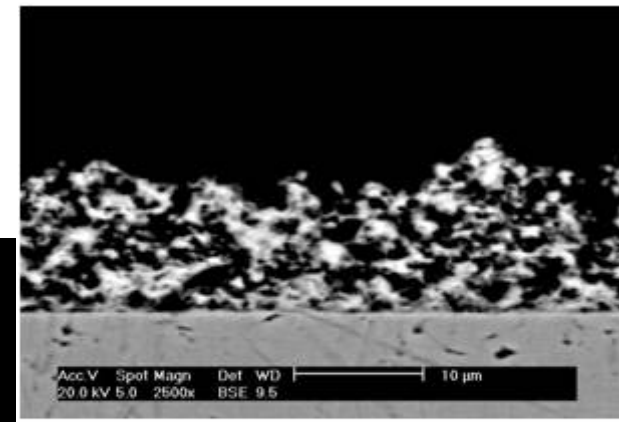
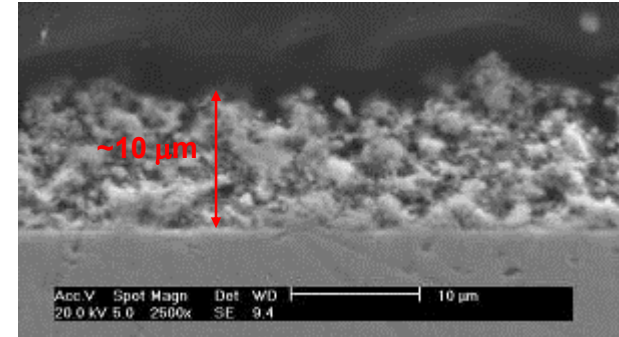


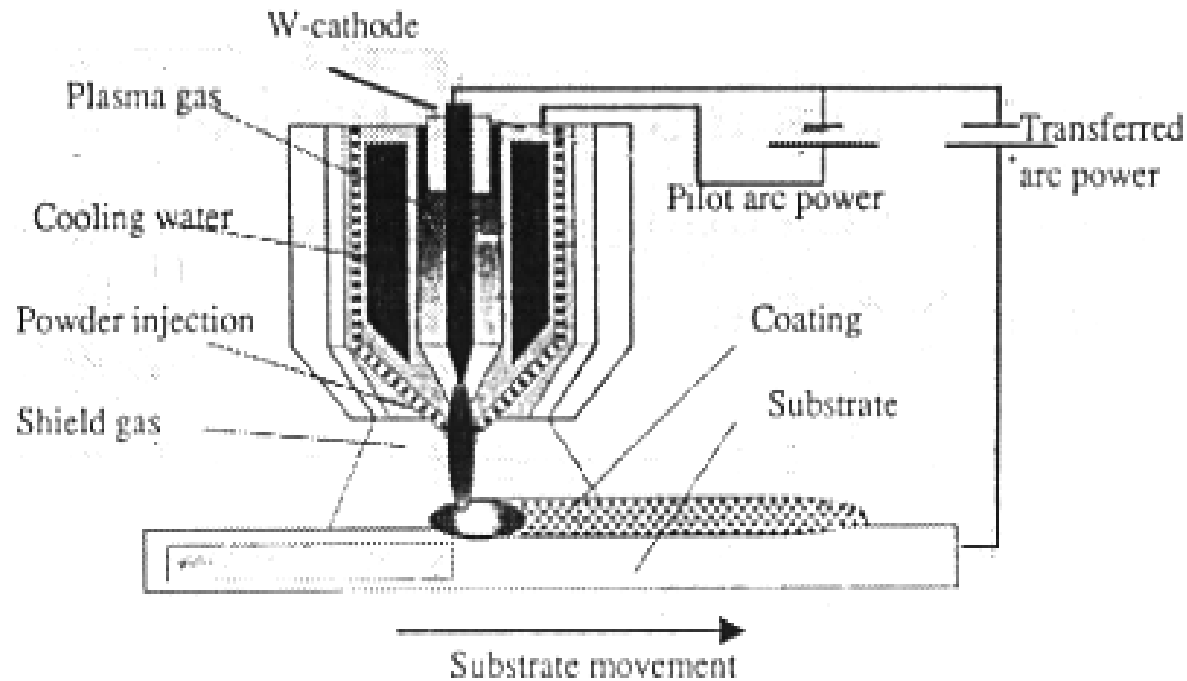
only in SPPS process where a chemical reaction takes place

SPPS: dissolved metallic salts



nickel VERY well dispersed in the coating

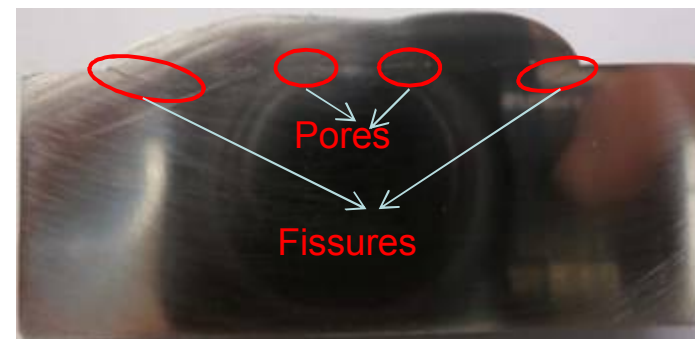
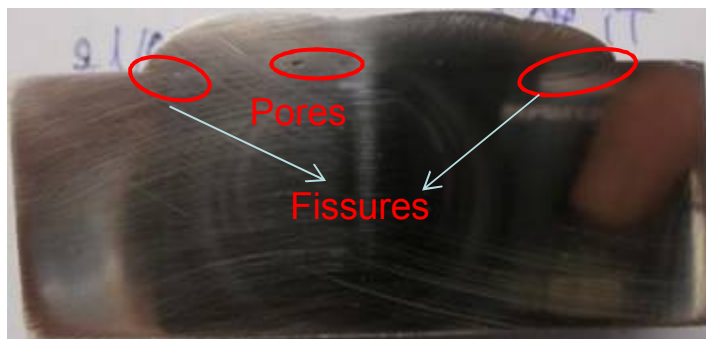
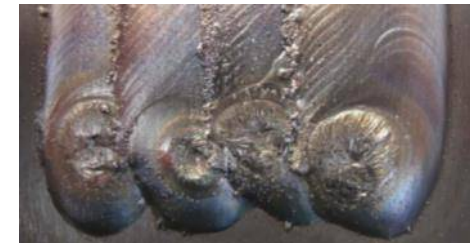
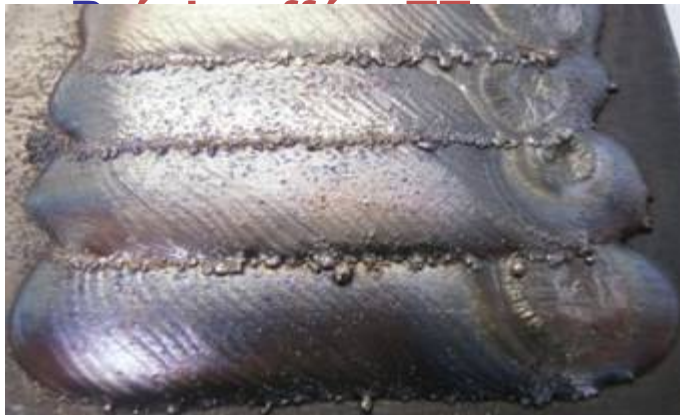


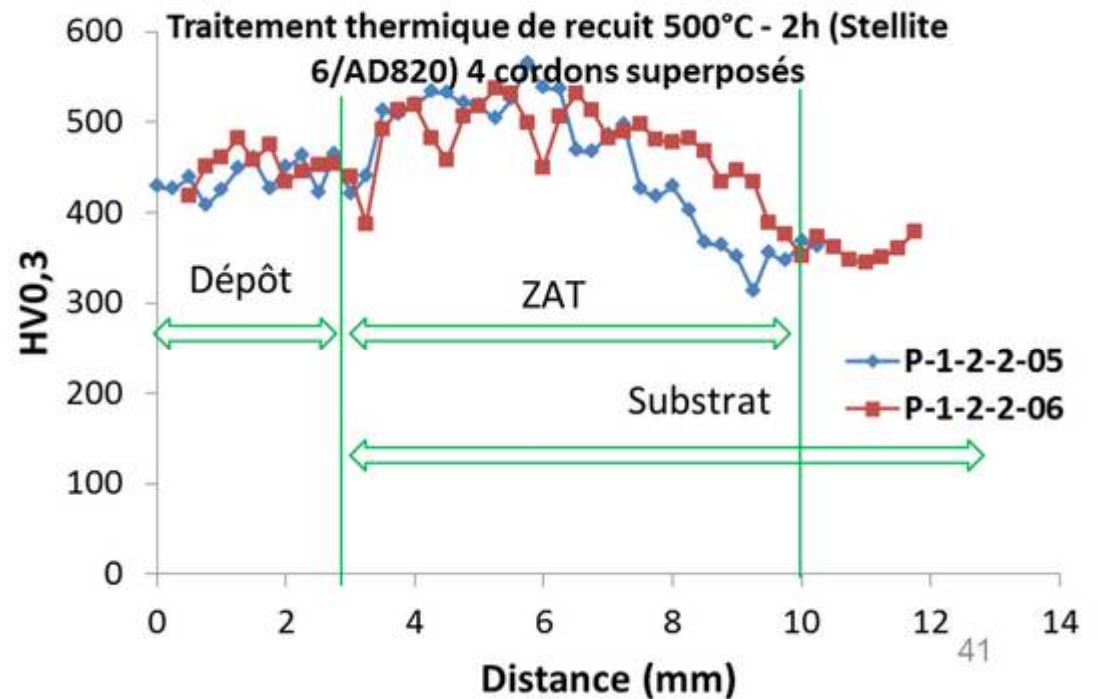
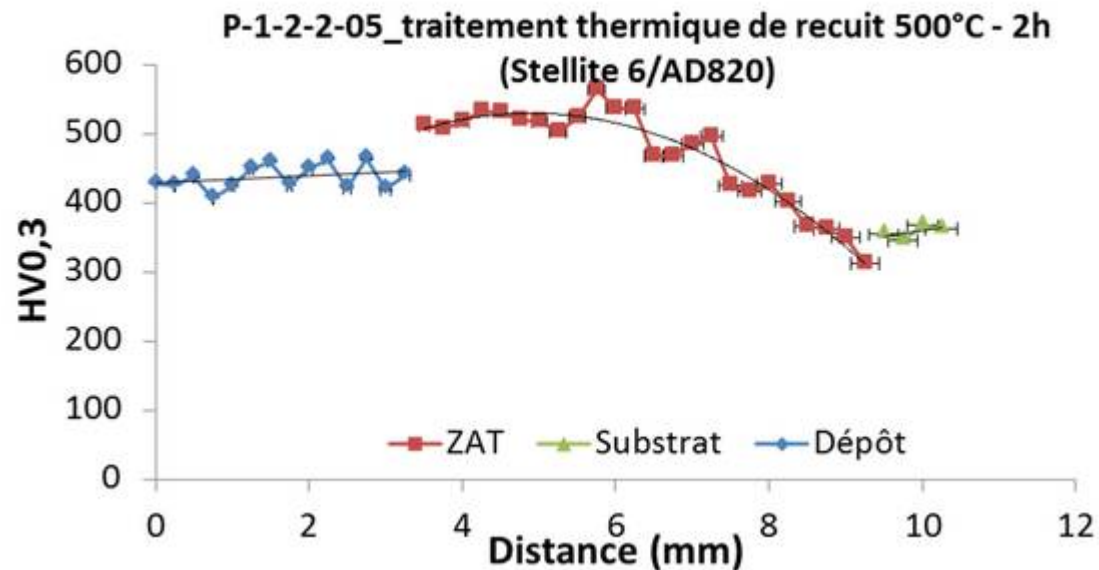


- Arc électrique transféré au substrat
 - chauffage maximum, fusion de surface
 - Arc pilote pour amorçage, stabilisation de l'arc
 - évite le refroidissement violent de l'arc par la poudre
- Injection de la poudre dans l'arc ou sur le substrat, fusion avec le substrat
 - liaison métallurgique
- Matériaux sous forme de fil, fil fourré, baguette
- Fort taux de dépôt 6 kg/h

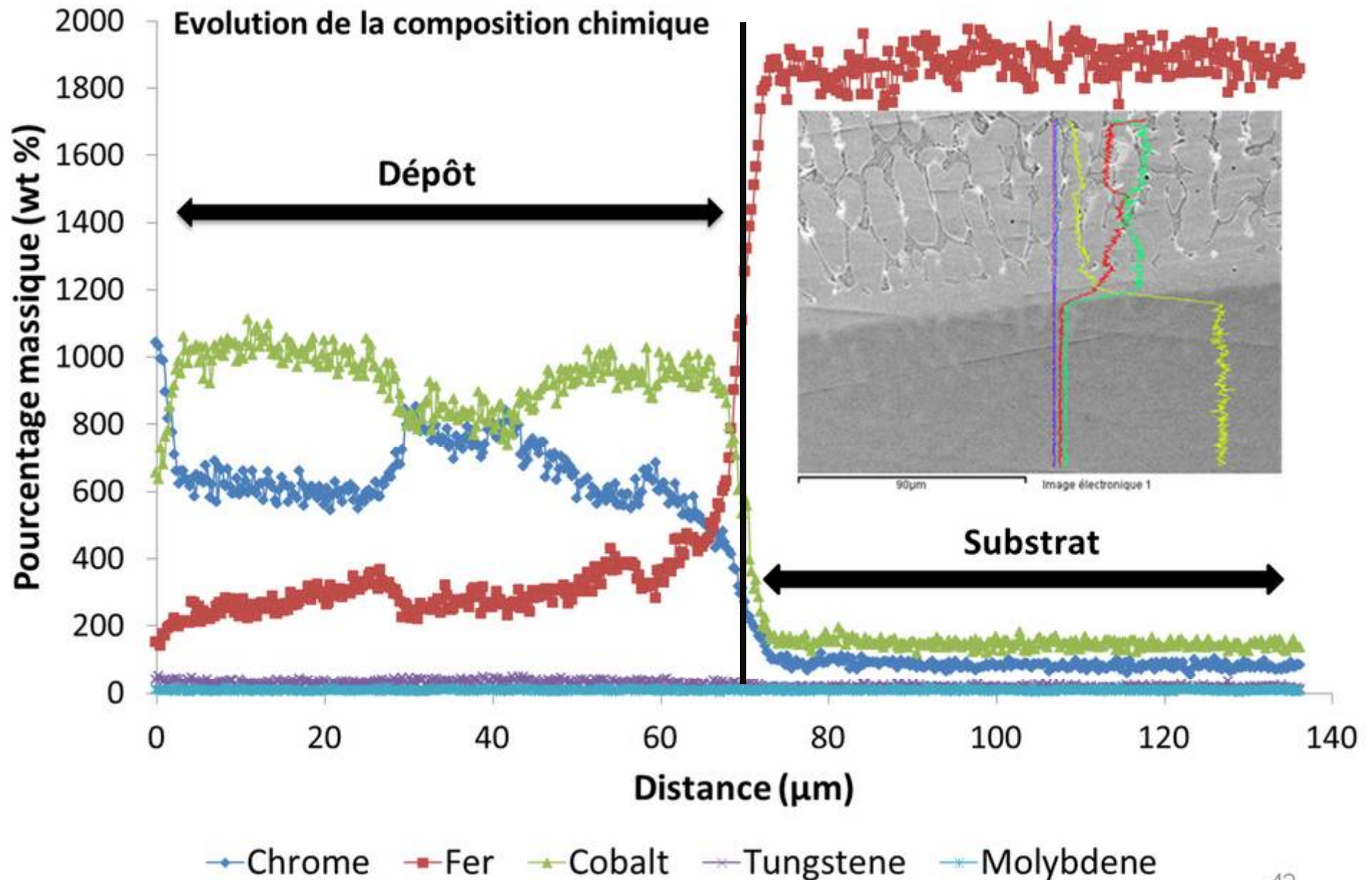
Exemple 3 - Dépôts PTA Stellite 6 – Aspect cordons

Substrats : 8 (21-03-2013) AD820 P-1-2-2-07 (50x50x23 mm) (n° 1007) –



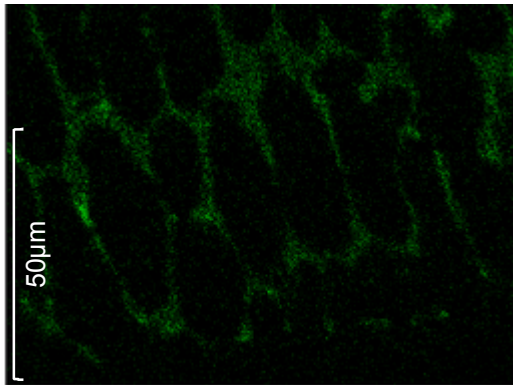
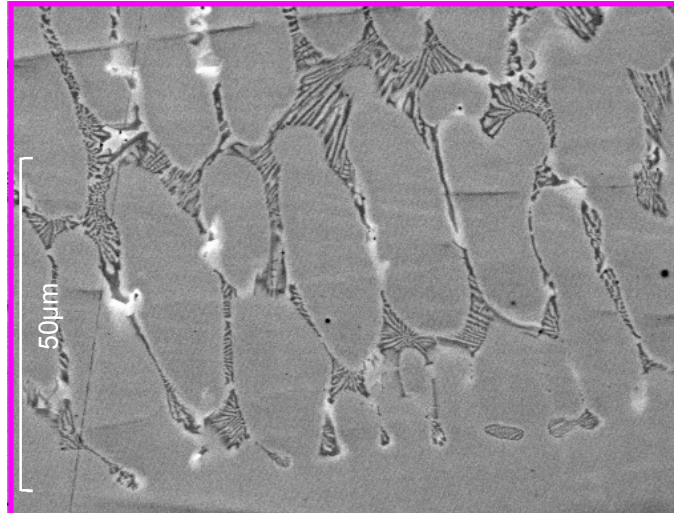


P-1-2-2-06

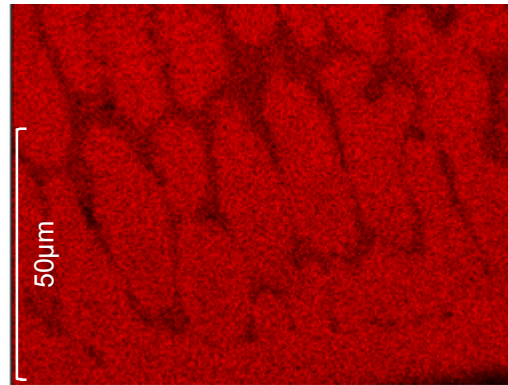


P-1-2-2-06

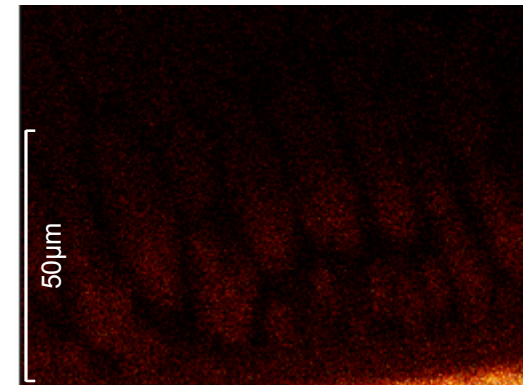
Cartographie éléments – zone diffusion



Cr Ka1 *

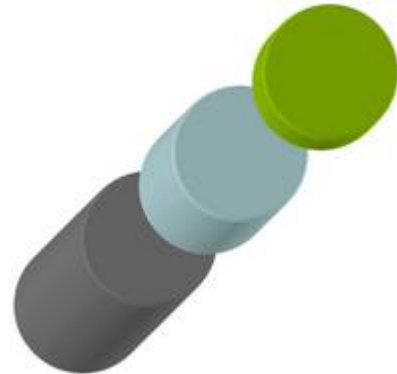


Co Ka1



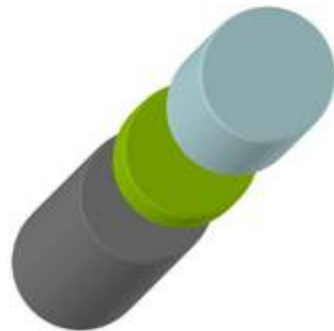
Fe Ka1

Duplex substrat-APS-PECVD : l'élaboration ne pose pas de problème ; étude de la porosité interconnectée



Duplex substrat-PECVD-APS : optimisation du film PECVD pour adhésion de la couche APS sur substrat poli

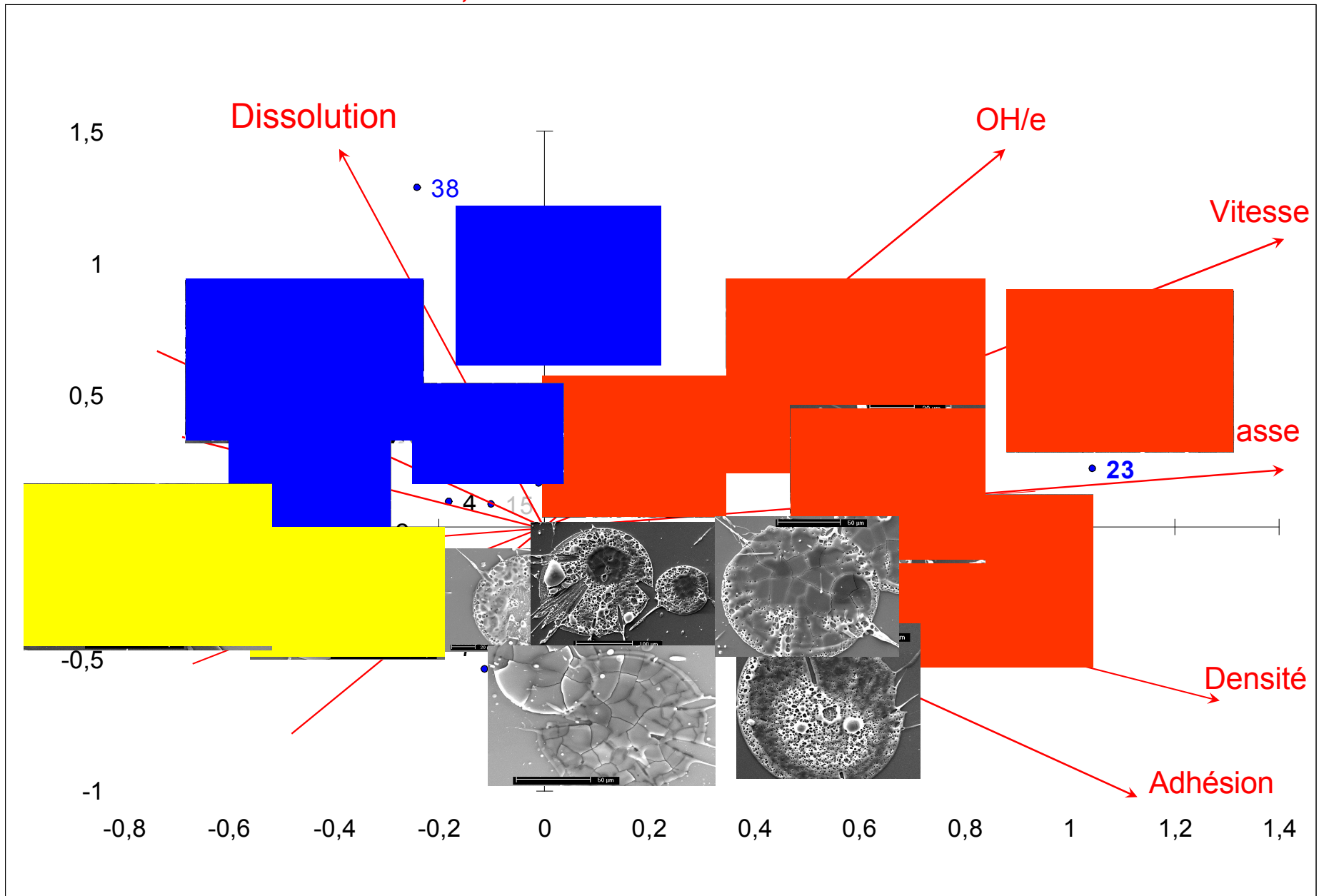
✓ Etude de l'interface : alumine PECVD – alumine APS



✓ Ecrantage du substrat

ACP : propriétés des films / morphologie des splats

En collaboration avec S. KARAM, A. BESSAUDOU - IRCOM





50 μm

Lamelle d'alumine sur une couche d'Alumine déposée par PECVD