

Alain DENOIRJEAN

Chargé de Recherche CNRS

**Section 10
INSIS**



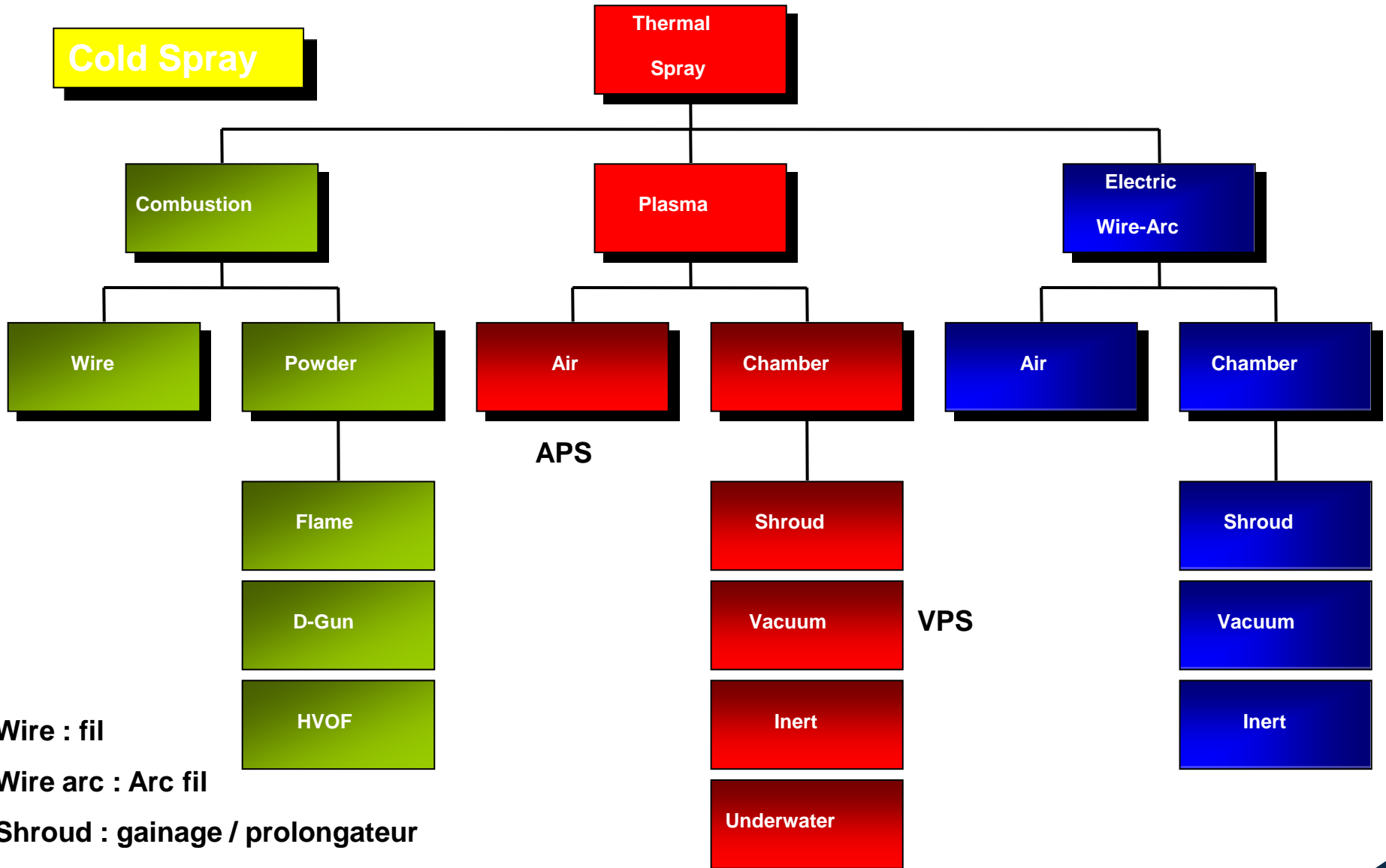
UMR CNRS 6638

**Dépôt par projection à plasma d'arc de poudres,
suspensions, solutions**

Architecture et propriétés fonctionnelles



Différents procédés de projection thermique utilisés dans l'industrie



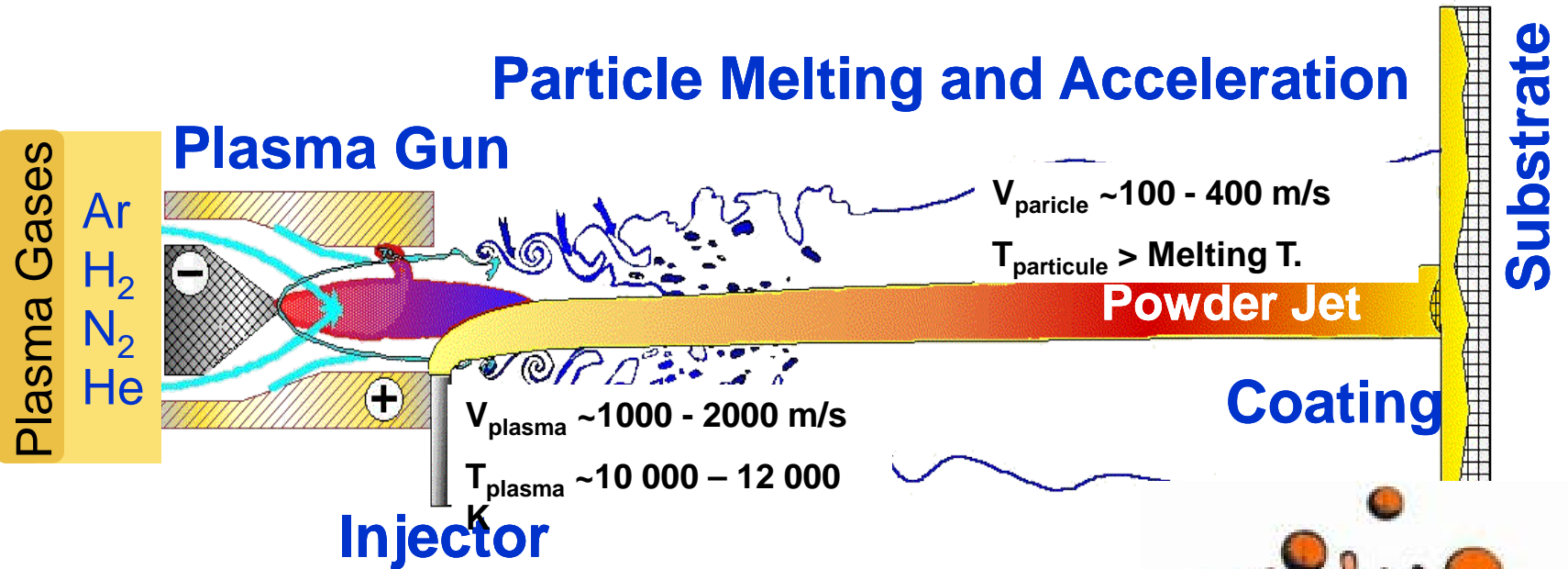
Wire : fil

Wire arc : Arc fil

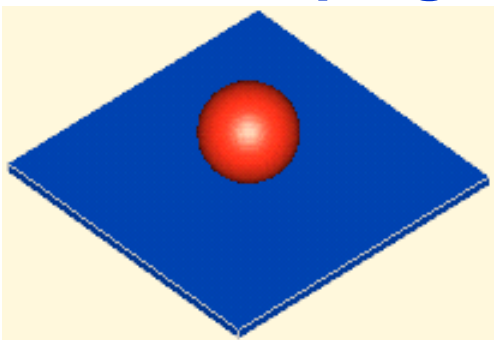
Shroud : gainage / prolongateur

Powder : poudre

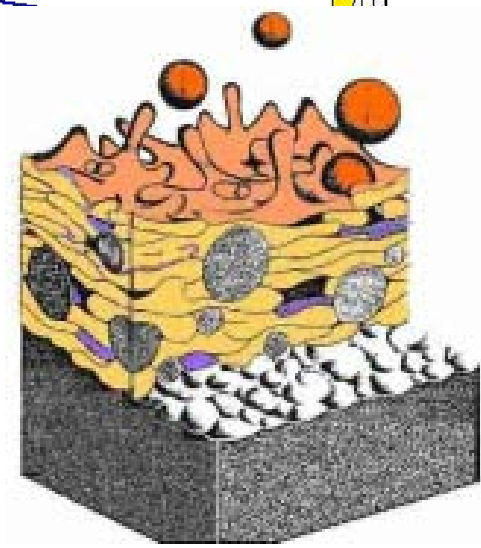
Introduction – Thermal Plasma Process




Particle Impingement



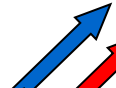

Splat Layering



Procédé de projection à la flamme oxyacétylénique

glaze powder 

substrate
(thermally sensitive)

oxygen 
acetylene 

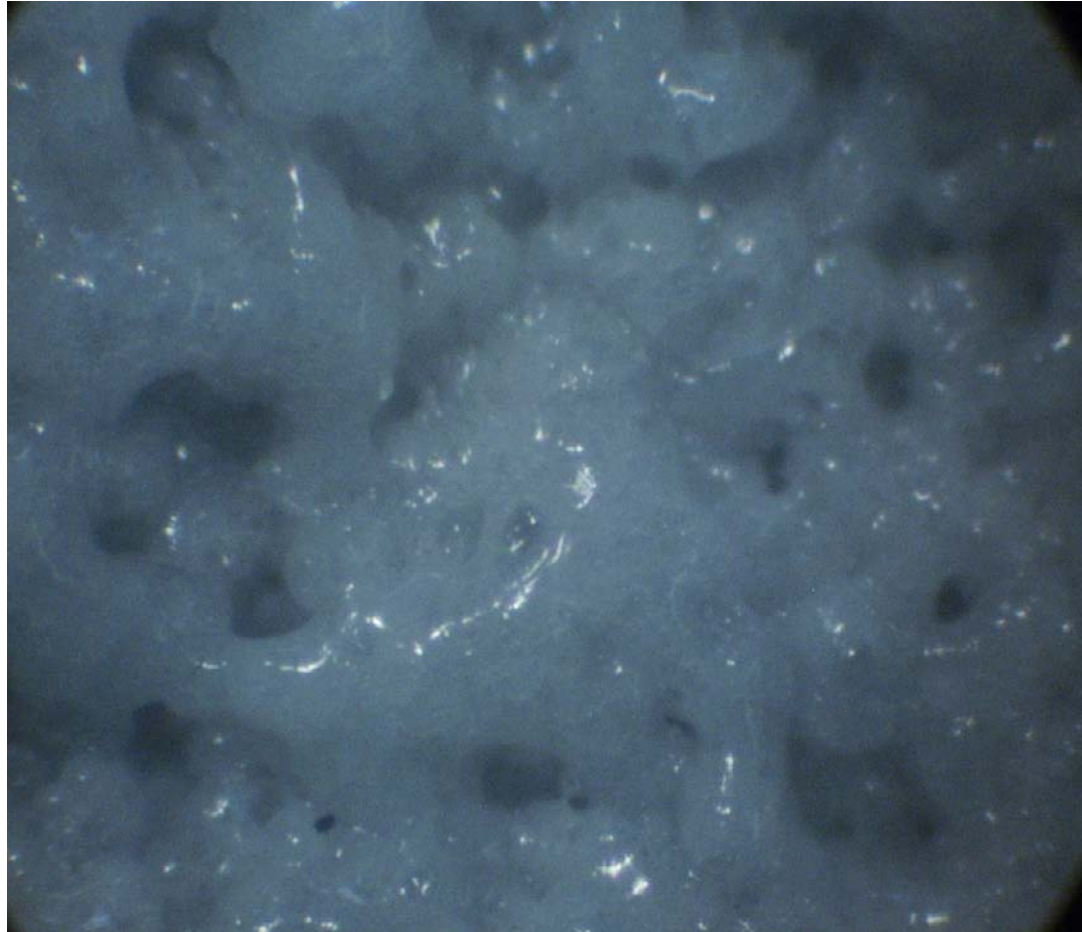
glaze coating

very large areas

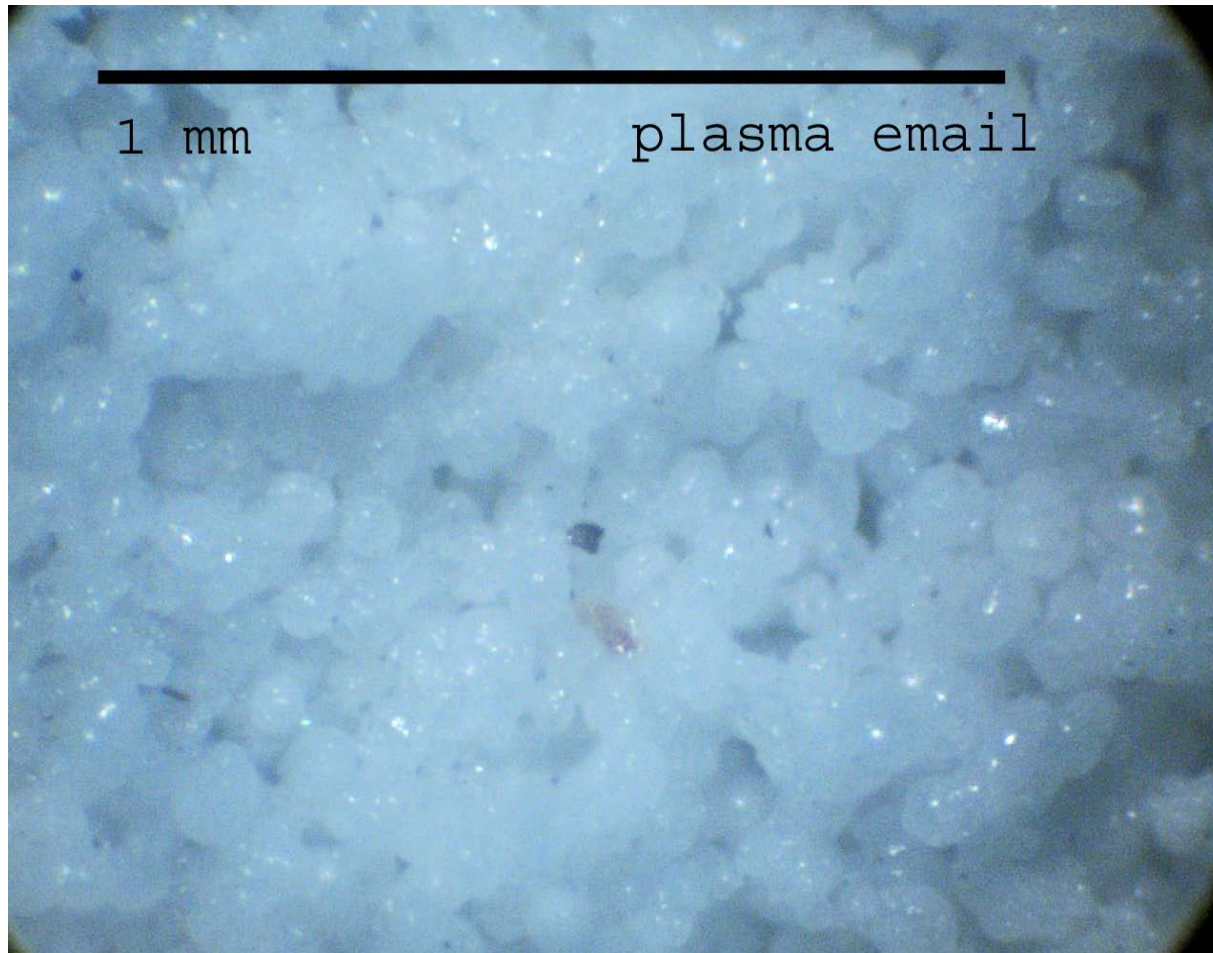
feedstock rate $\sim 3 \text{ kg.h}^{-1}$

low operating costs compared to other spraying techniques

Flamme silico-alumineux



Plasma silico alumineux structure poreuse



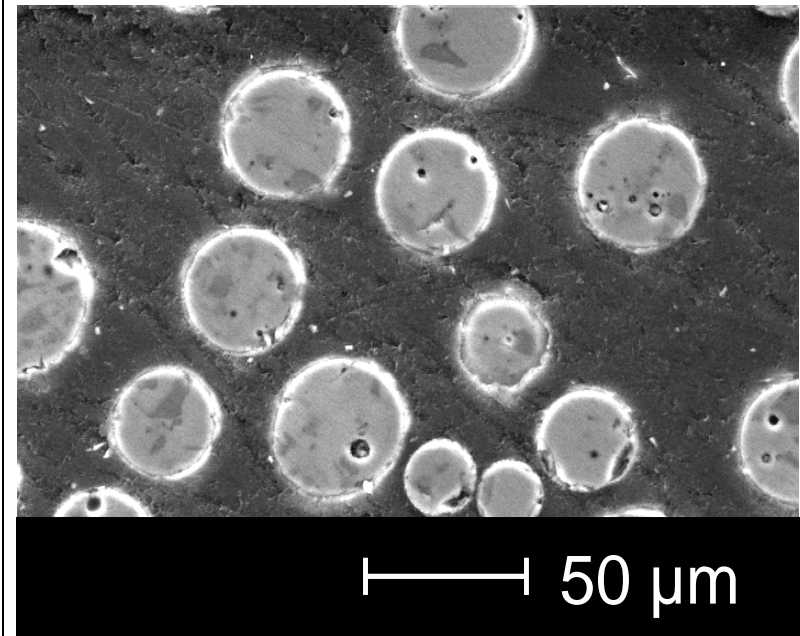
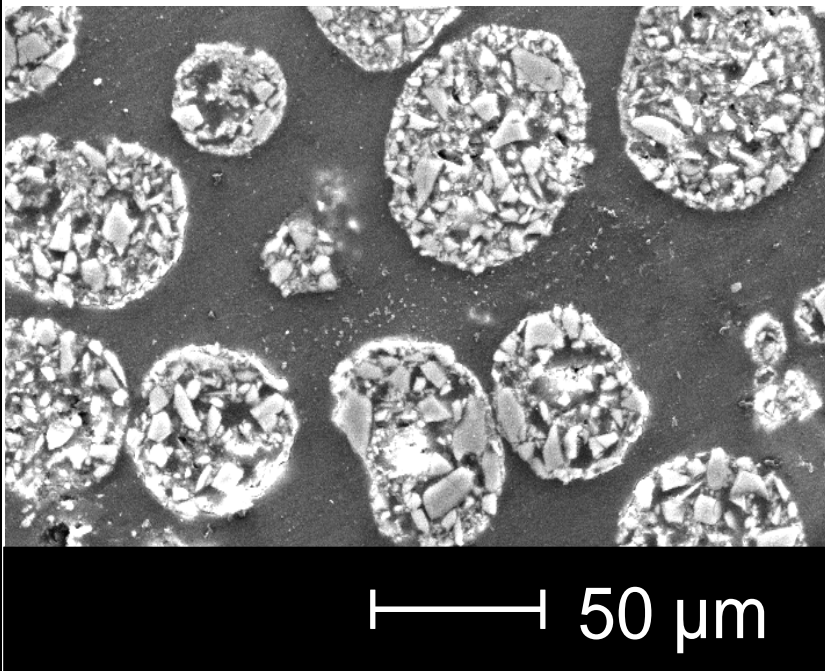
Optimisation de la poudre

- Composition spécifiquement mise au point par Imerys (propriétés physiques adaptées)

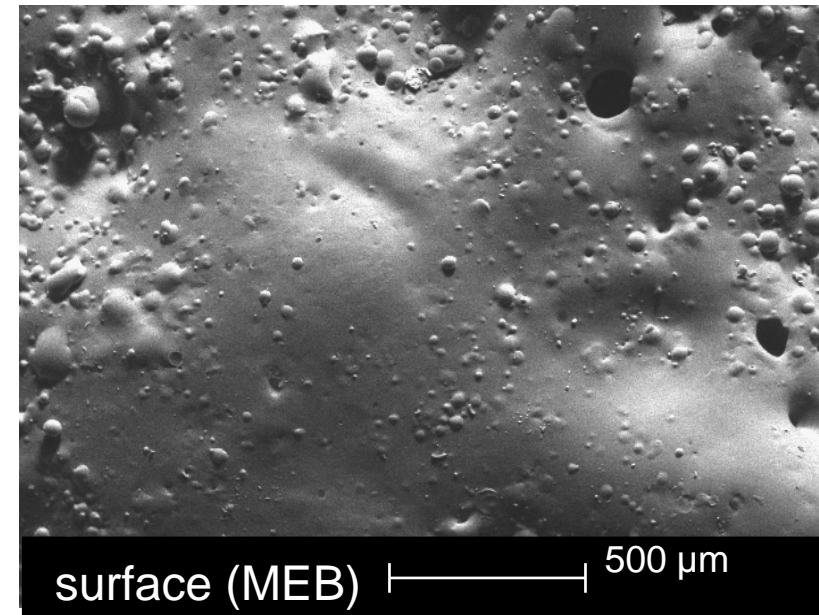
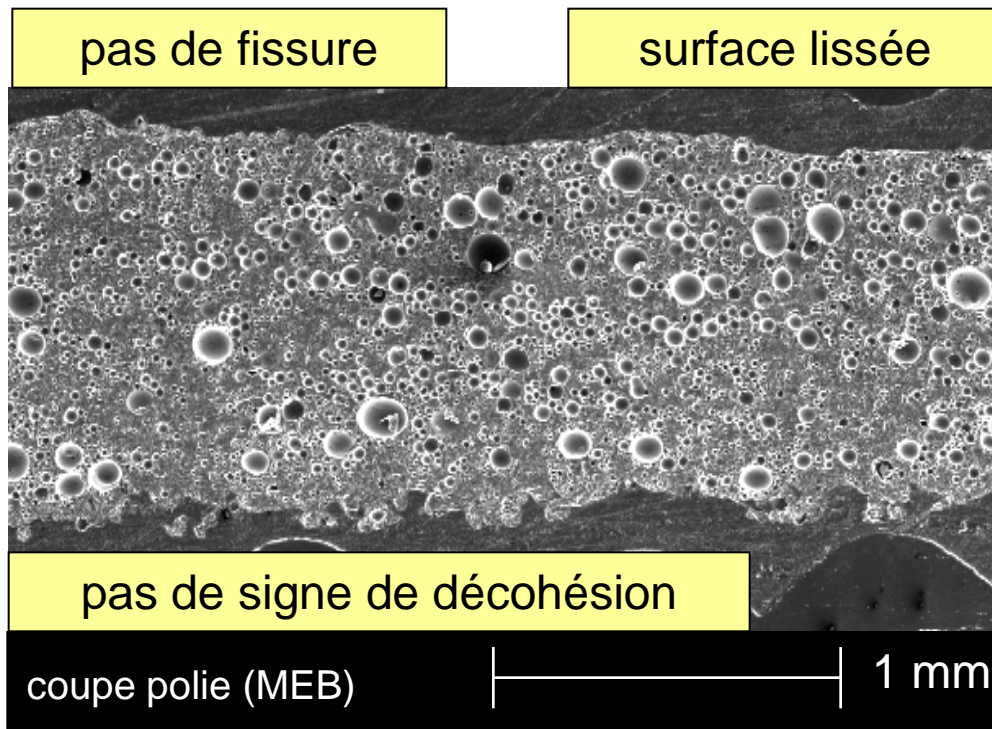
- Grains pré-densifiés à la flamme oxy-acétylénique



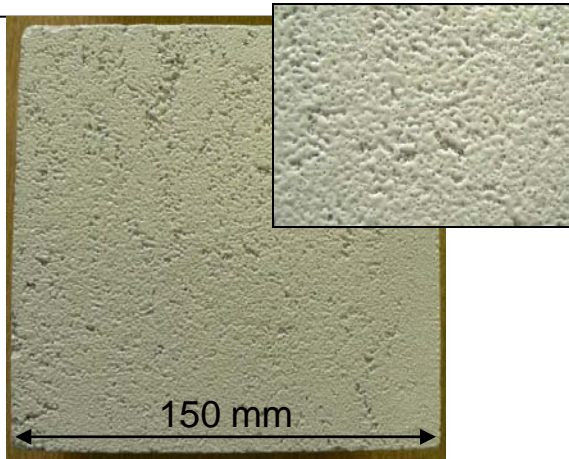
flamme $O_2-C_2H_2$



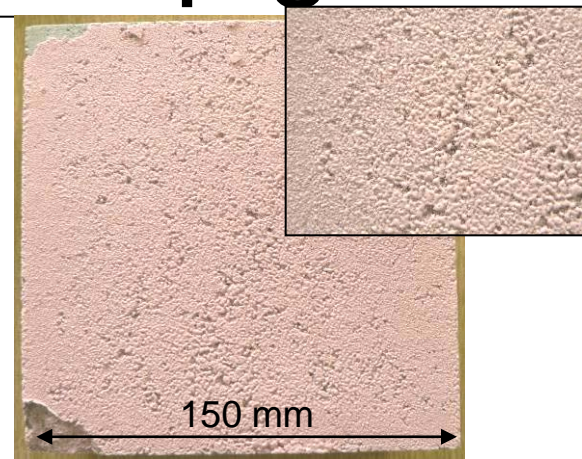
Optimisation des paramètres de projection-structure typique des dépôts



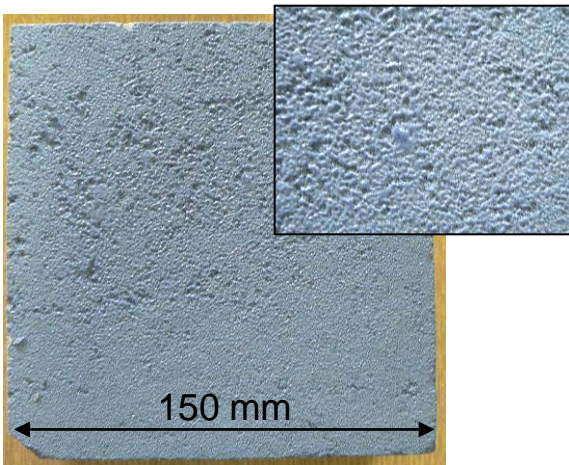
Surfaces de dépôts pigmentés



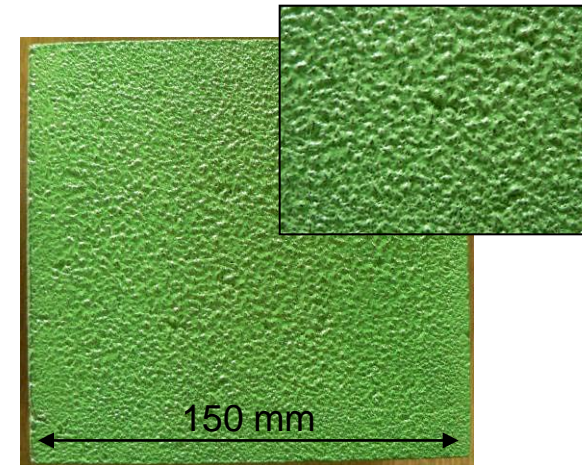
poudre optimisée



ajout de pigment rose

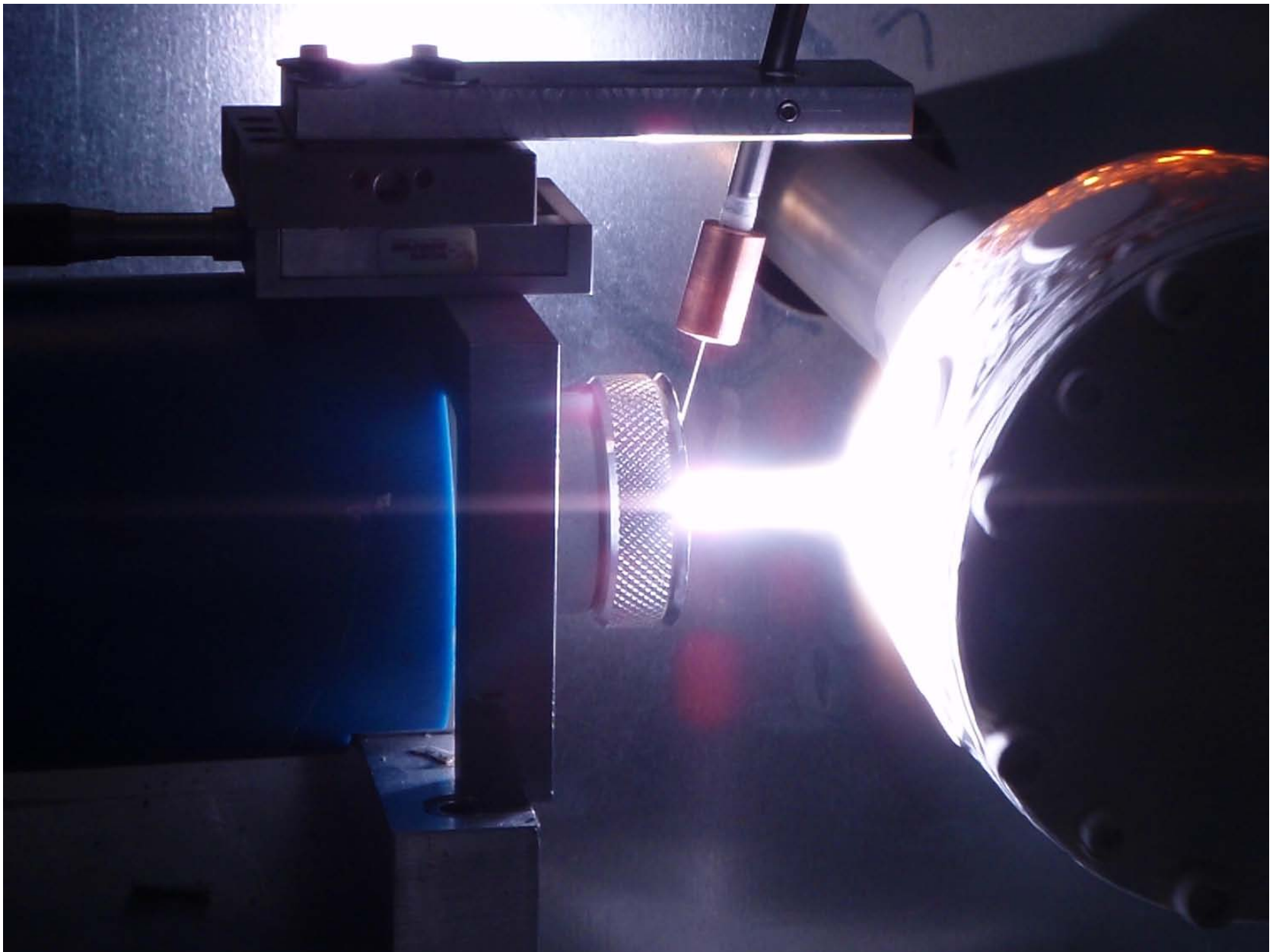


ajout de pigment bleu



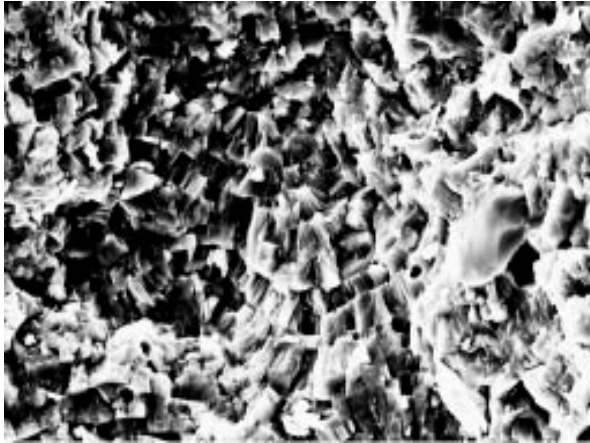
ajout de pigment vert





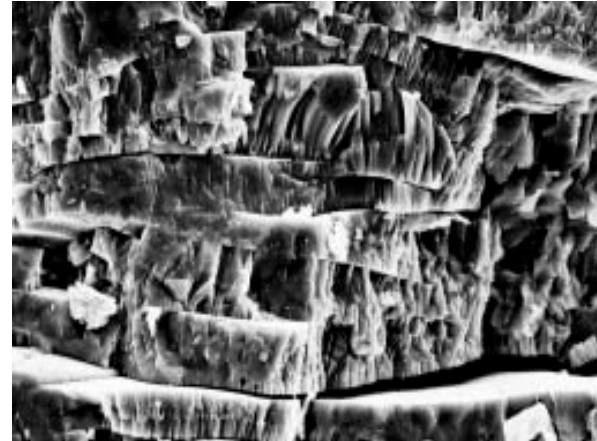
Exemple de dépôts

Dépôt conventionnel



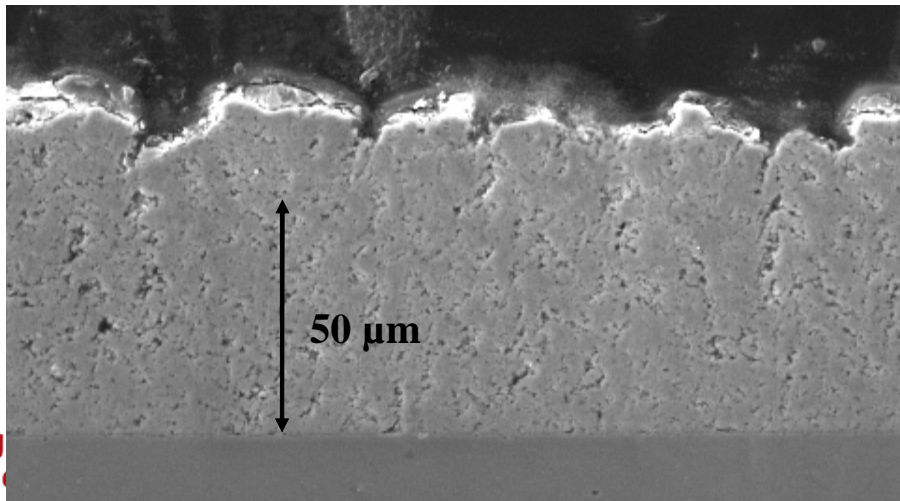
TiO₂

D.C. plasma spraying 10 μm

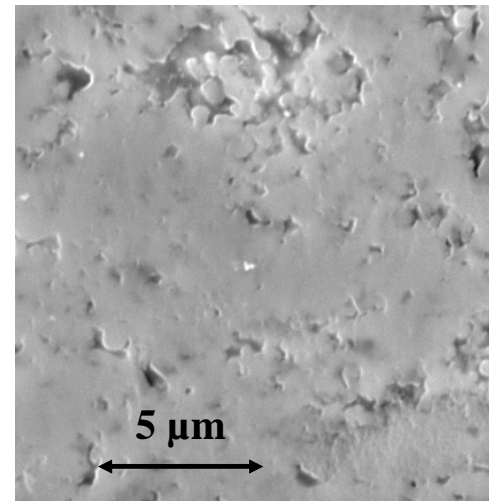


R.F. plasma spraying

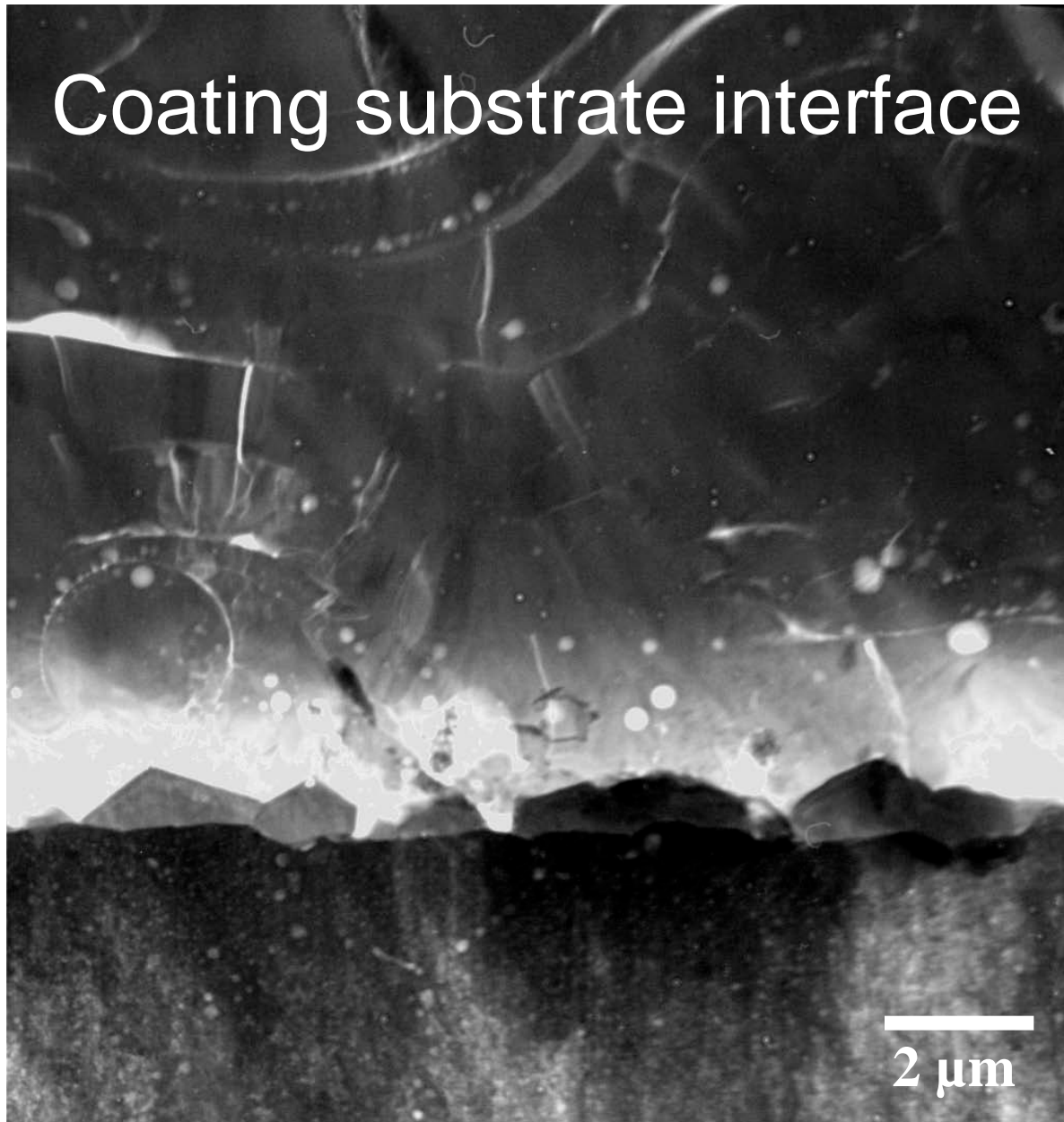
Dépôt Nanostructuré



ZrO₂



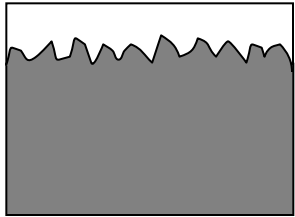
Coating substrate interface



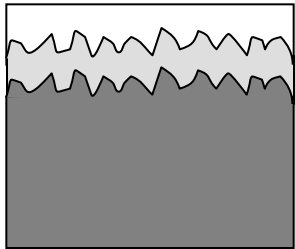
Which coating adhesion mechanism ?



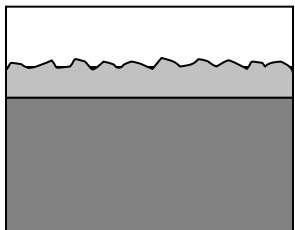
Ra ~ 0,06 μm 0 MPa
T < 100 C



Ra ~ 5 μm (RT ~ 50) 20 MPa Mechanical
T < 100 C



Ra ~ 5 μm 55 MPa Mechanical + Interfacial ?
T = 350 C



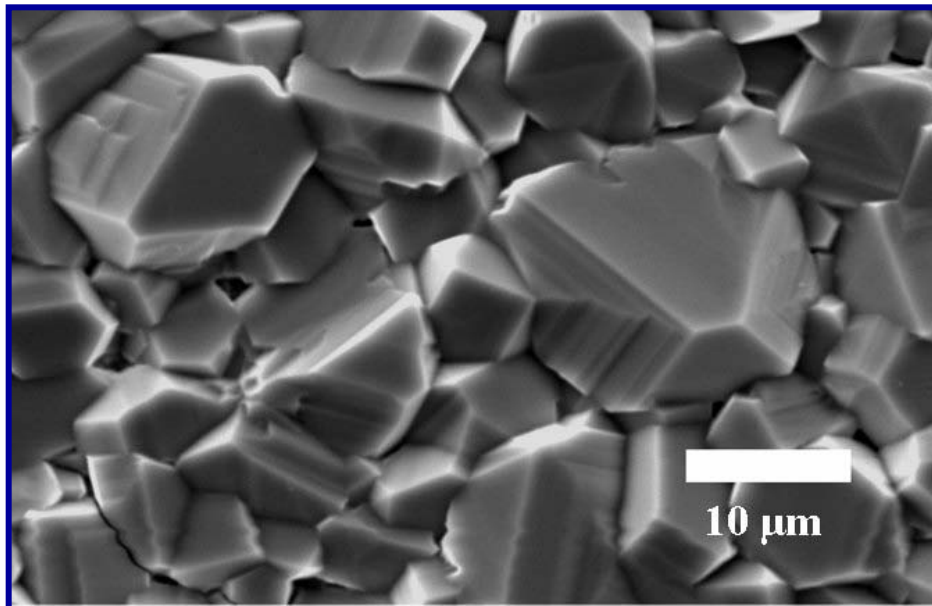
Ra < 1 μm > 55 MPa Interfacial – Mechanical ?
T = 350 C

Optimum preoxidation treatment

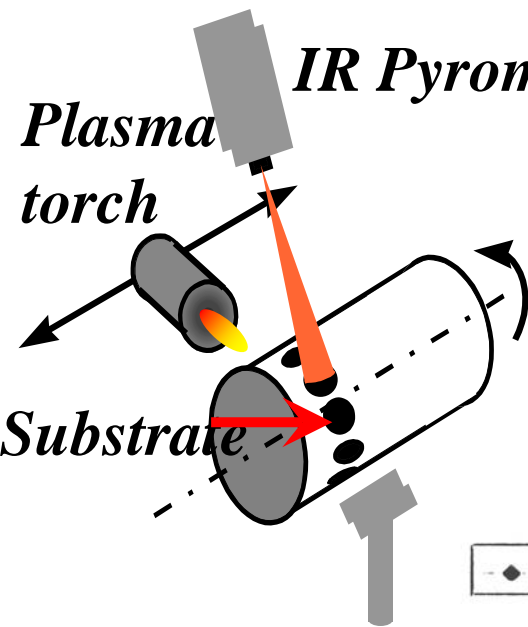
High pressure: $P_{\text{CO}_2} = 10^5 \text{ Pa}$

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

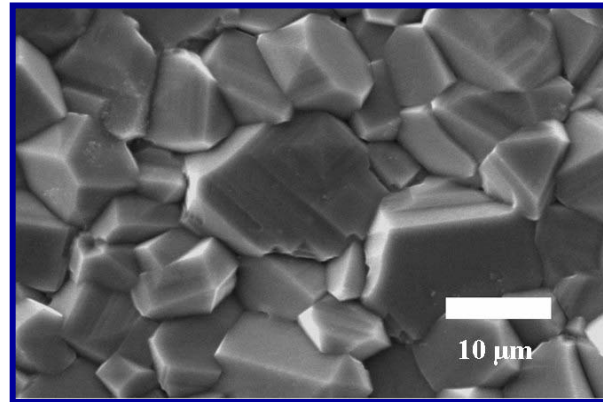
High Temperature: $T = 1000 \text{ C}$



Plasma preheating

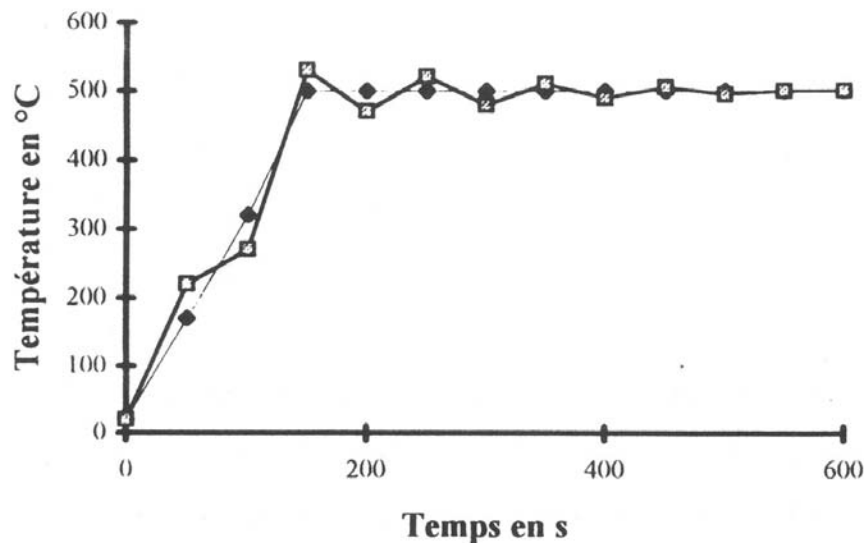


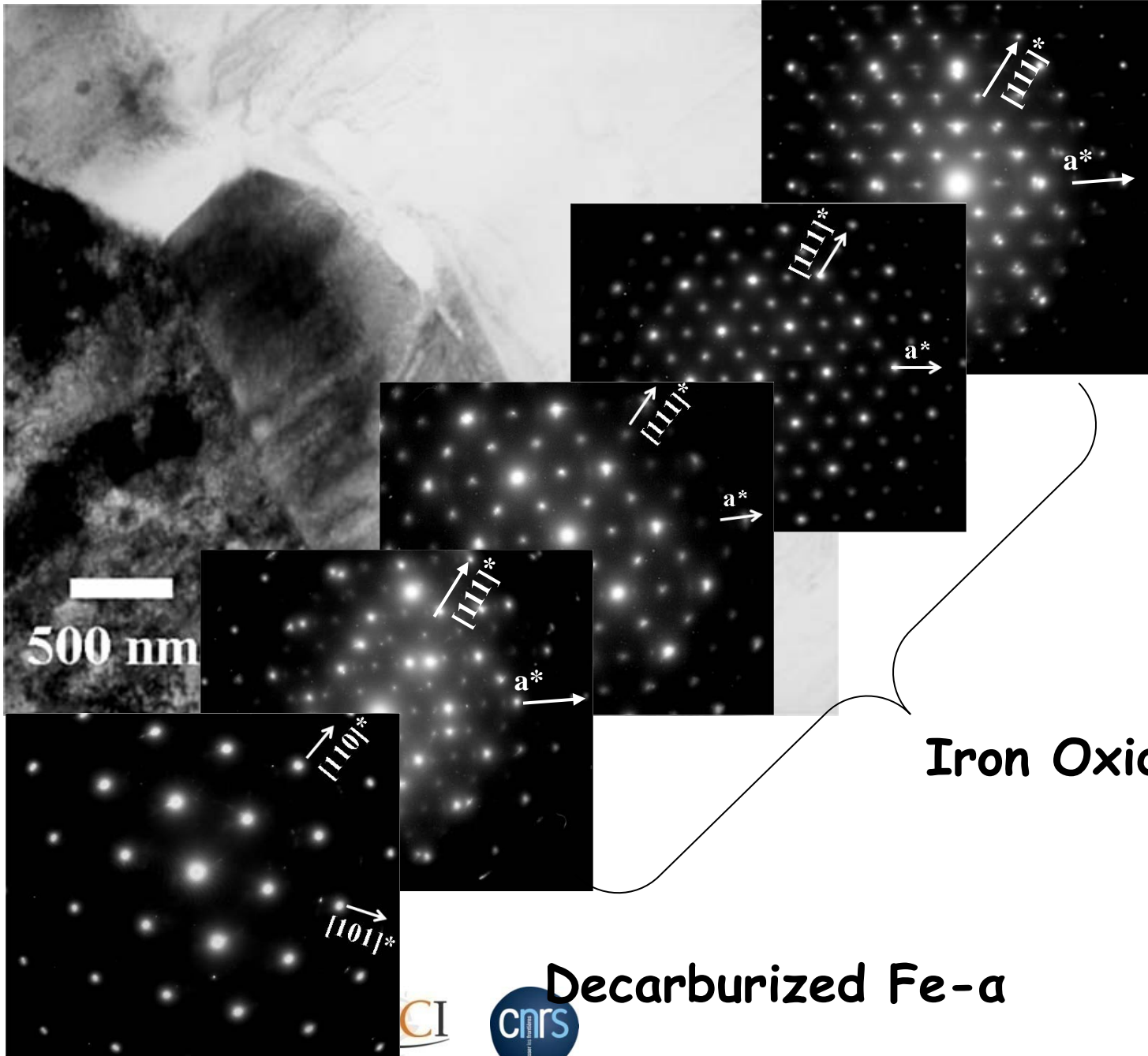
Preheating 1min 30 – 350 C



Plasma gas	Ar / H ₂
Gas flowrates (l/min)	45 / 15
Arc current (A)	550
Voltage (V)	52
Stand off distances (mm)	100
Preheating T (C)	350
Carrier gas flowrate (l/min)	5,5

—●— Courbe de consigne —■— Courbe expérimentale





γ Alumina

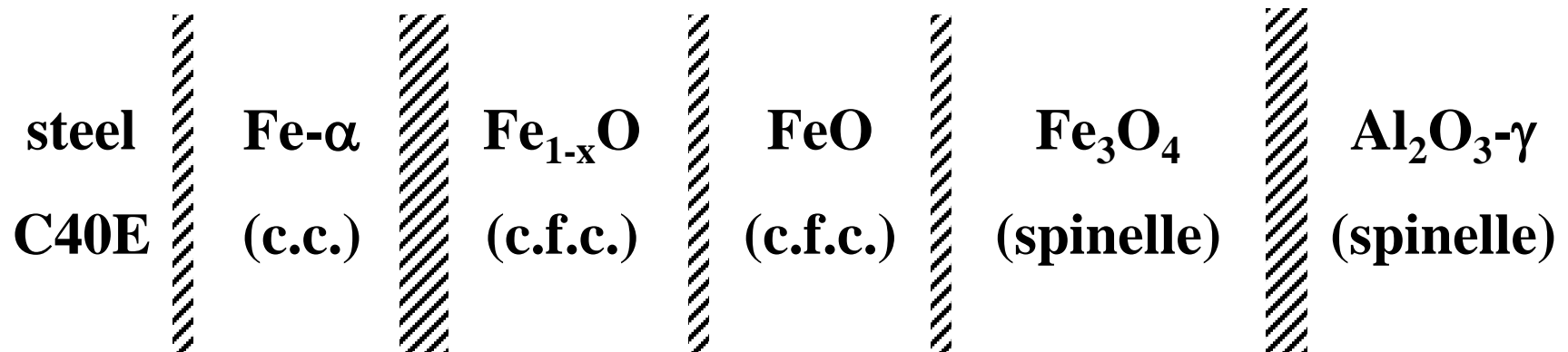
Iron Oxides

Decarburized Fe-a

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

Continuity of the cristal network

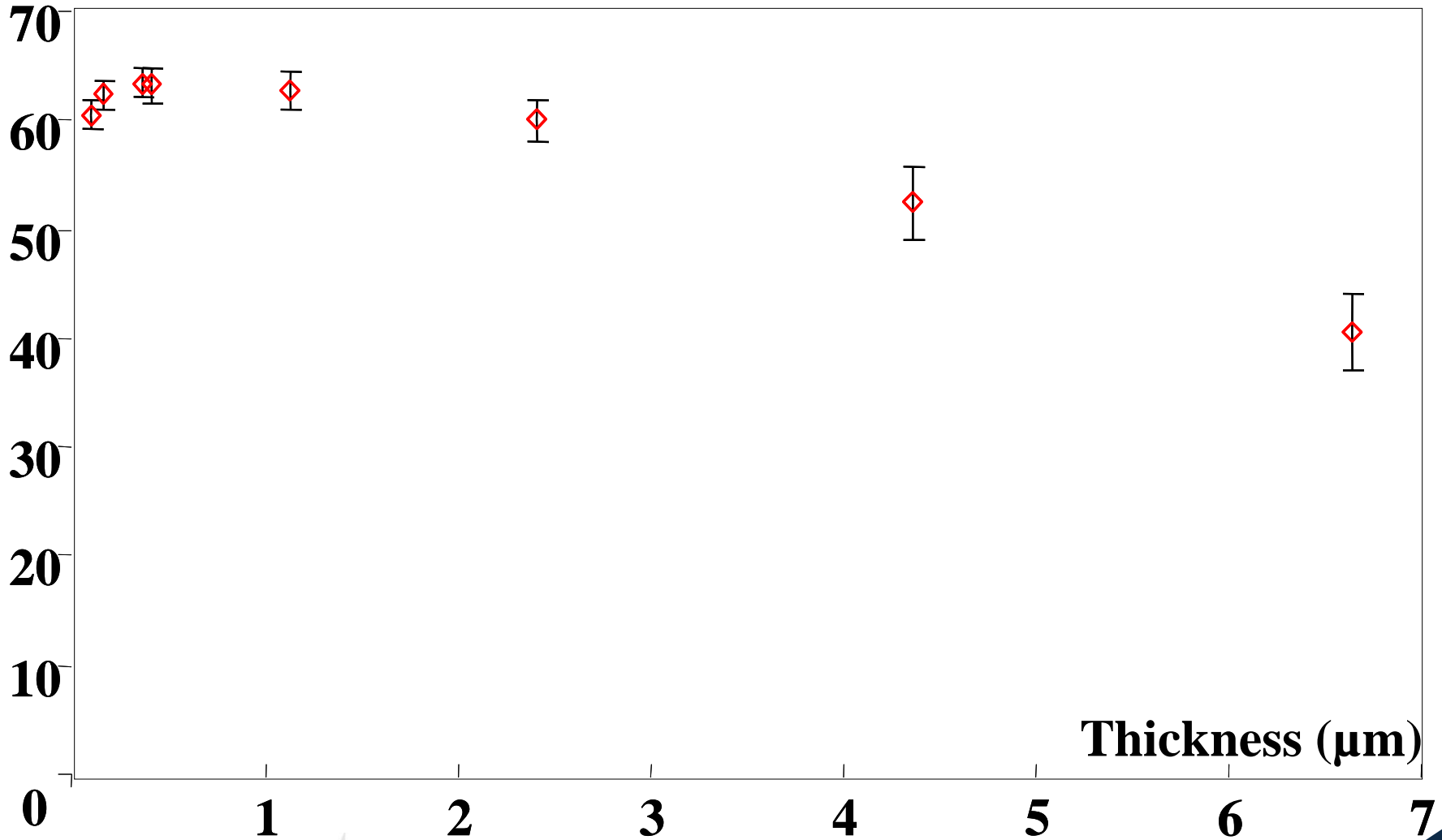
- physical-chemical adhesion



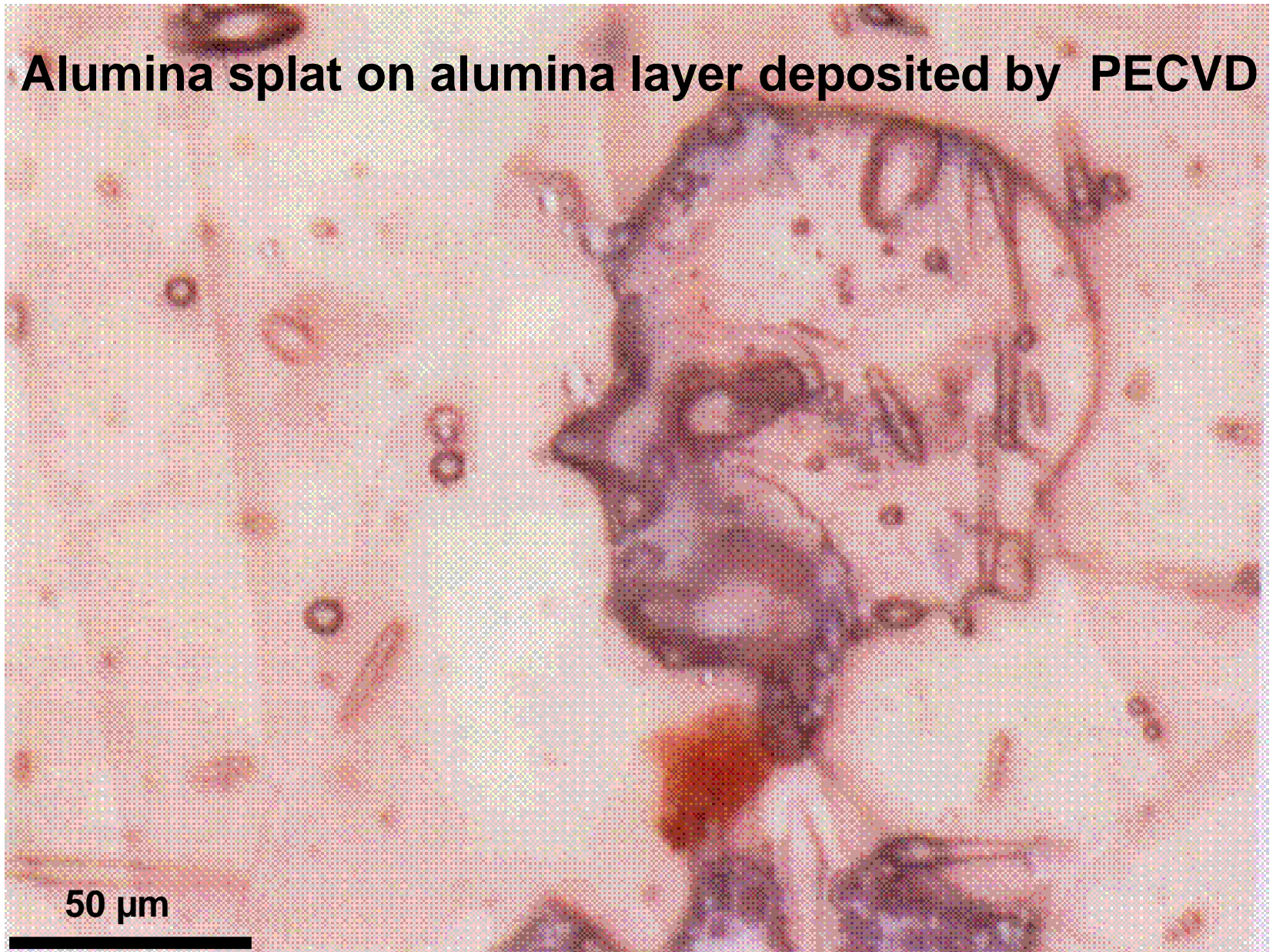
←—————→
homoaxial Heteroepitaxy

Preheating in furnace under CO₂ atmosphere

Adhesion (MPa)



Alumina splat on alumina layer deposited by PECVD

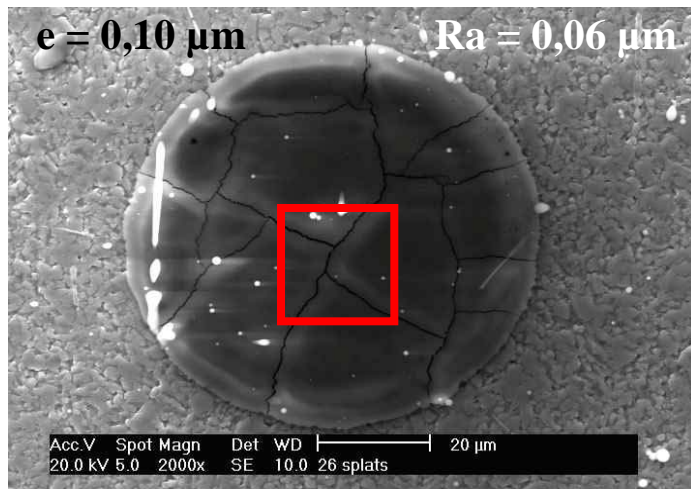


Alumina splat morphologies on oxidized metallic substrates (APS)

Microstructure
et nanostructure
of alumina
lamellae



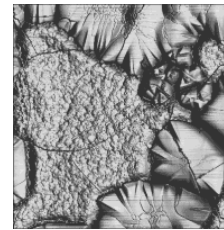
Surface state in
contact with



AL₂O₃ ON 304L SUBSTRATE

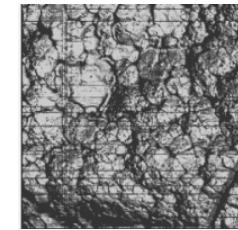
Area with
bad contact

27.5 μm



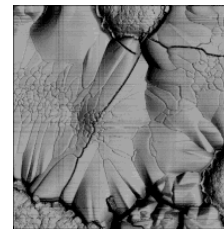
Area with
good contact

3 μm



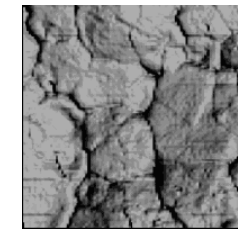
General view

15 μm

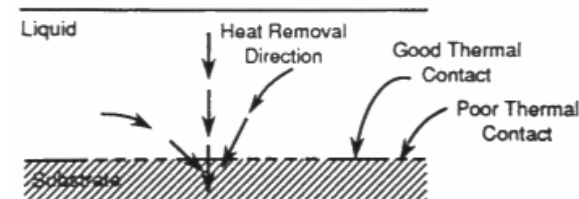


Detail of big cristal

1 μm

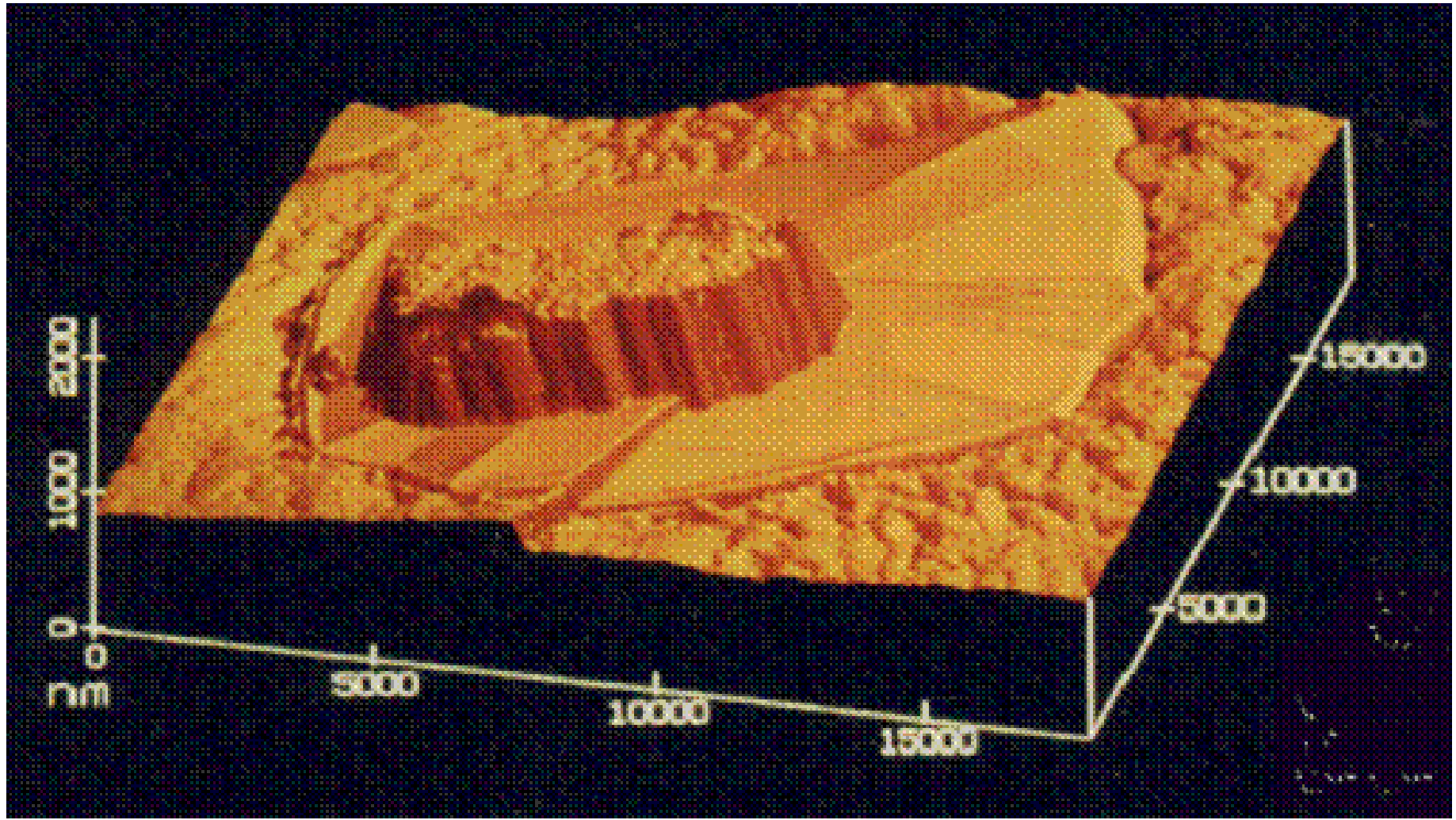


detail of columnar structure


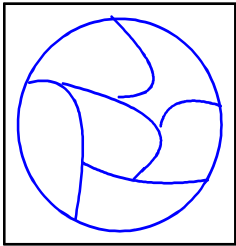
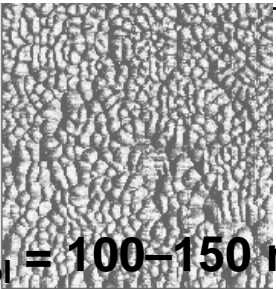
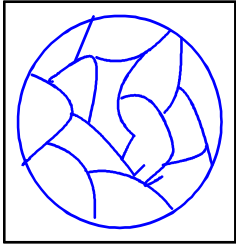
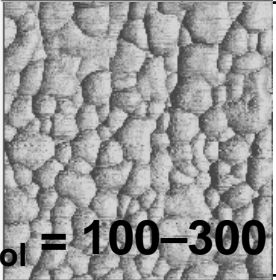
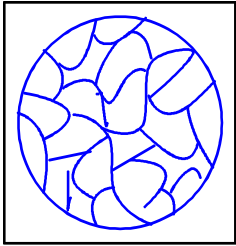
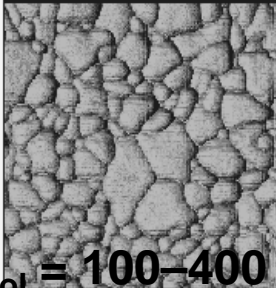


Heat flux Withdrawal in the splat

Alumina splat deposited by RF plasma torch under oxidized metallic substrate (APS)

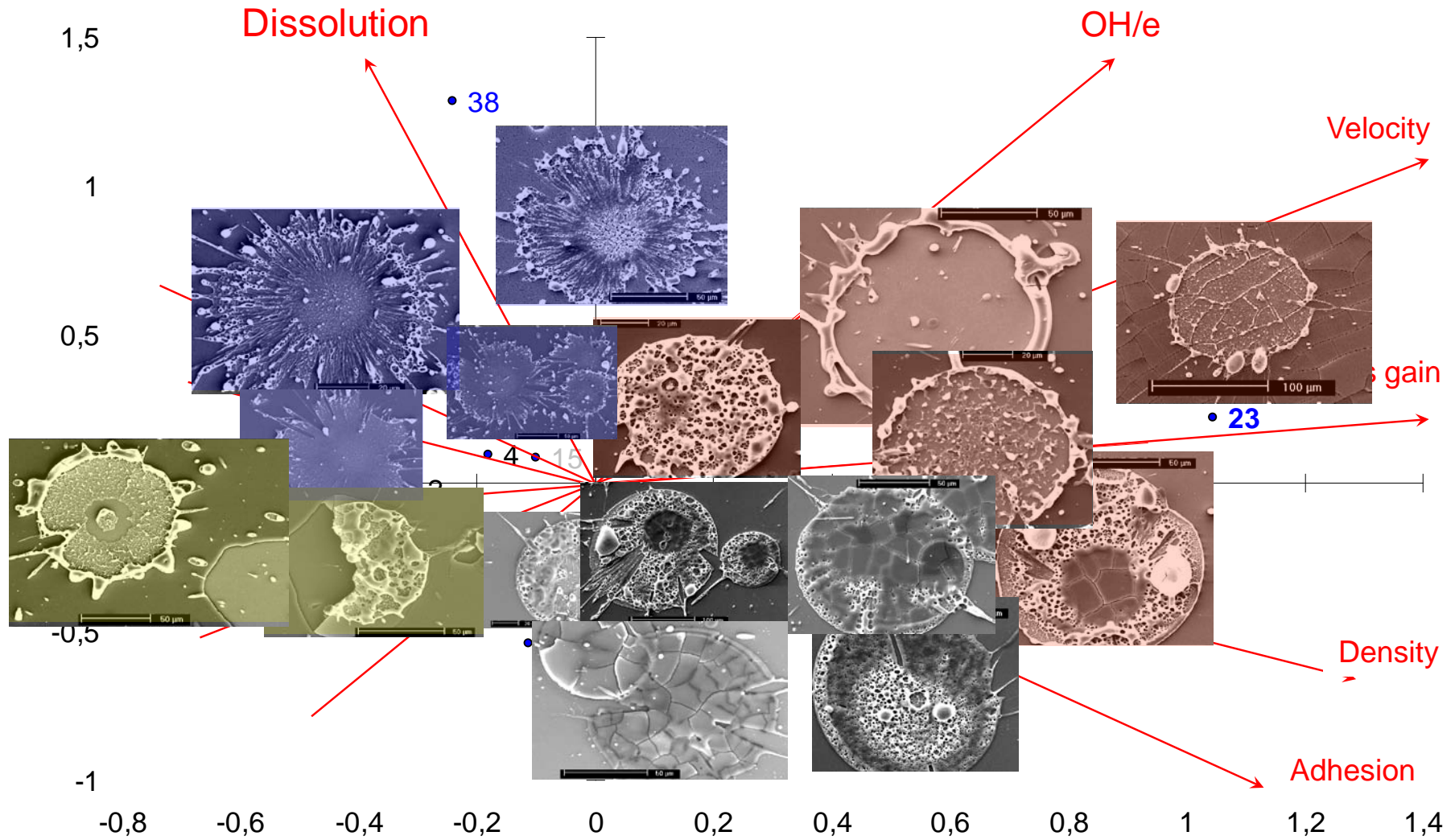


Plasma-sprayed alumina coating on polished alumina substrate (APS)

Substrate	Microcrack network	Adhesion/Cohesion (MPa)		AFM picture 3 μm 
		<i>Ra</i> < 0.4 μm	<i>Ra</i> ~ 1.3 μm	
γ alumina Columnar microstructure		35 \pm 3	40 \pm 3	 $\Phi_{\text{col}} = 100\text{--}150 \text{ nm}$
α alumina Columnar microstructure		3 \pm 1	5 \pm 1	 $\Phi_{\text{col}} = 100\text{--}300 \text{ nm}$
α Granular microstructure		No adhesion of coating		 $\Phi_{\text{col}} = 100\text{--}400 \text{ nm}$

ACP : relationship between film properties and splat morphologies (Alumina PECVD underlayer)

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

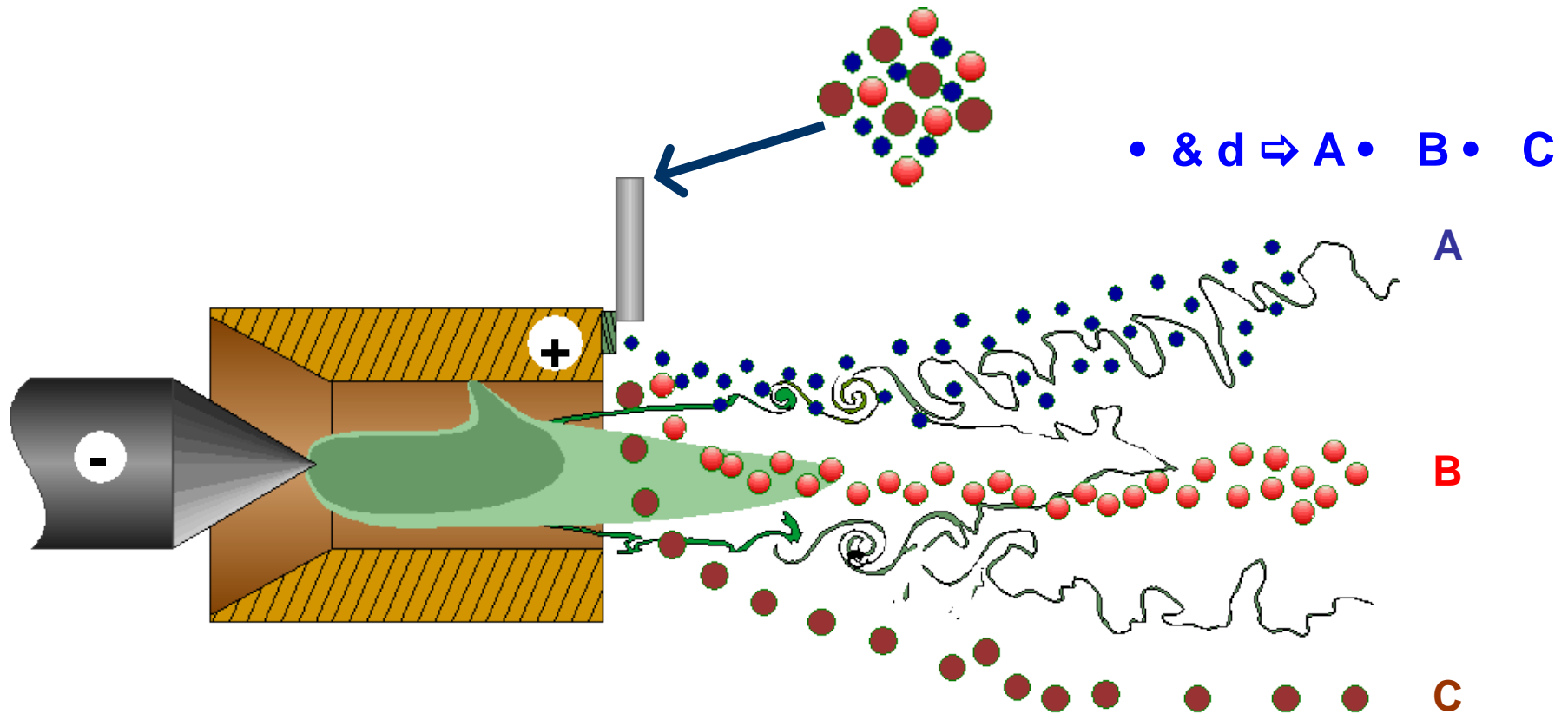


Coating properties and functionality



Cermet Fabrication Techniques

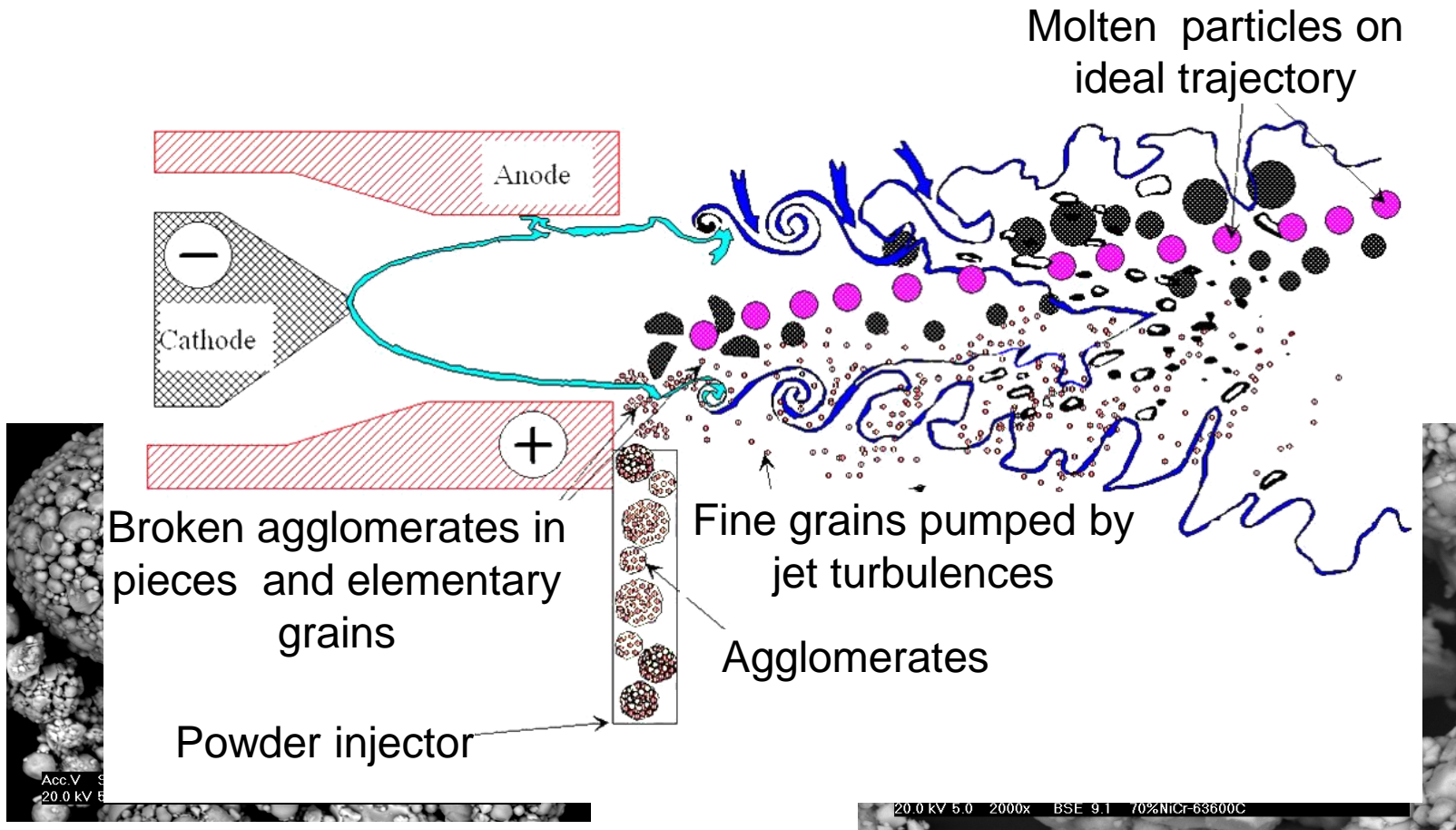
Pre-mixed Powder



Spray drying

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

Yttria Stabilized Zirconia / NiCr

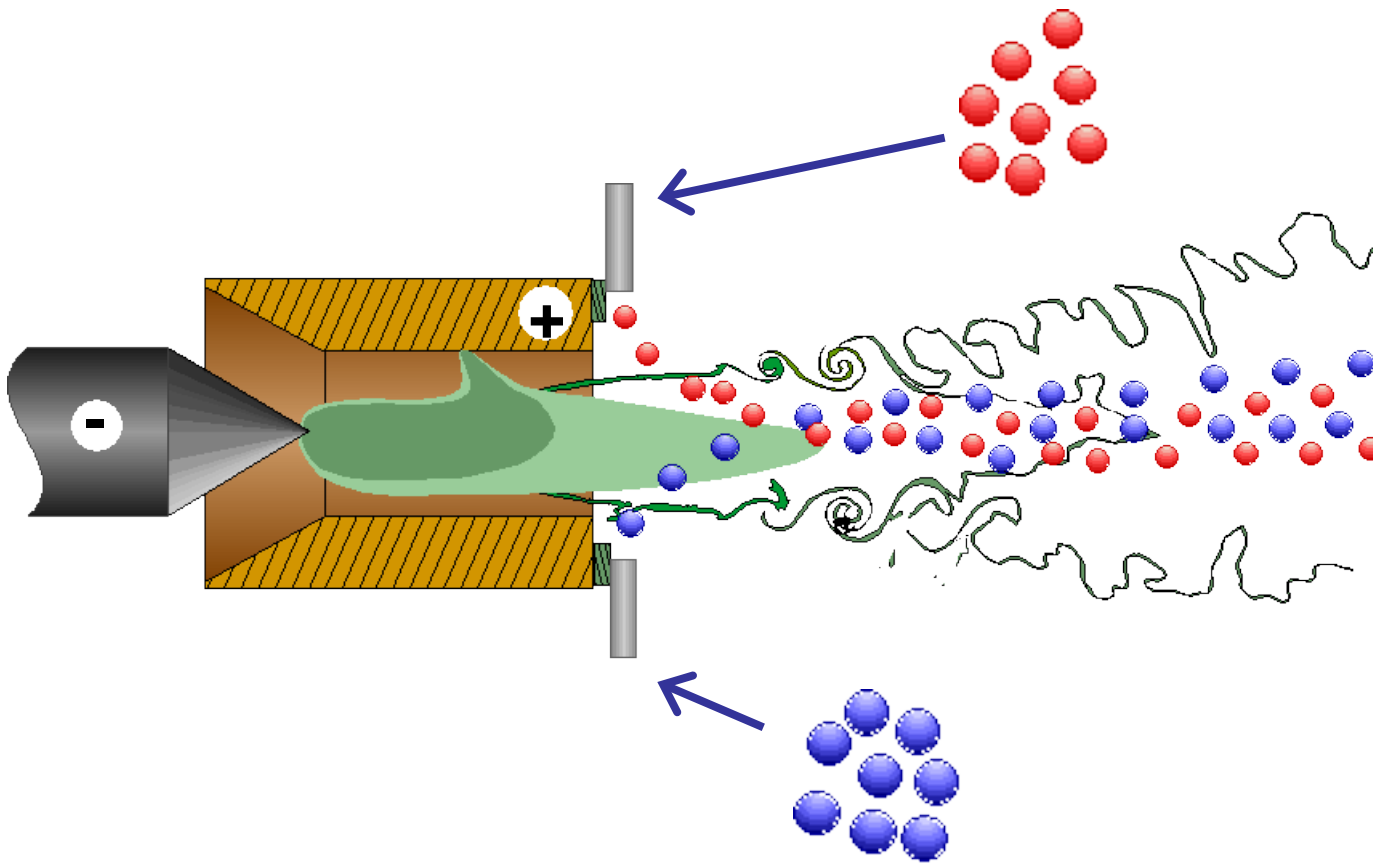


Agglomerated particles

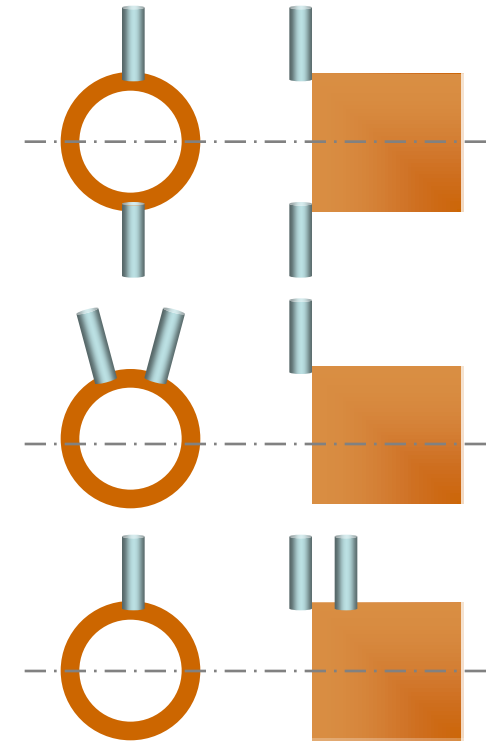
Agglomerated and sintered particles

Cermet Fabrication Techniques

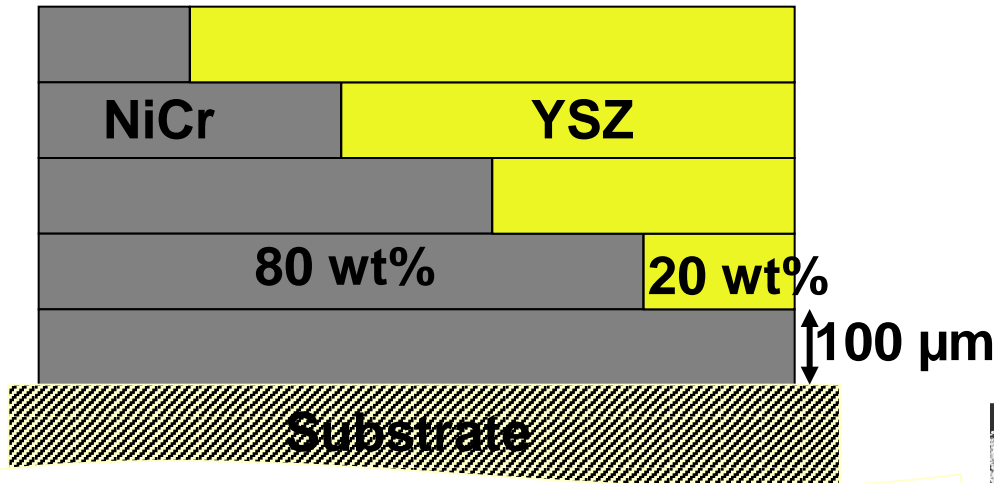
Co-spraying



Multi-injector Configurations

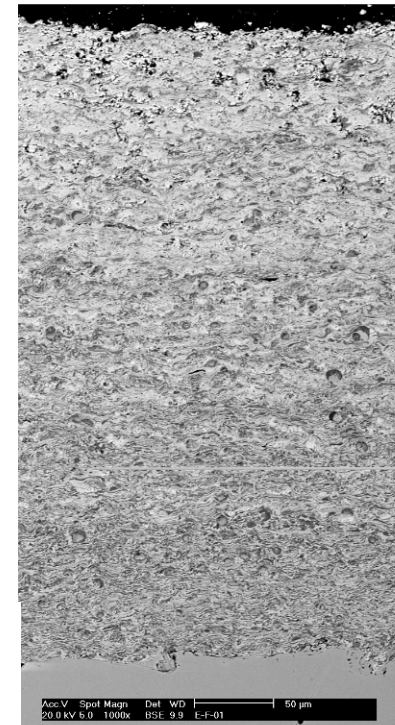
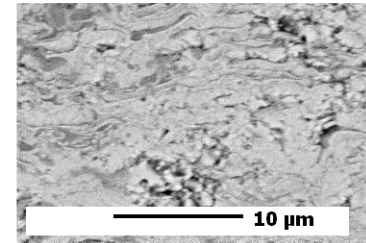
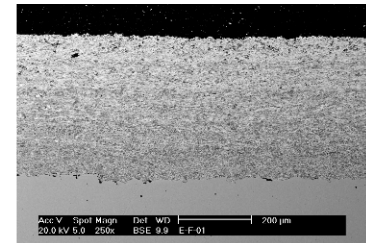
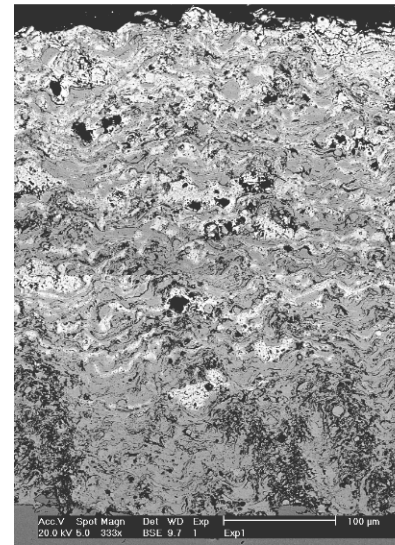
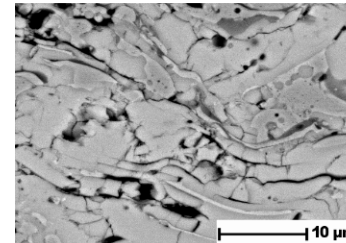
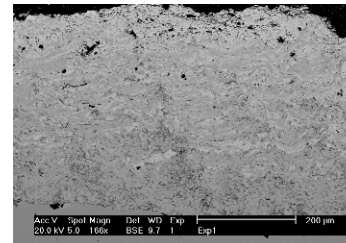


Multilayer coating with composition gradient



Results

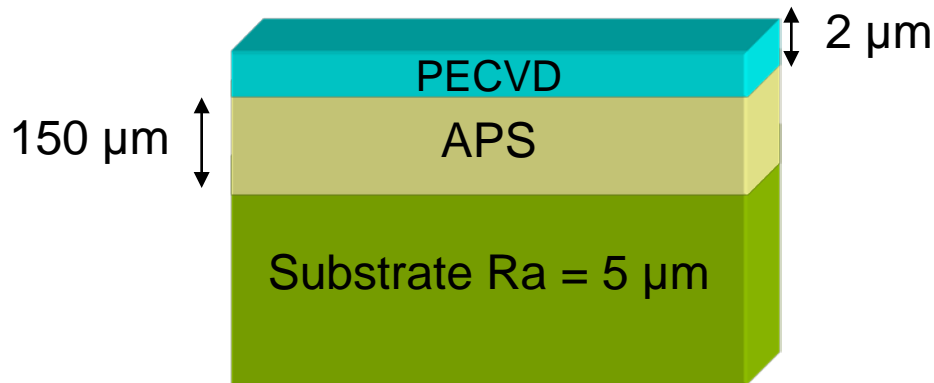
- Increase of thermo-mechanical resistance
- Insufficient thermal insulation



Finely structured coating: Particles gas transported

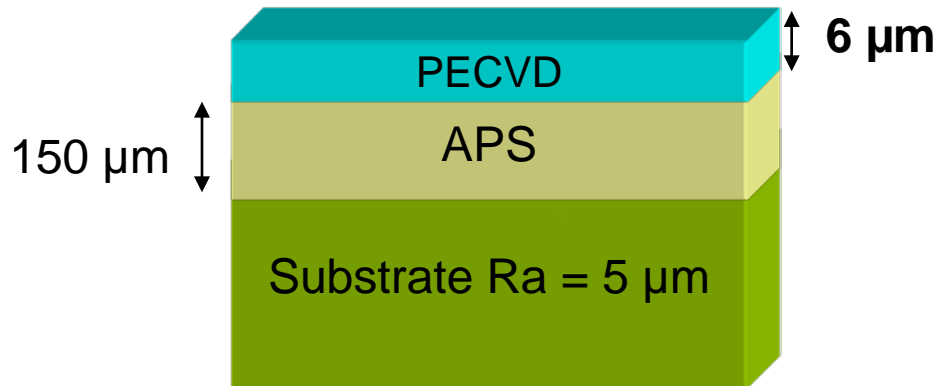
Multilayer coating by multi-process

Decreasing of open and interconnected porosity



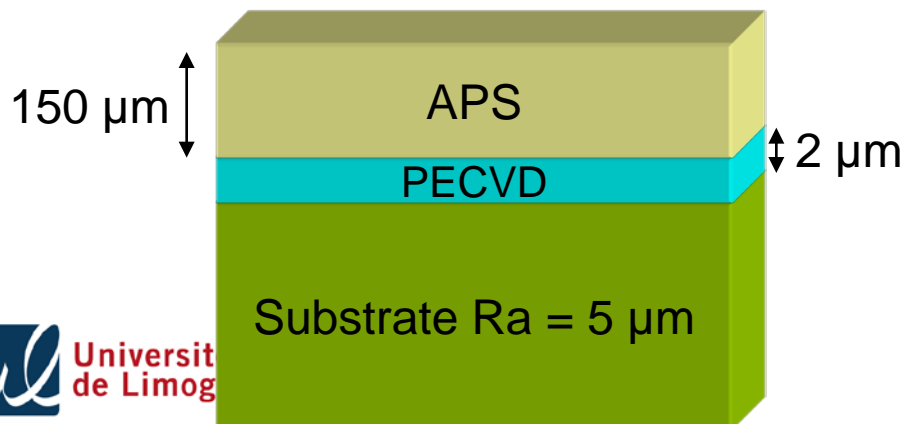
Porosity level = 1,1 %

Decreasing by 40 %



Porosity level = 0,2 %

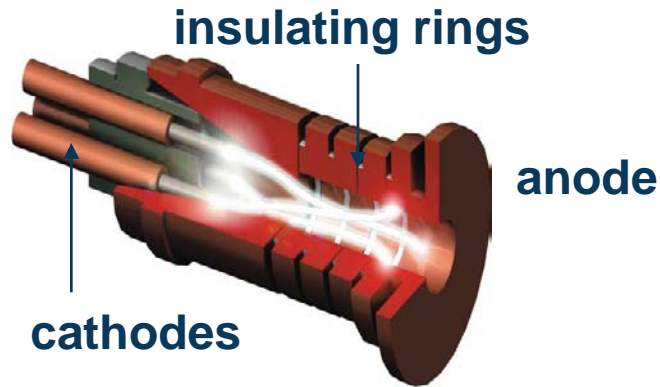
Decreasing by 90 %



Porosity level = 0,4 %

Decreasing by 80 %

tri-cathodes plasma torch (Triplex)

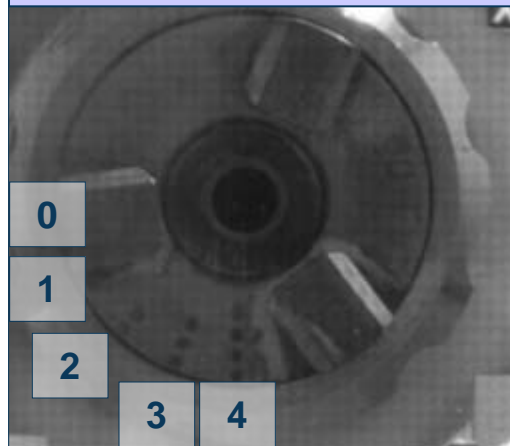


• $V/V < 0.1$

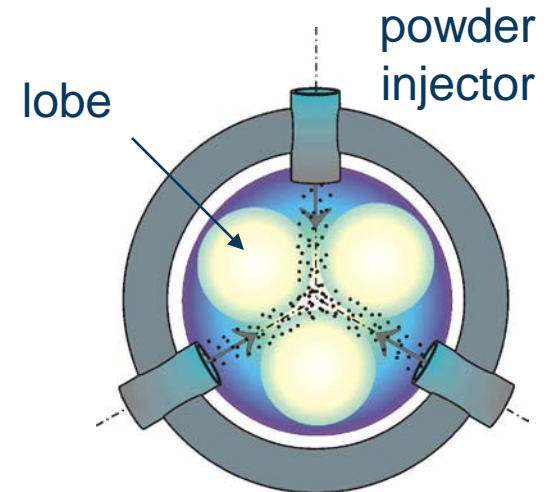
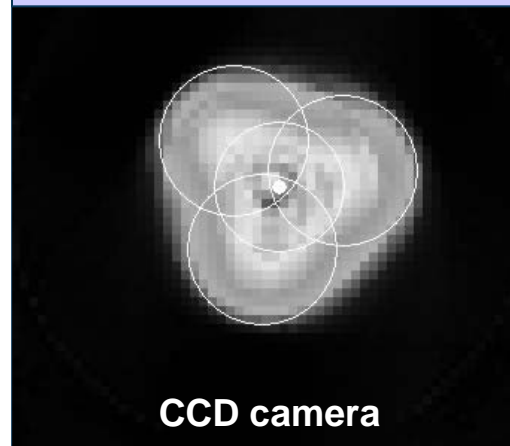
usual operating conditions

nozzle i.d. [mm]	plasma gas mixture	arc current [A]	injector positions
5	Ar	100 to 500	0 - 4
6.5	Ar-He	(depending upon plasma gas mixture)	
9	Ar-N ₂		
11			

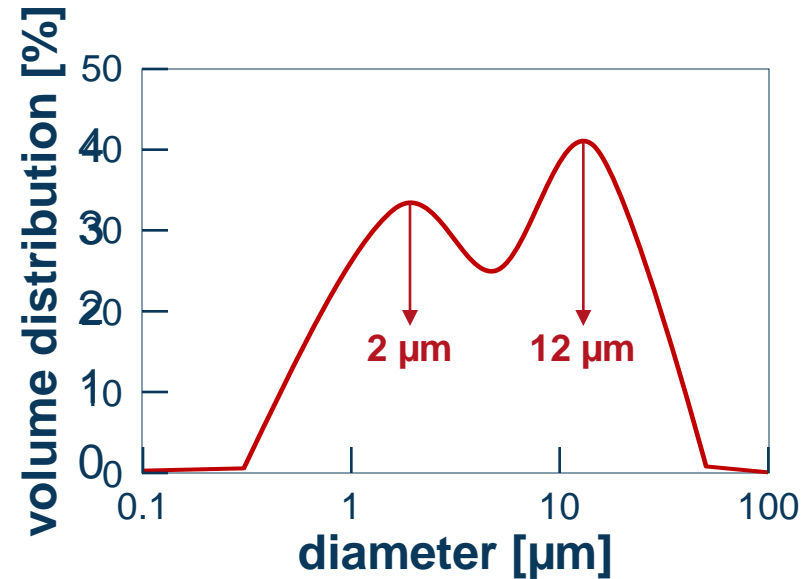
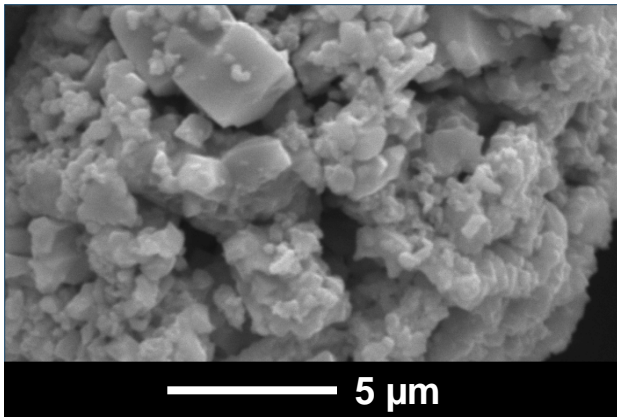
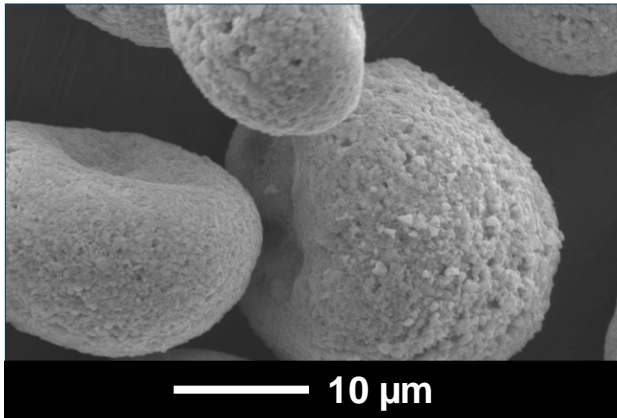
torch nozzle exit



plasma lobes



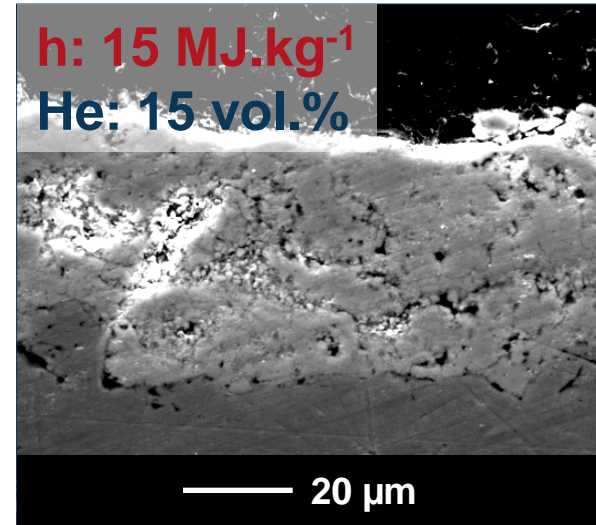
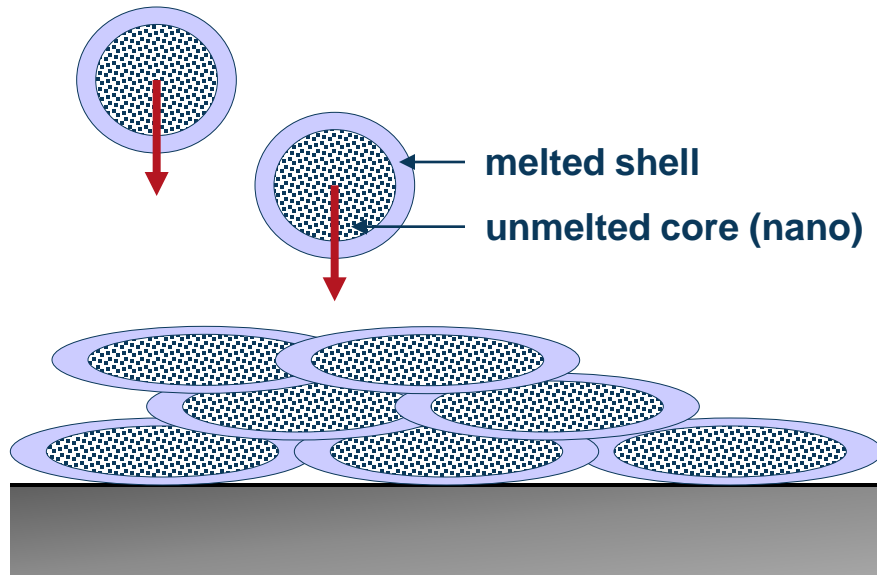
nano-agglomerated $\text{La}_{0,8}\text{Sr}_{0,2}\text{MnO}_3$ (Inframamat)



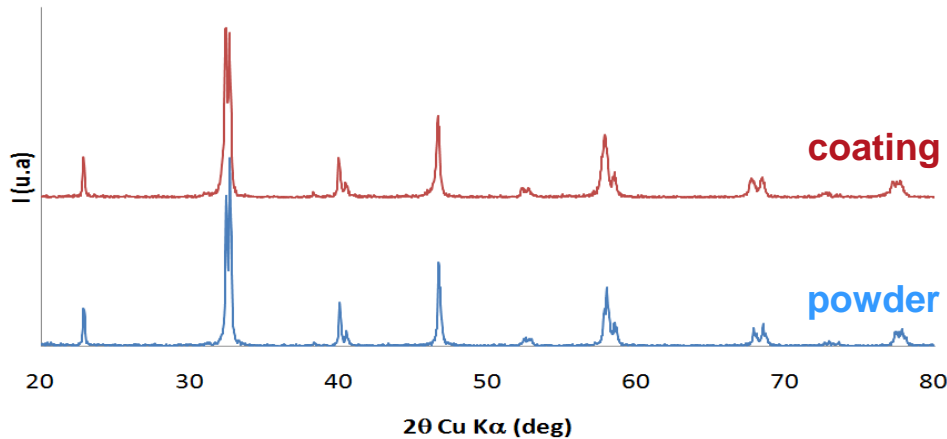
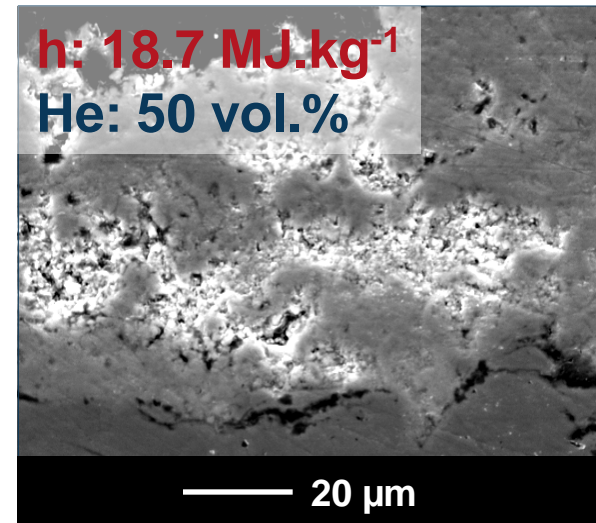
d_{10}	d_{50}	d_{90}
1.01 μm	5.25 μm	21.26 μm

specific surface = 2.94 m².g⁻¹ (BET)

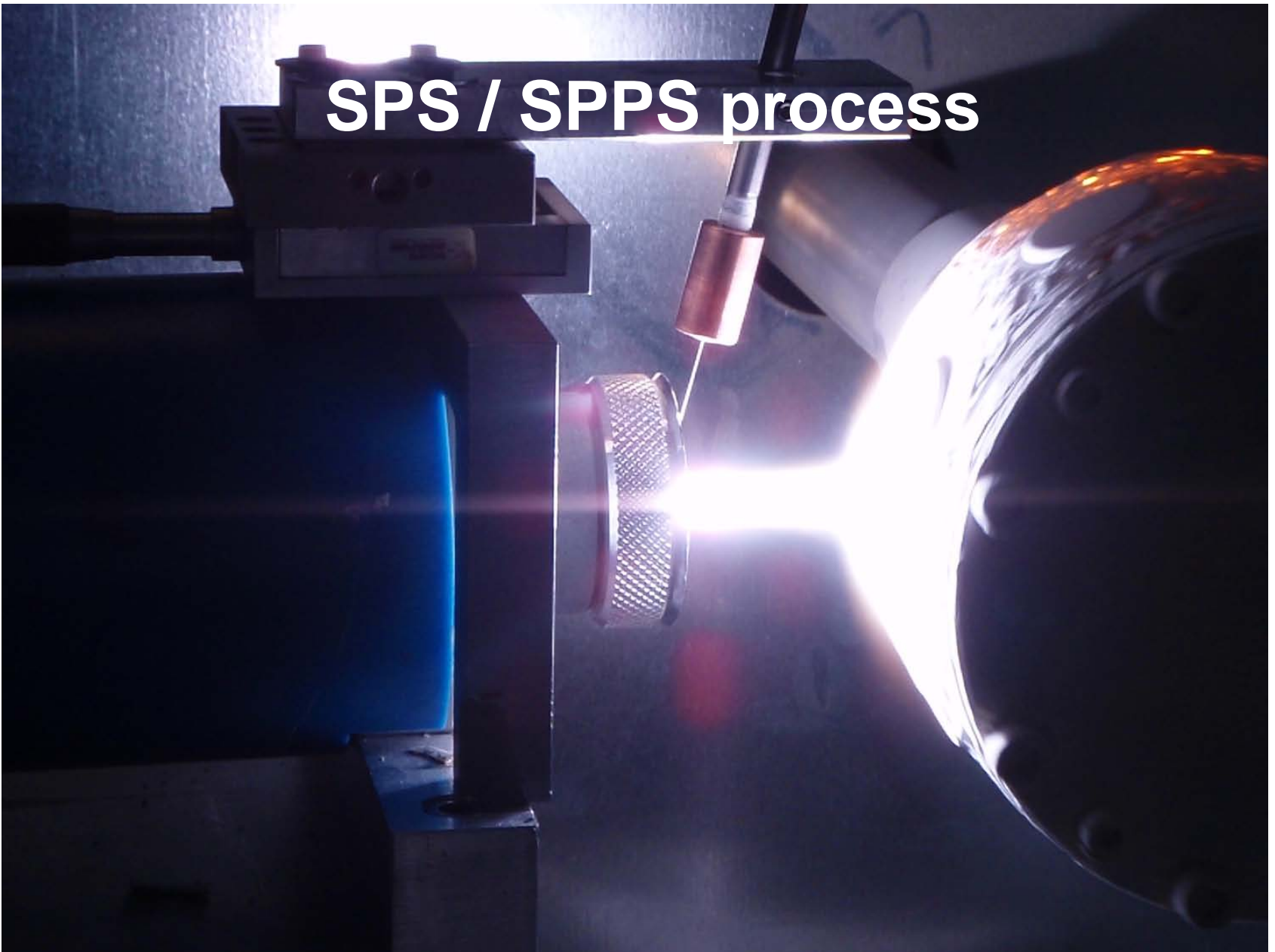
nano-agglomerated $\text{La}_{0,8}\text{Sr}_{0,2}\text{MnO}_3$ coating elaboration strategy



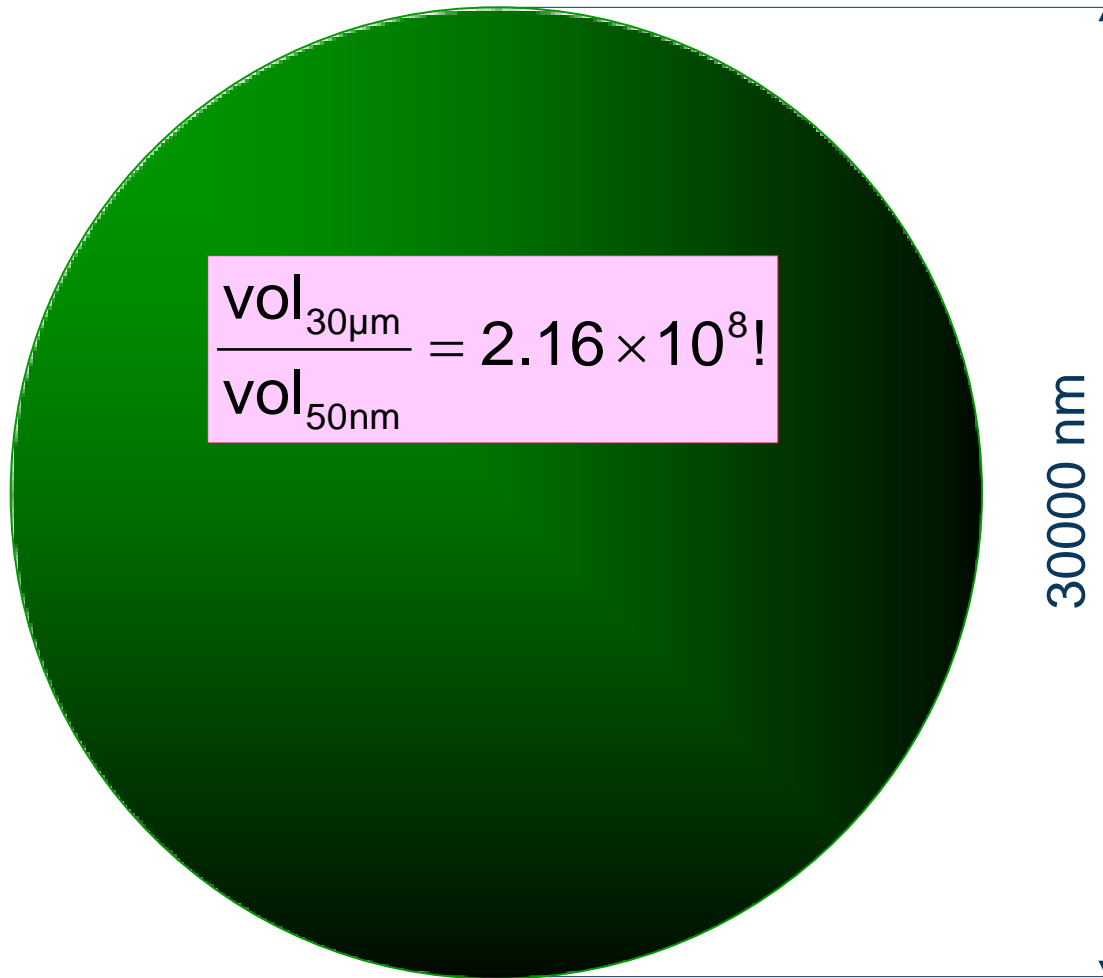
nozzle i.d.: 6.5 mm



SPS / SPPS process

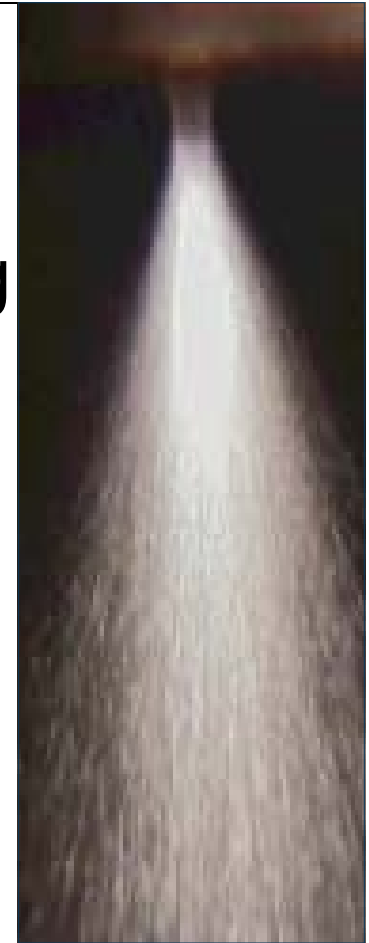


Coating architecture: APS vs. SPS

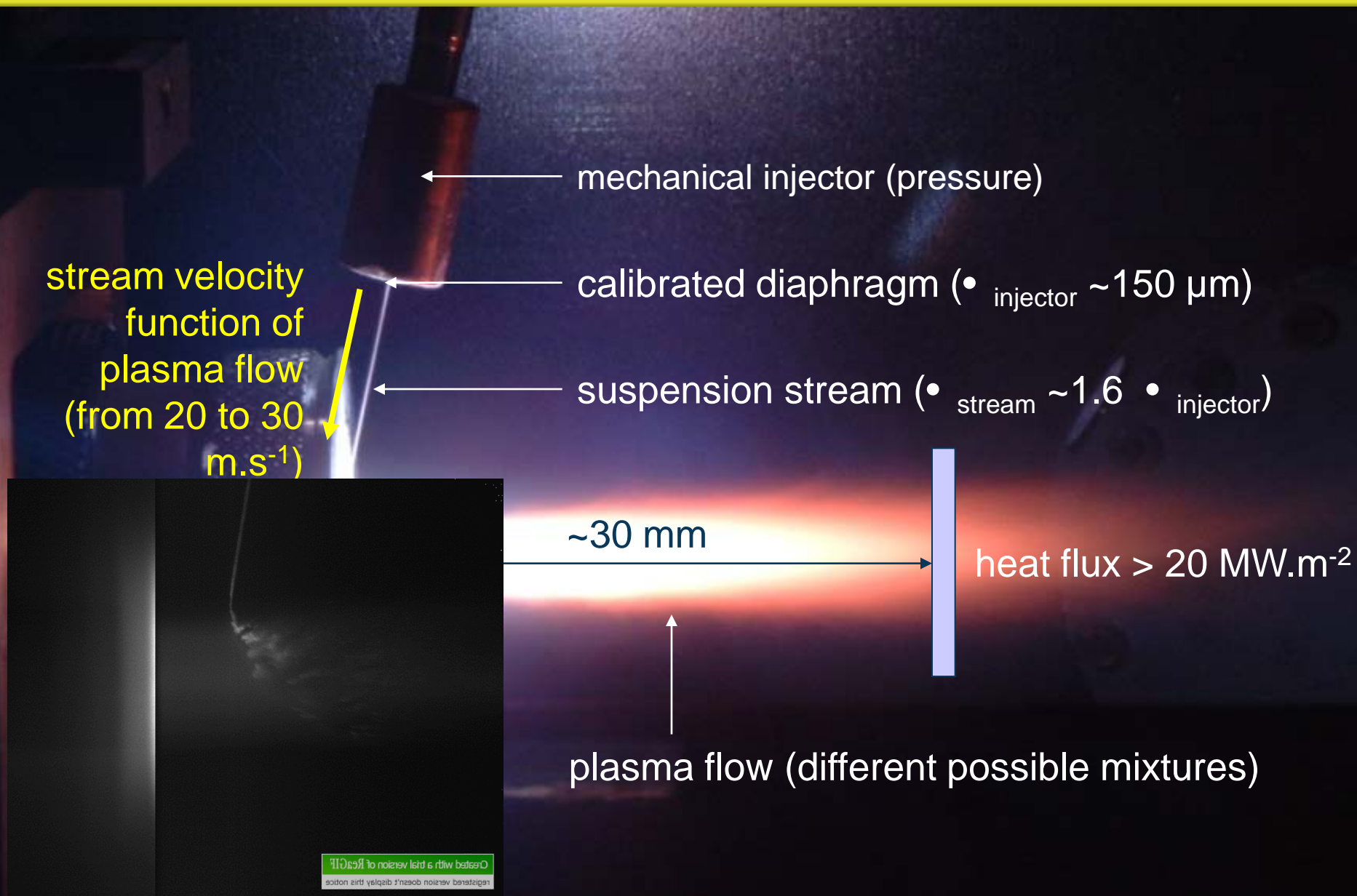


pneumatic injection (secondary atomization)

- atomization by a secondary gas flow
- divergent jet of droplets
- plasma flow perturbation by atomizing gas



Suspension plasma spraying (SPS)

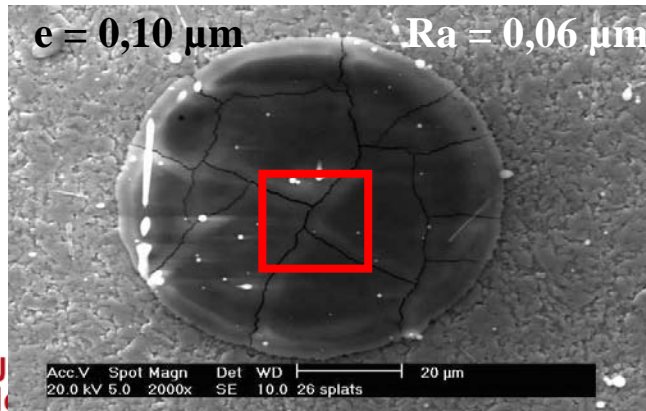
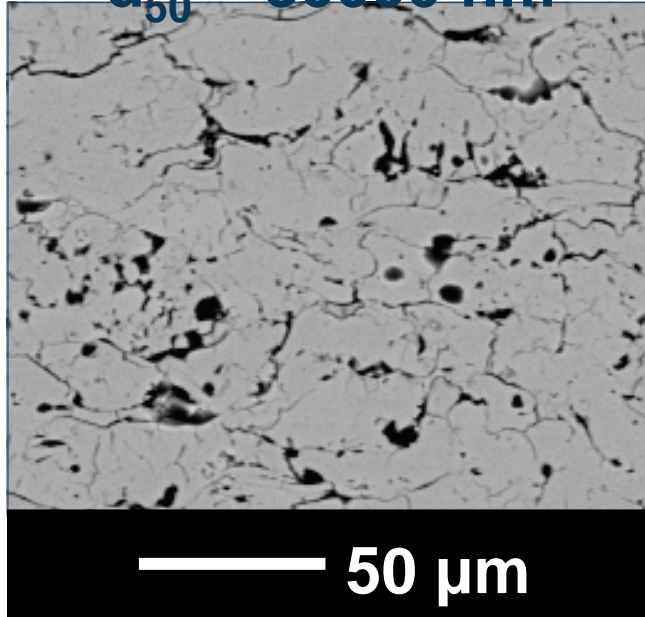


plasma torch mass enthalpy: from 8 to 14 MJ.kg^{-1}

Coating architecture: APS vs. SPS

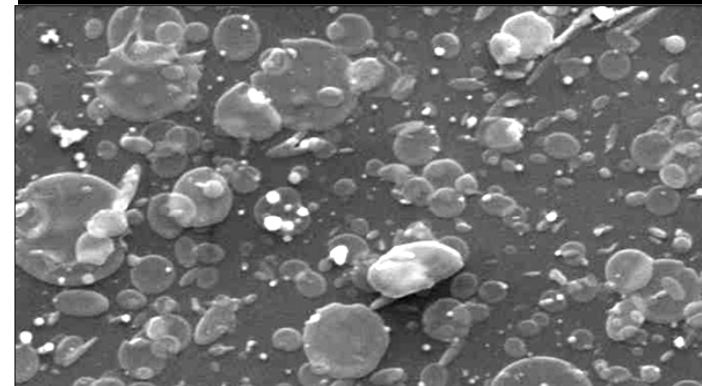
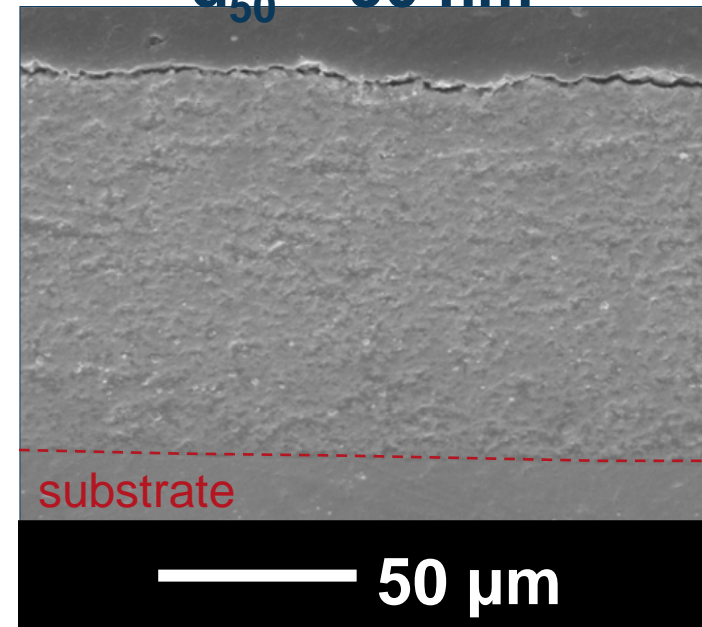
APS

micrometer-sized
 $d_{50} \sim 30000 \text{ nm}$



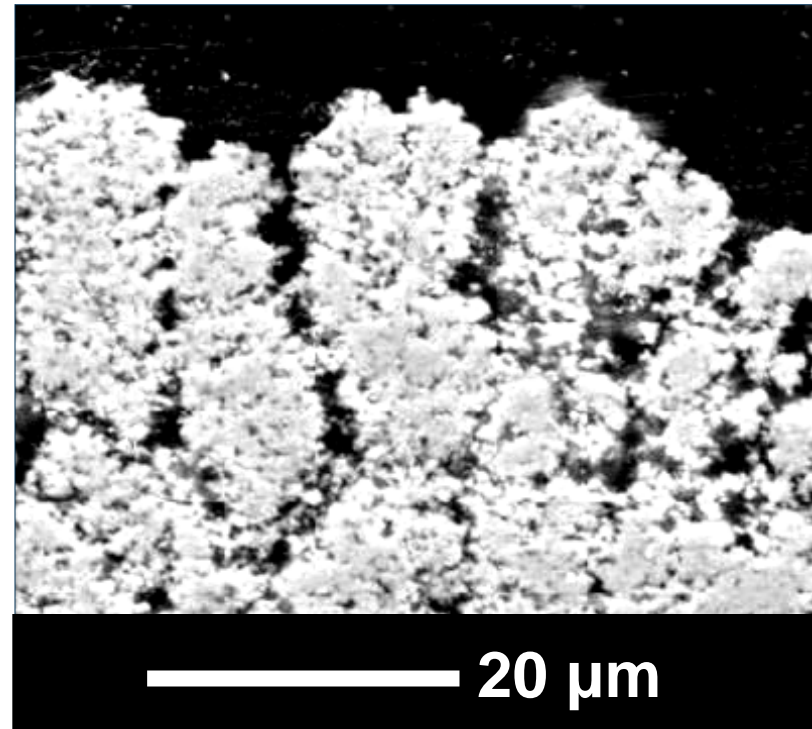
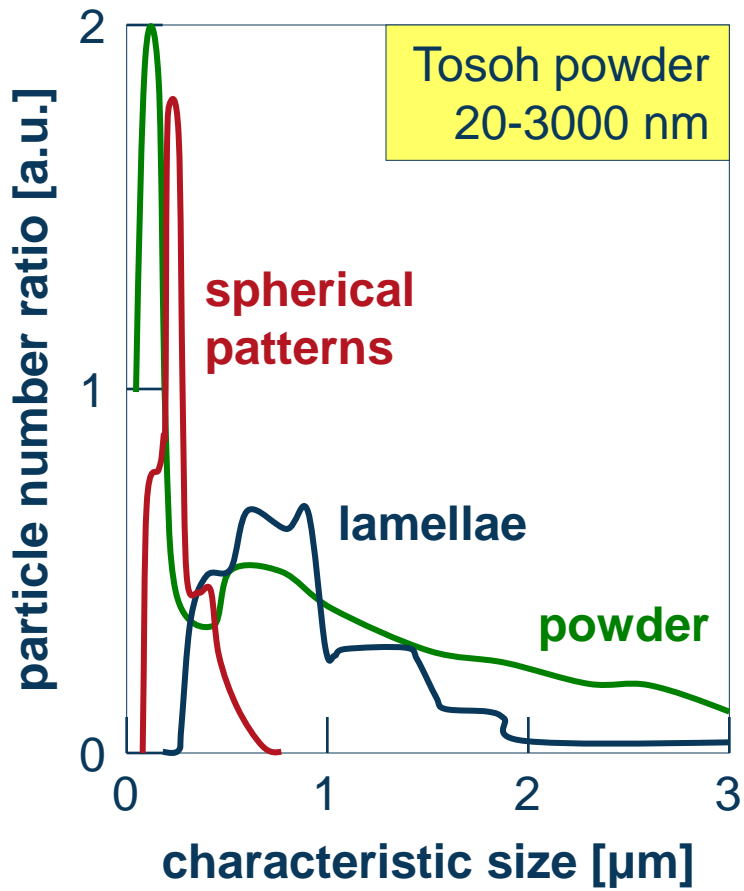
SPS

nanometer-sized
 $d_{50} \sim 50 \text{ nm}$



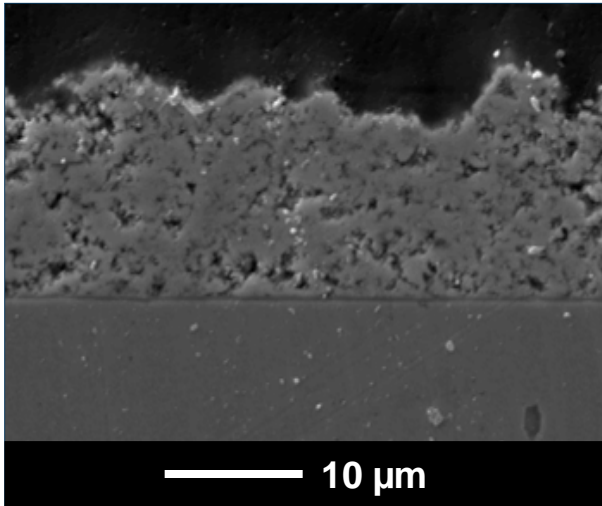
coating architecture

YSZ nano-sized particles with agglomerates and aggregates

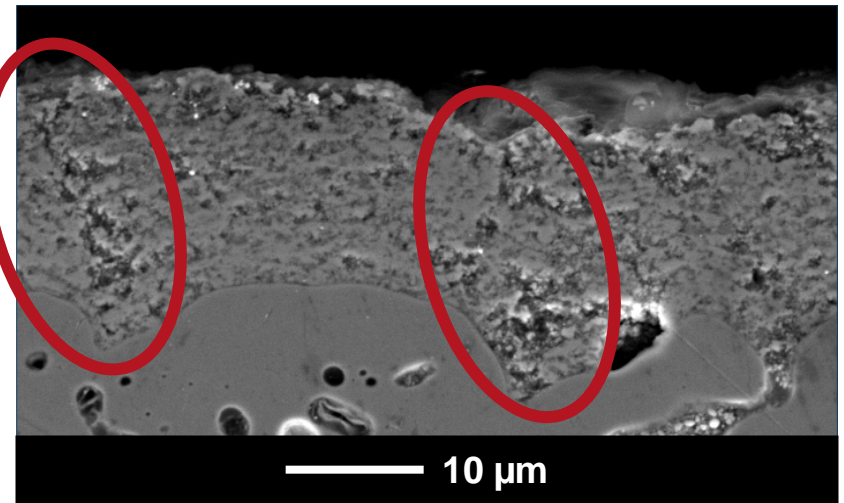


plasma: Ar-H₂ (25 vol.%)
• V / V > 1.1

coating architecture

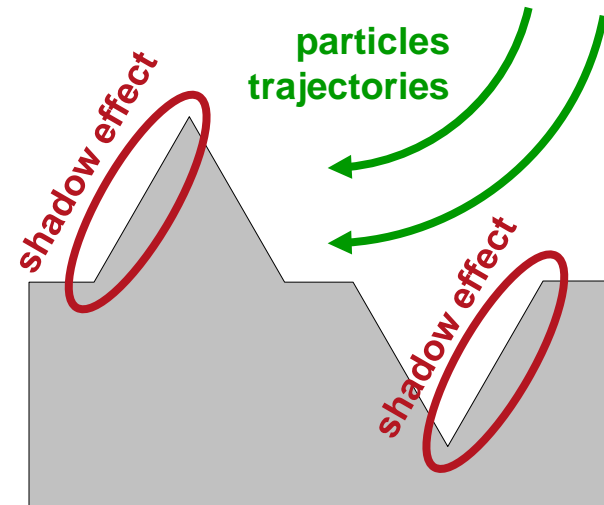


$Ra / d_{50} = 2$

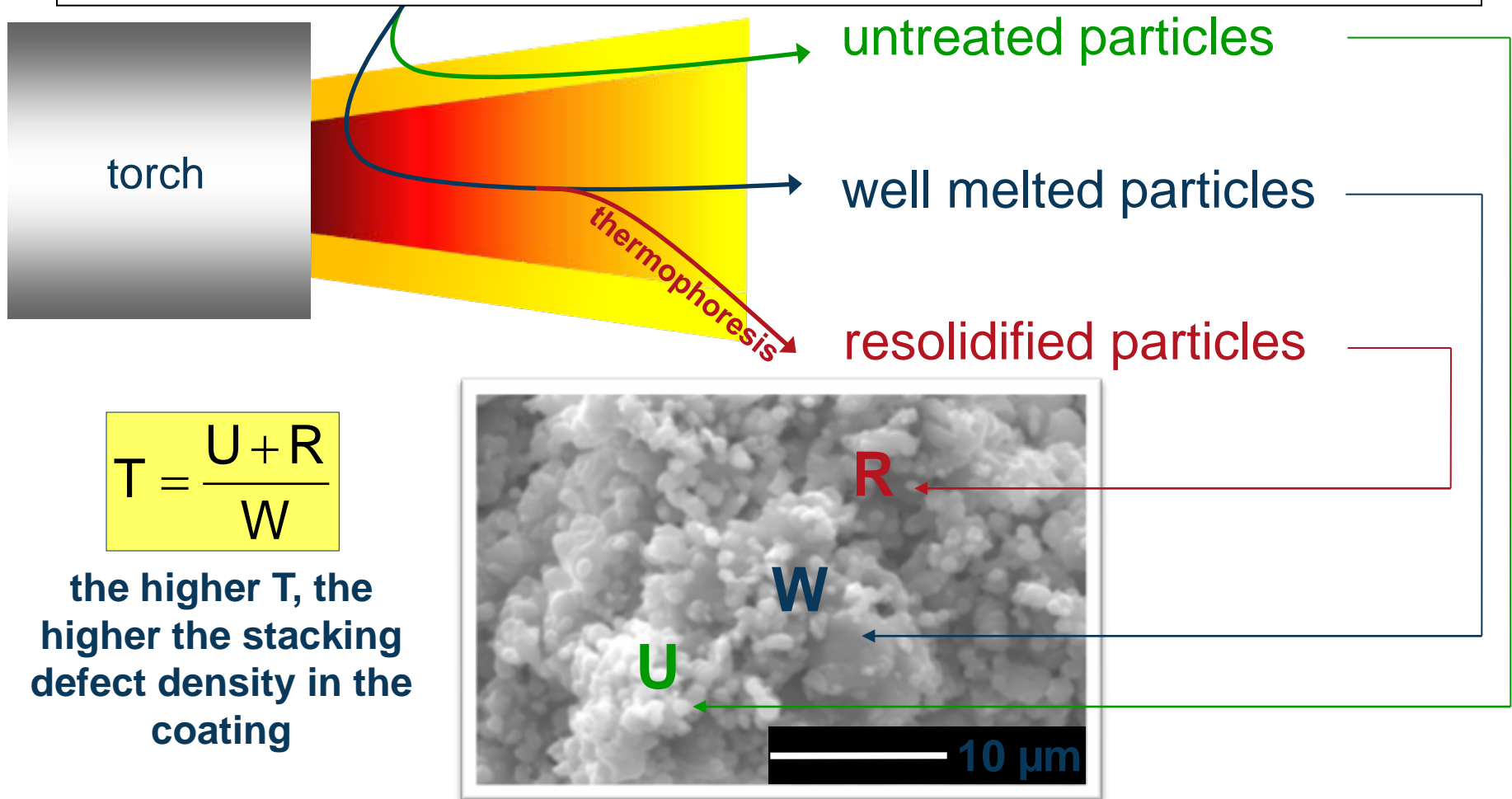


$Ra / d_{50} = 75$

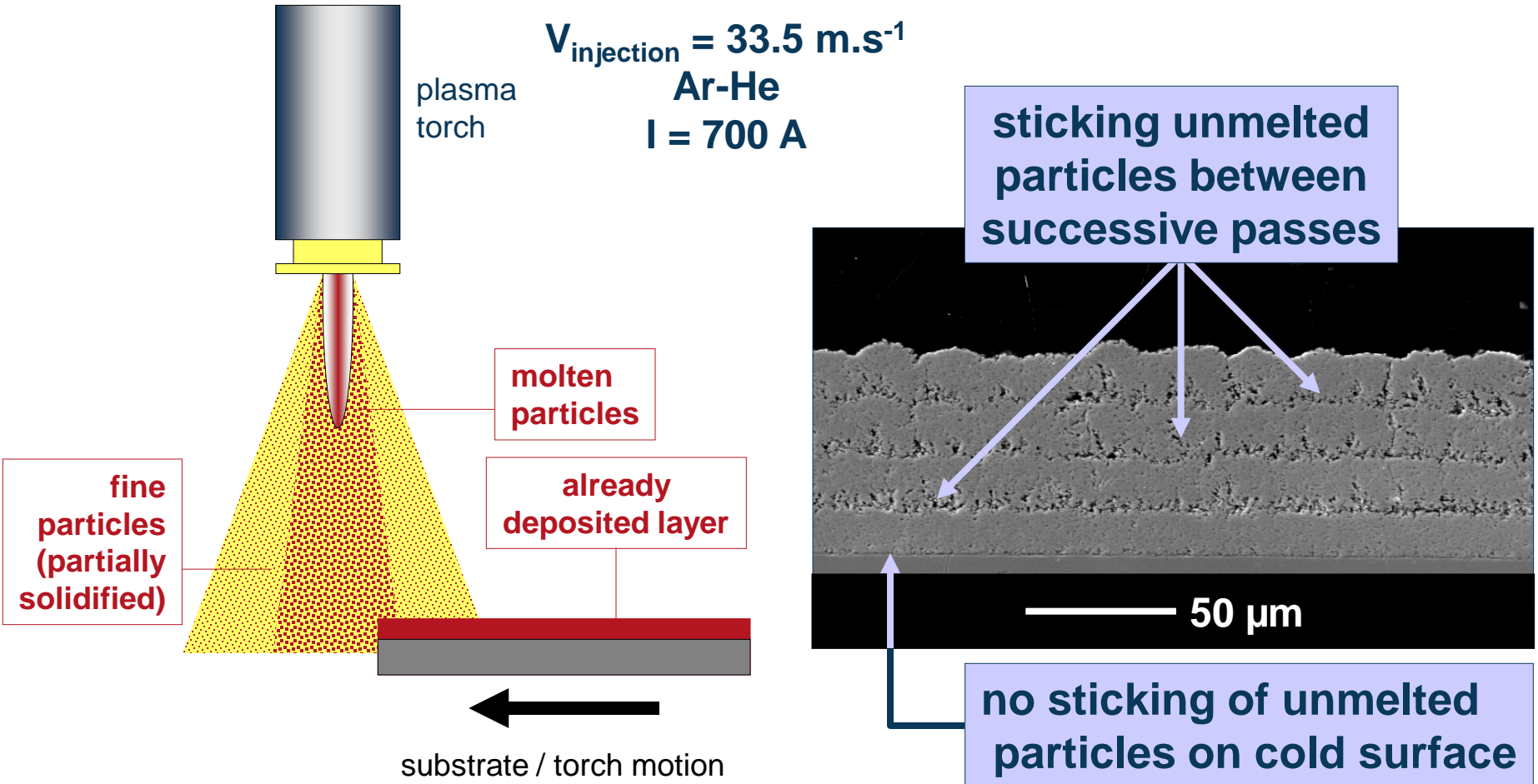
necessity to spray on smooth surfaces



a peculiar coating structure

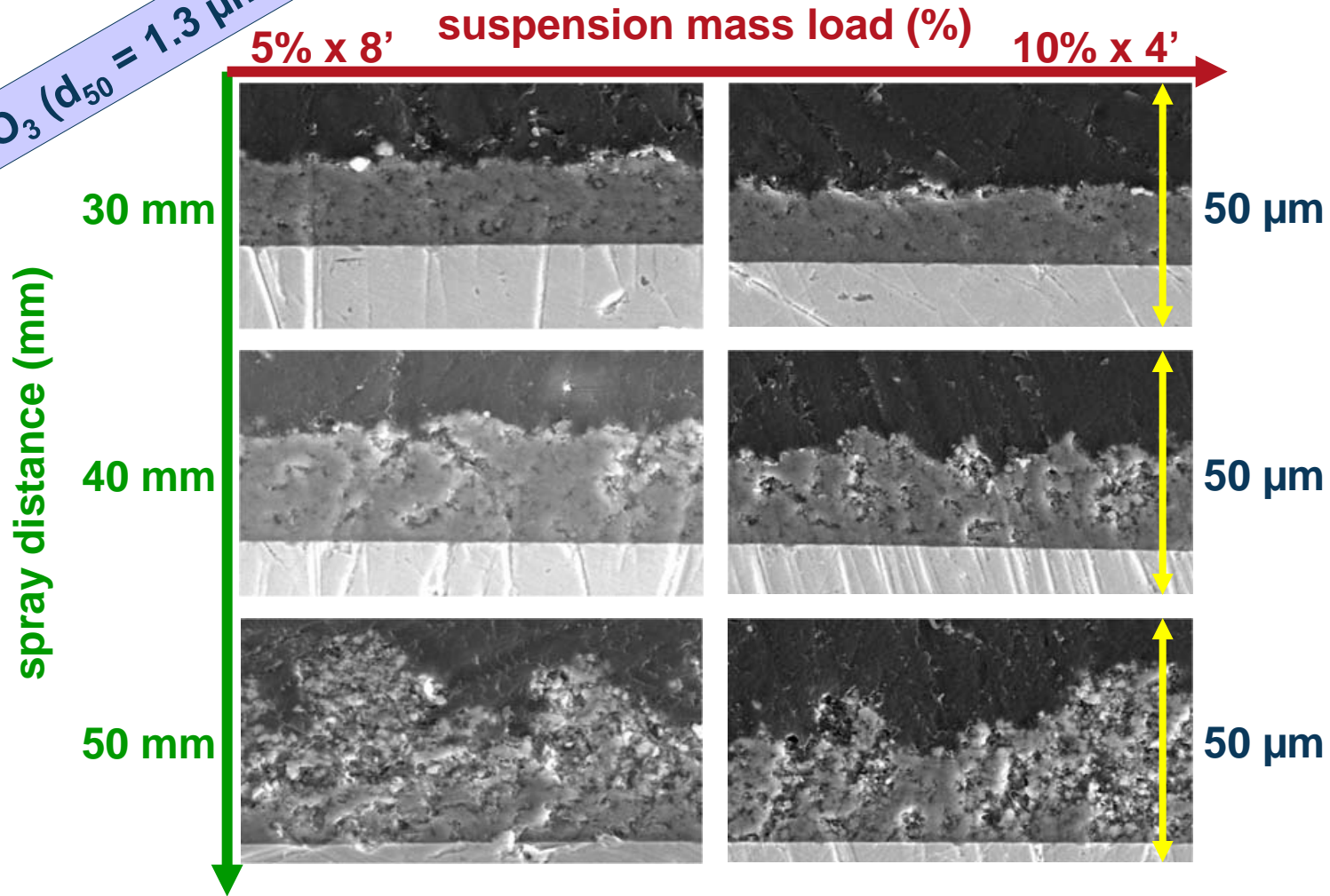


coating manufacturing mechanisms

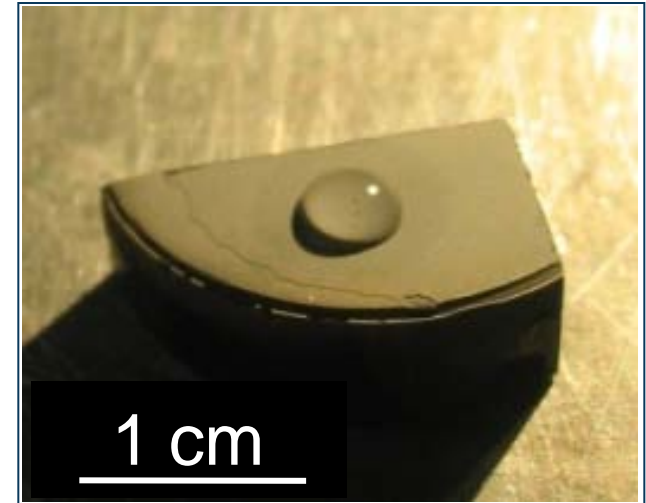
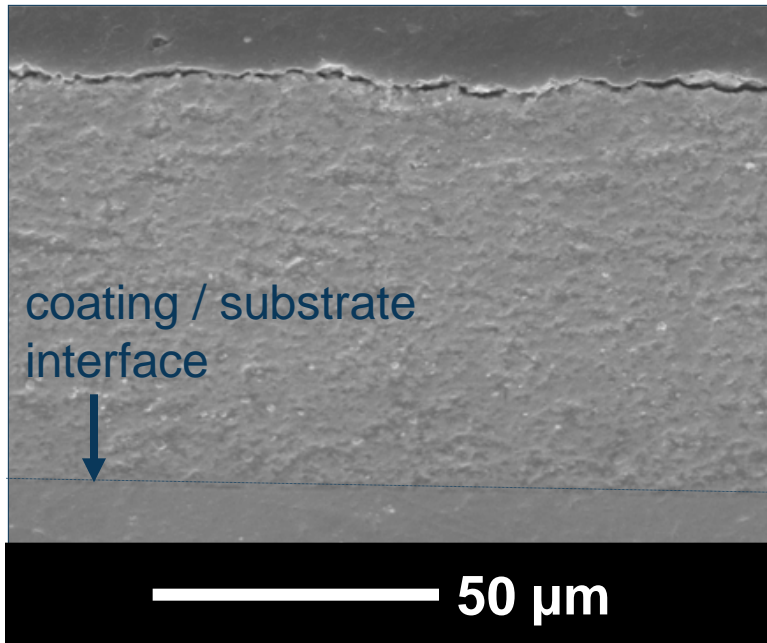


some effects of operating parameters

$\alpha\text{-Al}_2\text{O}_3$ ($d_{50} = 1.3 \mu\text{m}$)



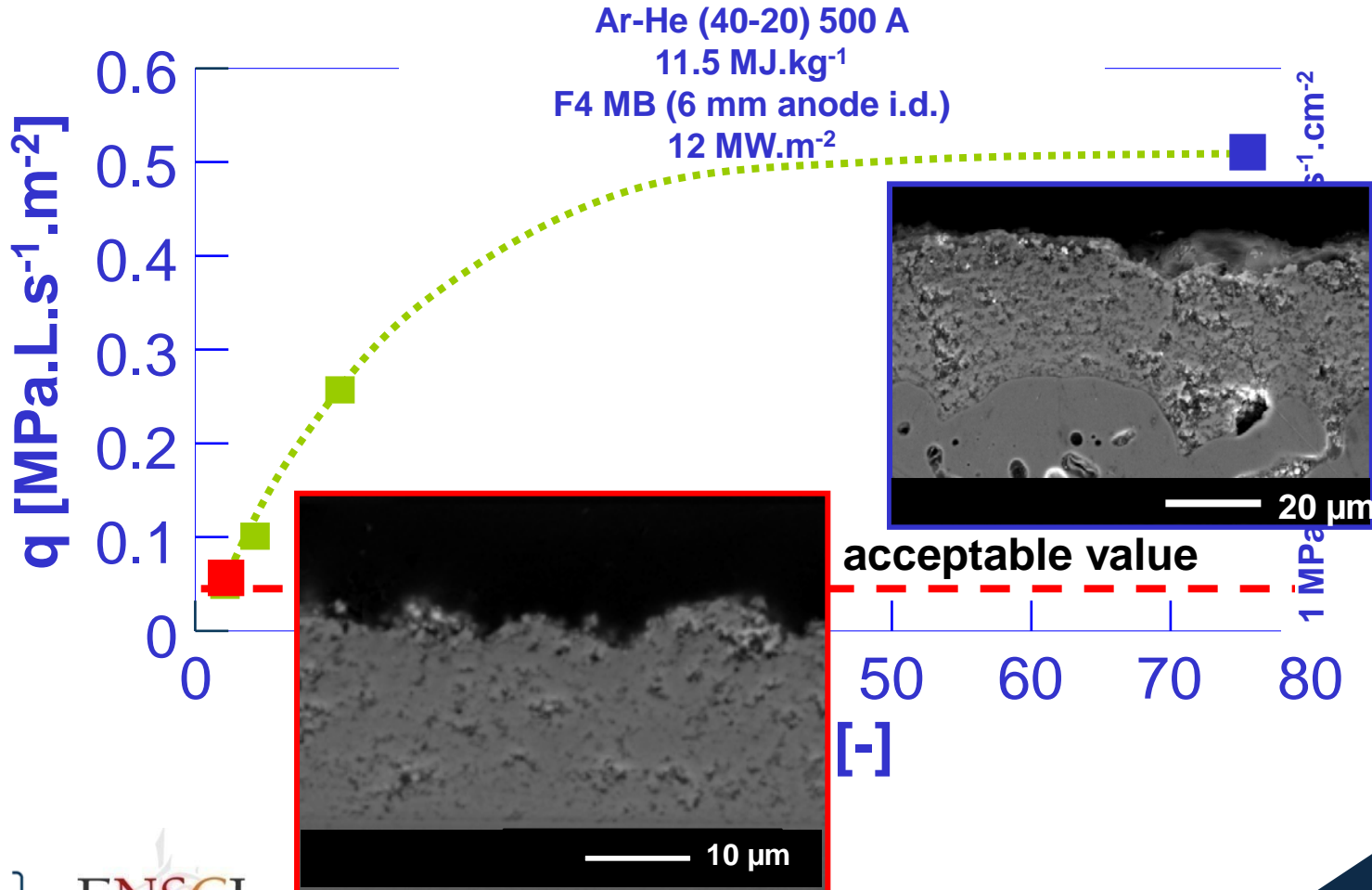
coating architecture



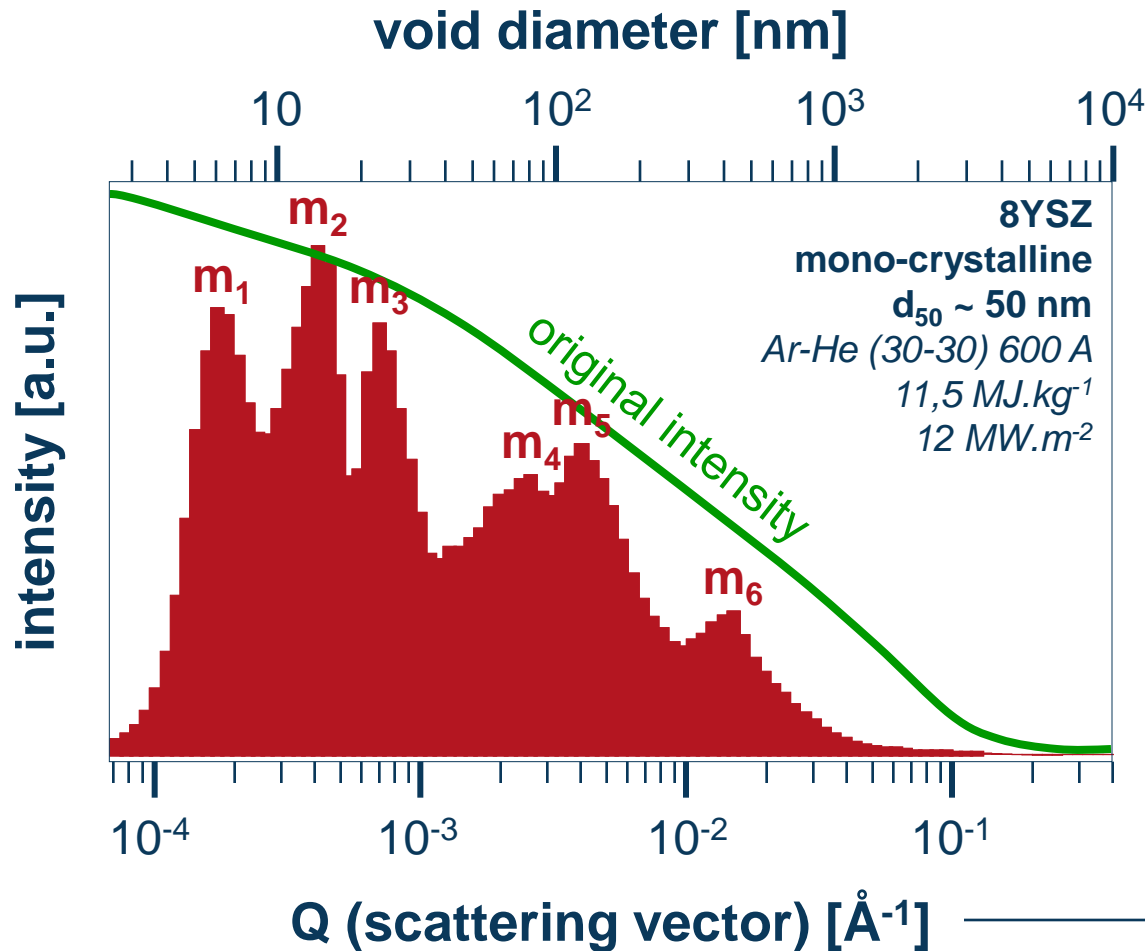
- compared to APS coatings, SPS ones exhibit higher toughness (4-7 times)
 - **superior abrasive wear resistance**
 - **very difficult to polish**

Gas permeability

torche conventionnelle



Typical void size distribution (USAXS)

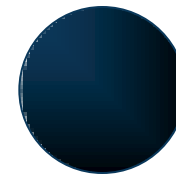


multimodal size distribution

- m_1 : ~ 5 nm
- m_2 : ~ 15 nm
- m_3 : ~ 30 nm
- m_4 : ~ 80 nm
- m_5 : ~ 120 nm
- m_6 : ~ 300 nm

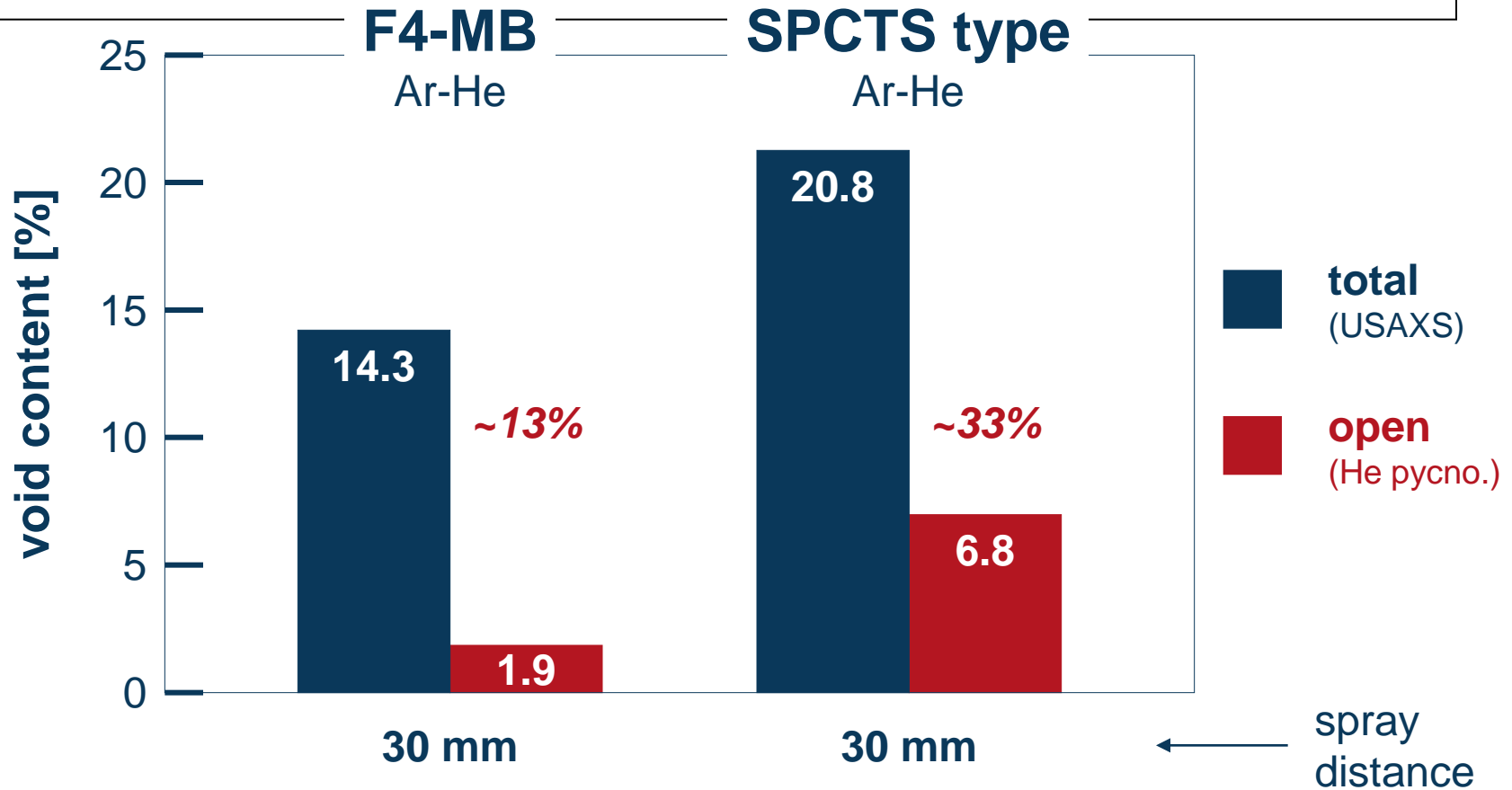
cumulated void content

10 to 20% (!)

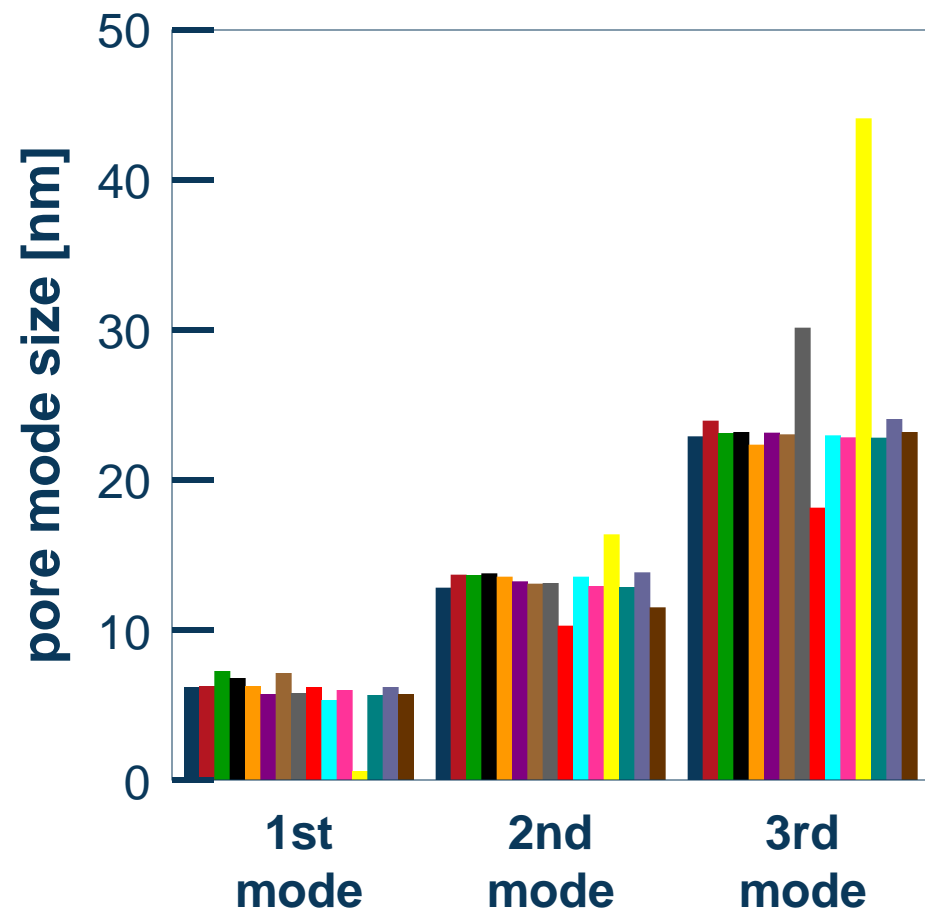
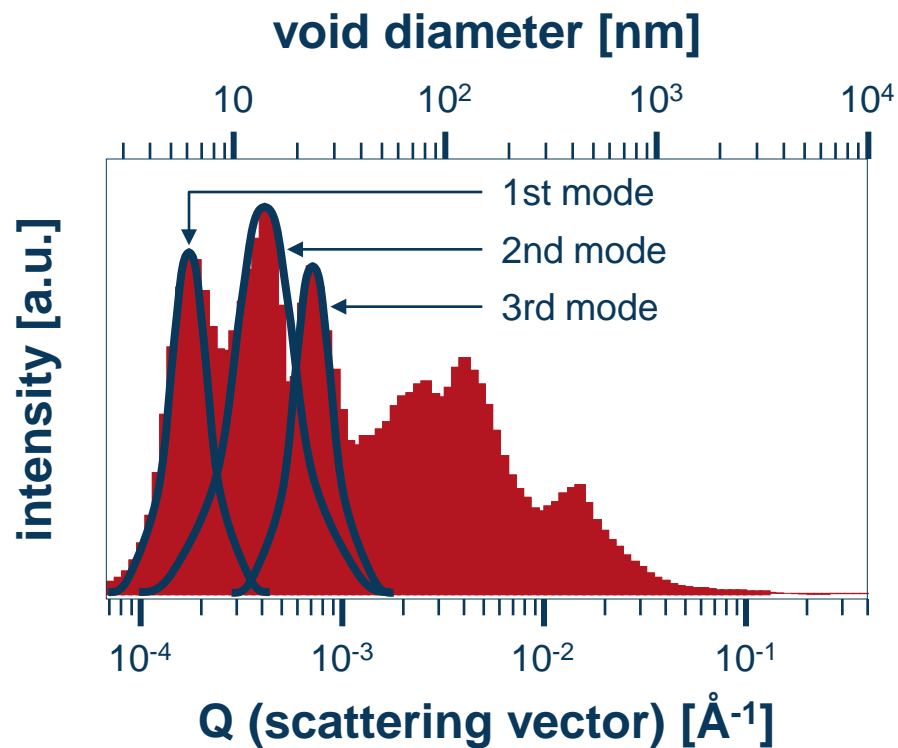


voids modeled
as spheres

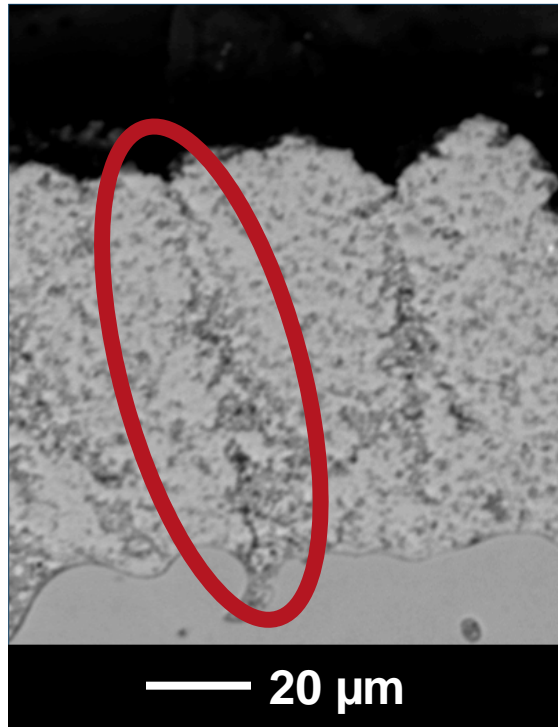
porosity measurement



Void average sizes (USAXS)

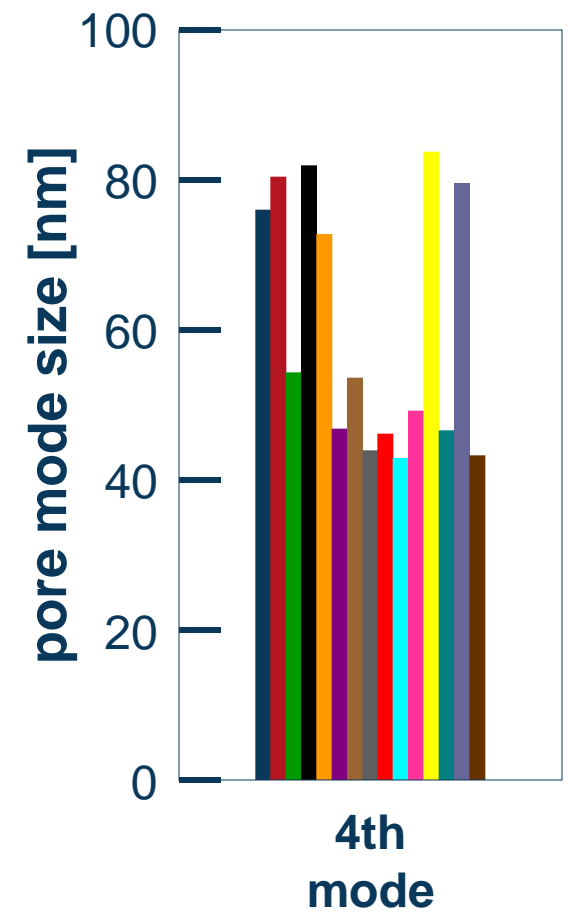


Void average sizes (USAXS)

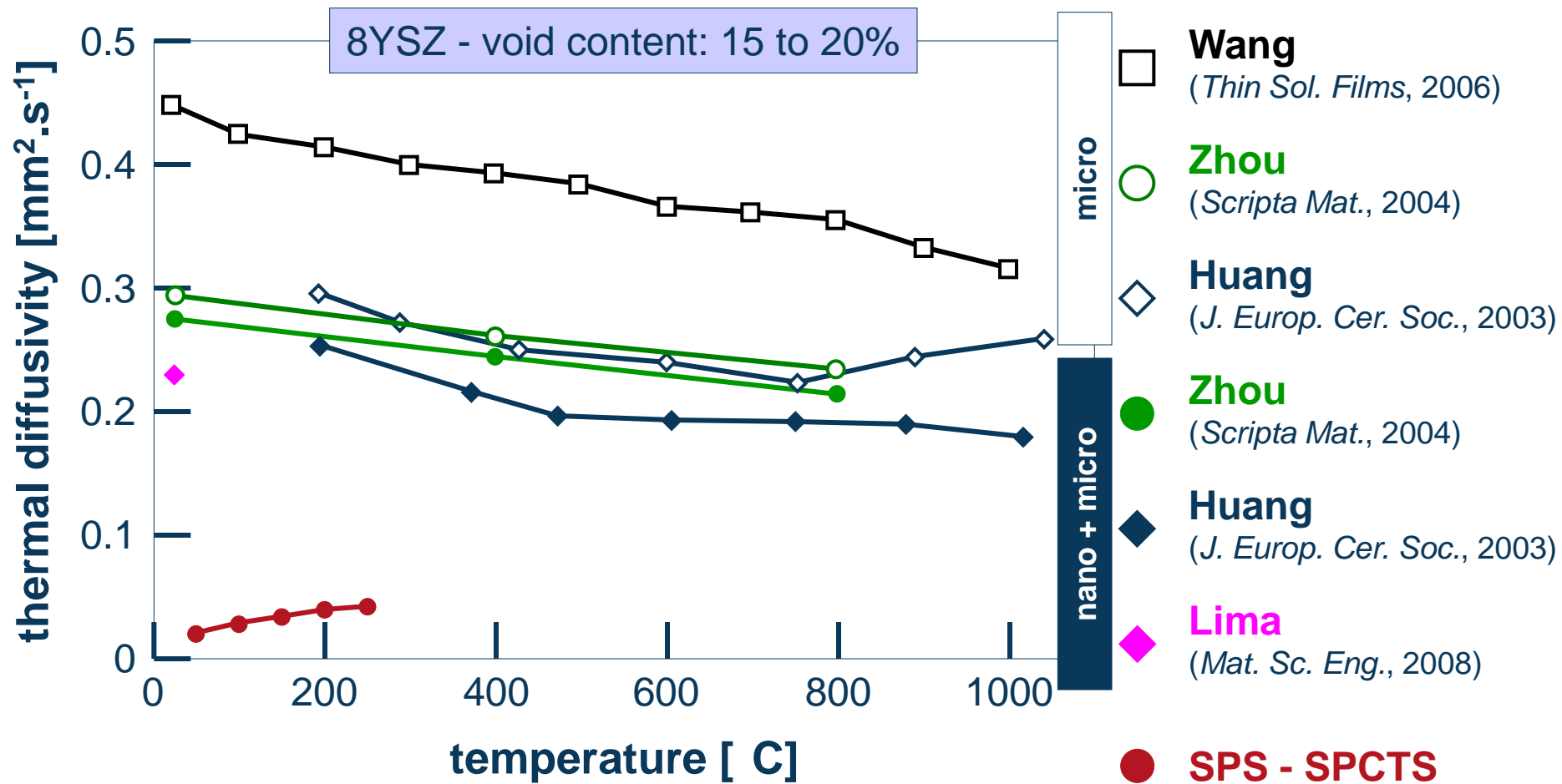


bigger voids
↓
stacking defects

if defect $\gg d_{50}$
↓
stacking defect
develops through
the coating
thickness and
amplifies

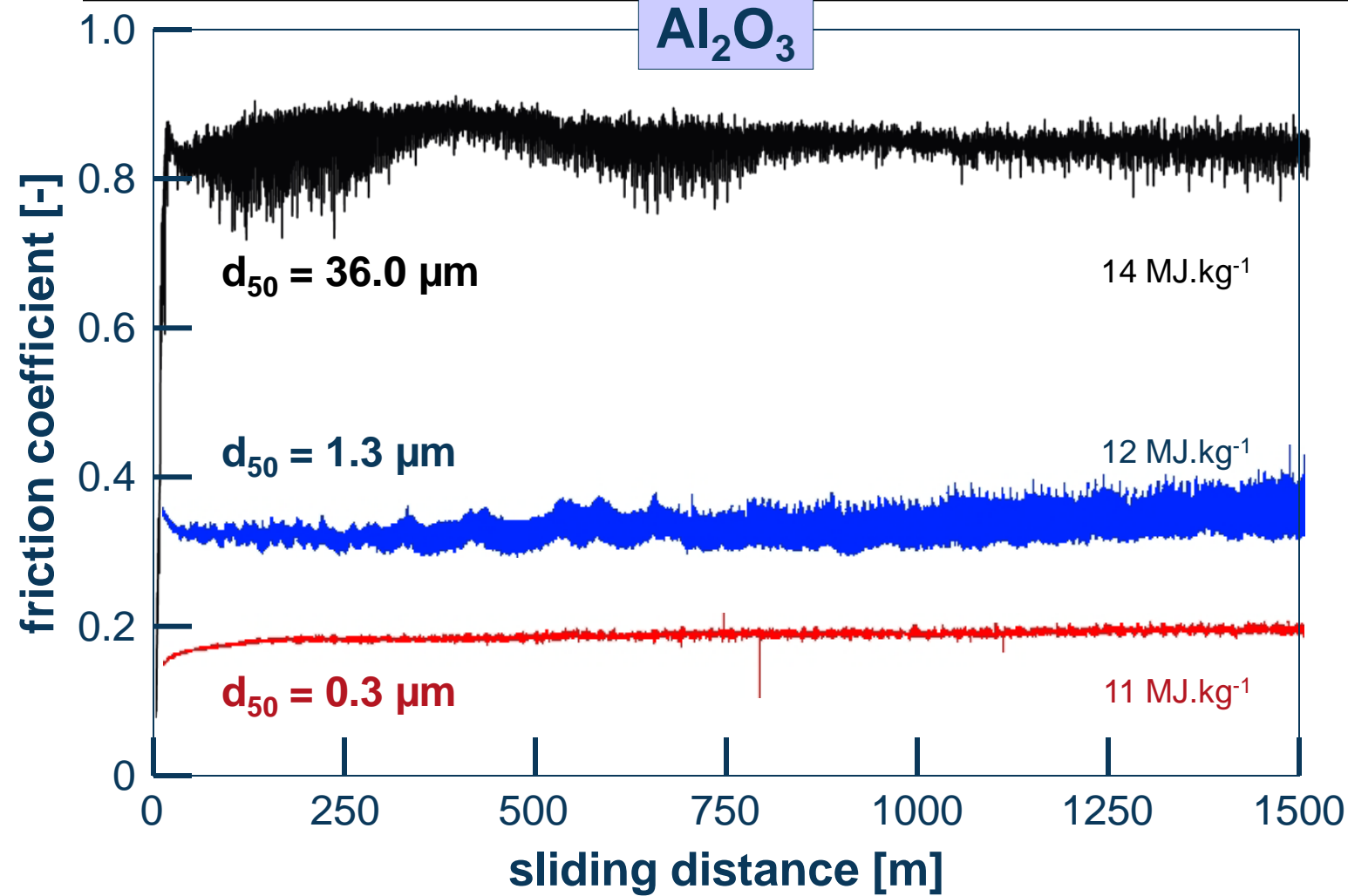


YSZ thermal barrier coatings (TBCs)



friction coefficient vs sliding distance

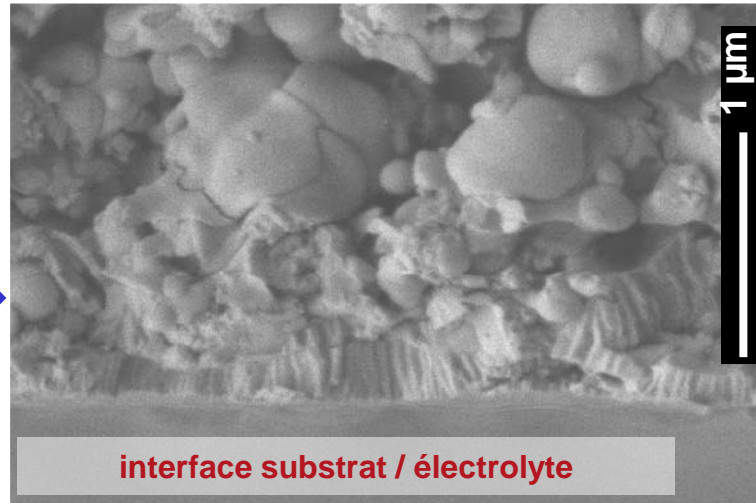
Al₂O₃



radius (mm)	10
length (m)	1500 (23873 cycles)
load (N)	2
speed (m.s ⁻¹)	0.1
conditions	dry / blew
ball	Al ₂ O ₃ • 6 mm

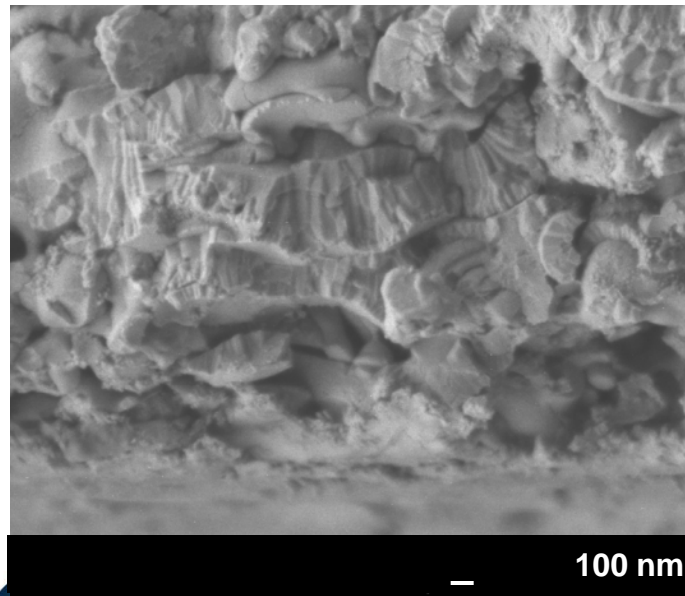
Electrolyte Y-PSZ

Conventional
SPCTS torch

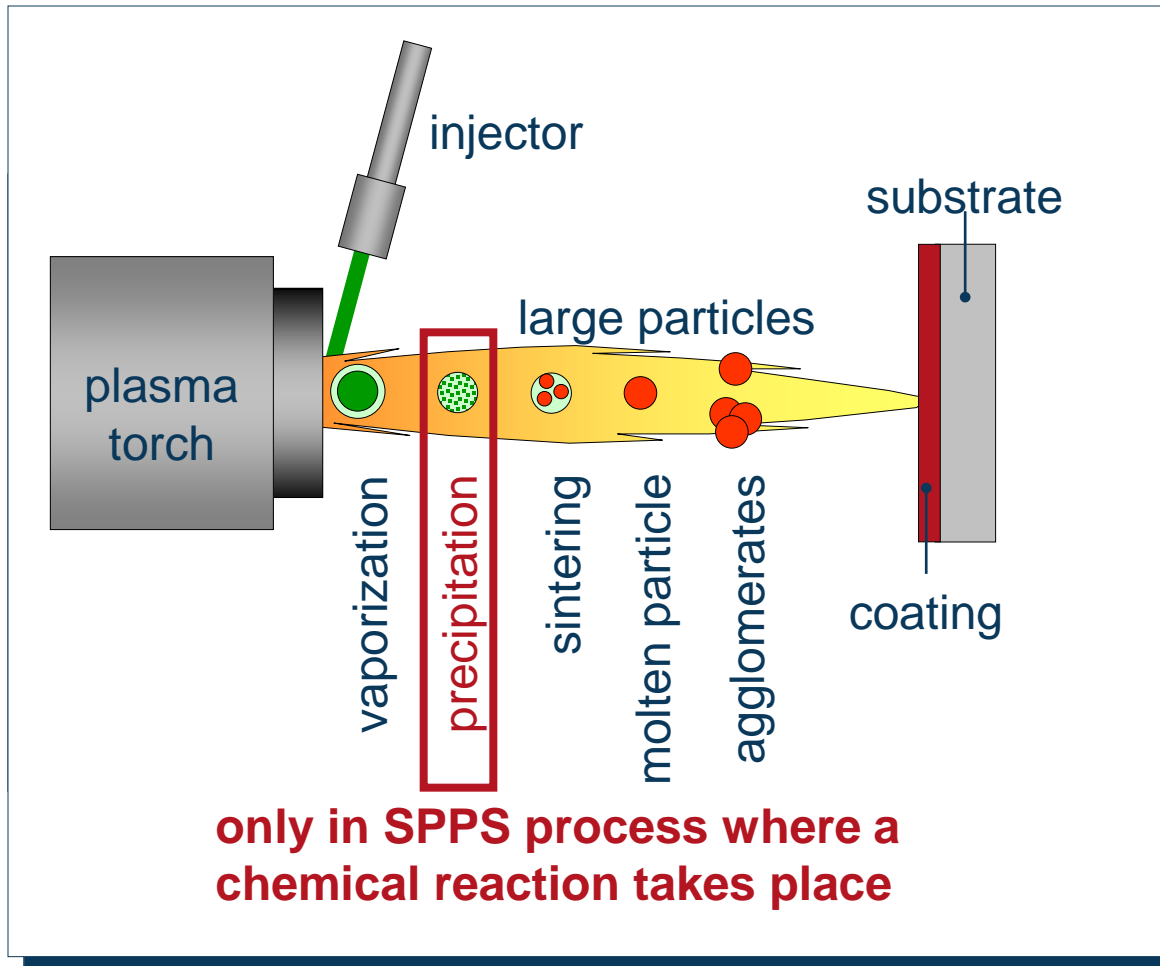


Ar: 30 L/min
He: 30 L/min
I: 600 A
h: 11,5 MJ.kg⁻¹

TriplexPro 200
torch



Ar: 50 L/min
He: 10 L/min
I : 300 A
h: 11.5 MJ.kg⁻¹
D: 40 mm
D_{nozzle}: 9 mm
Pos: 2



liquid precursor plasma spraying (SPPS)

SPPS: solution (torch F4)

nickel nitrate : $\text{Ni}(\text{NO}_3)_2, 4\text{H}_2\text{O}$

yttrium nitrate : $\text{Y}(\text{NO}_3)_3, 6\text{H}_2\text{O}$

zirconyl nitrate : $\text{ZrO}(\text{NO}_3)_2, 2\text{H}_2\text{O}$

dissolution in Et-OH
20 wt.% of dry material

Et-OH

final required layer composition
Ni / 8YSZ
50-50vol.%

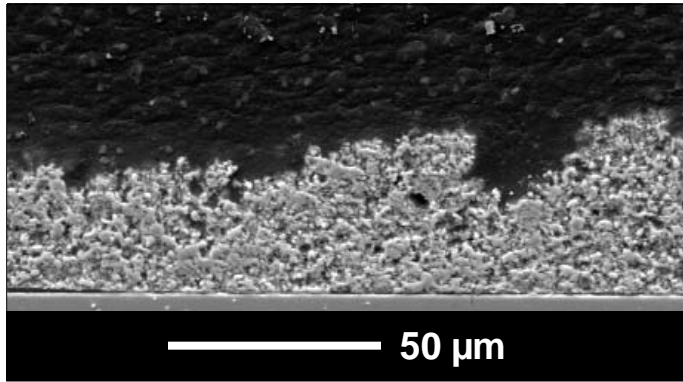
viscosity
 $6.7 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$

SPPS: layer architecture (torch F4)

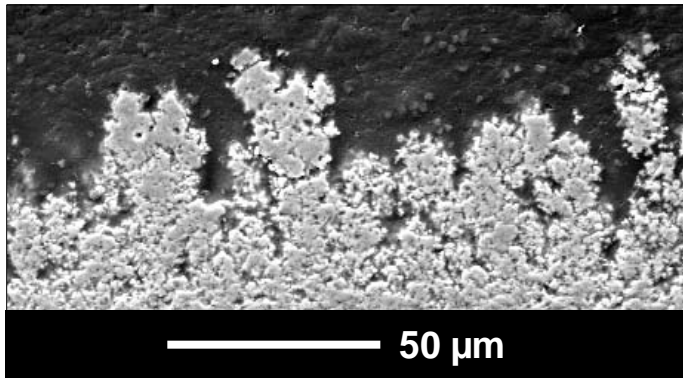
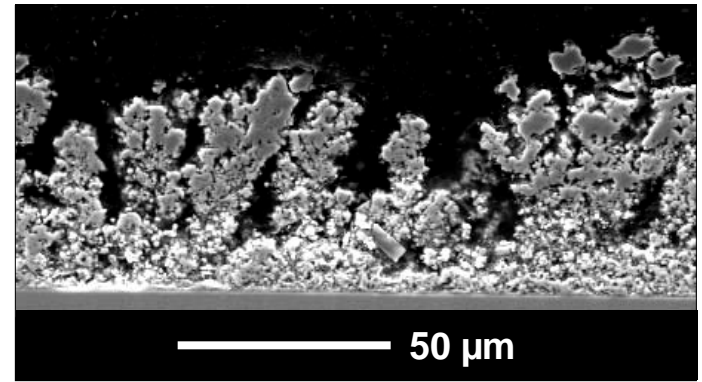
Ar-He

spray distance

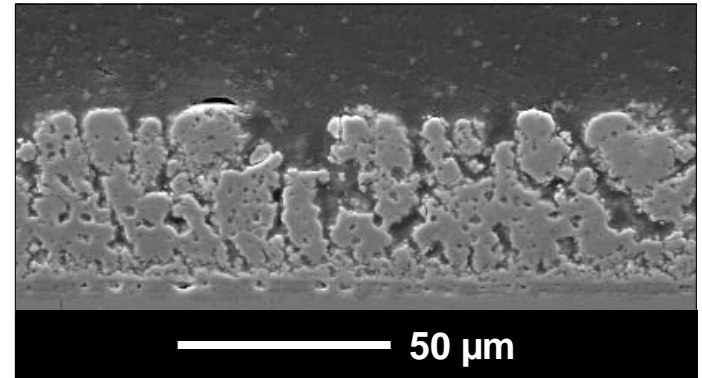
Ar-H₂



50 mm



20 mm

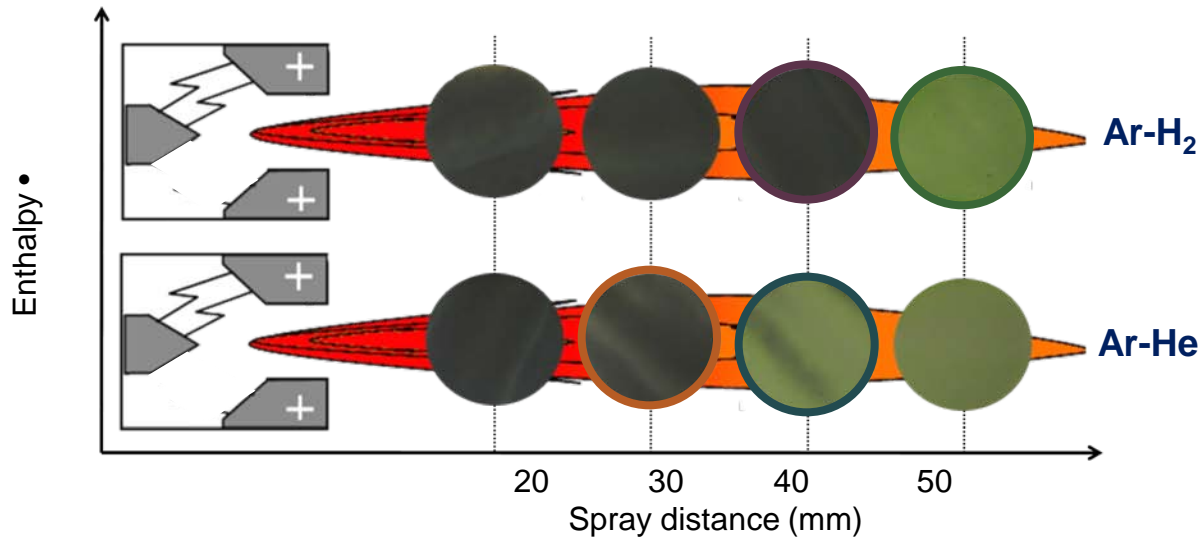
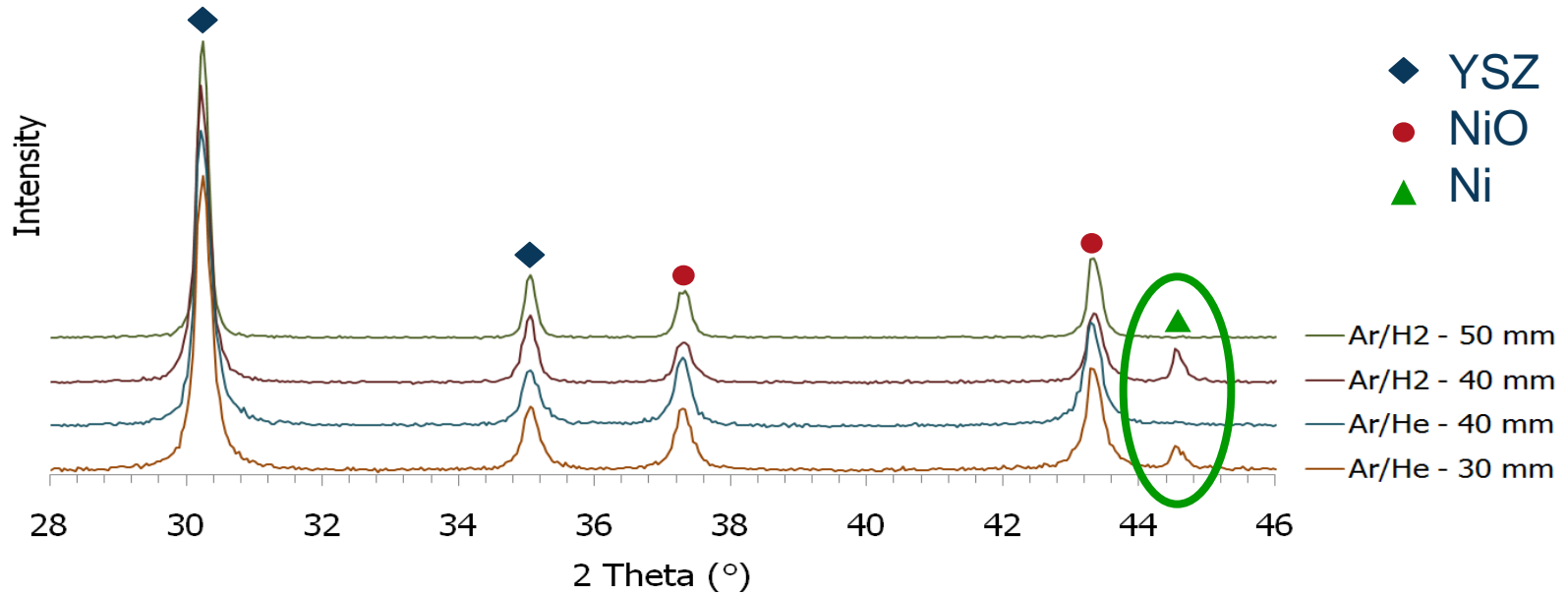


11.5 MJ.kg⁻¹

13.5 MJ.kg⁻¹

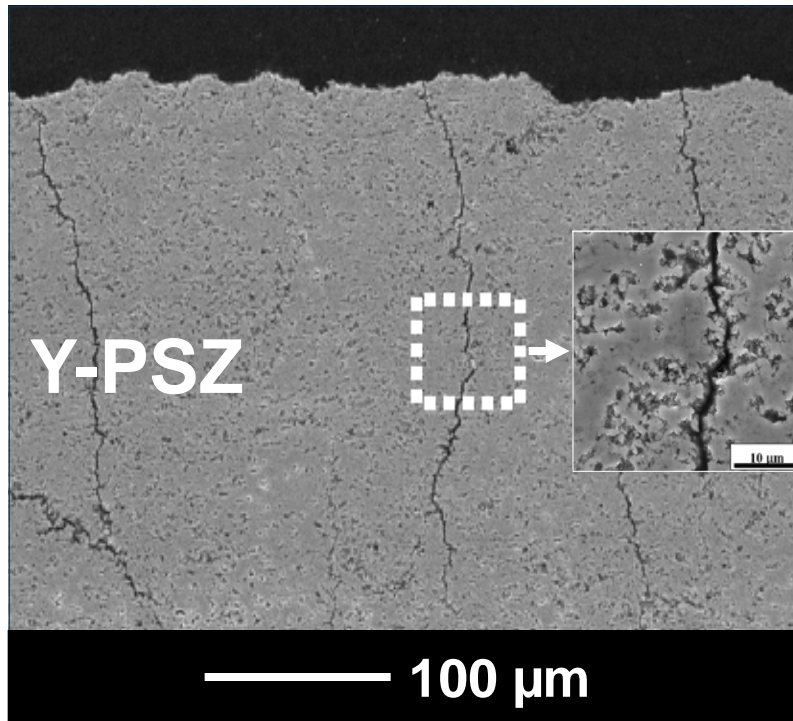
denser at 50 mm spray distance
more achieved pyrolysis treatment

SPPS: nickel oxidation state

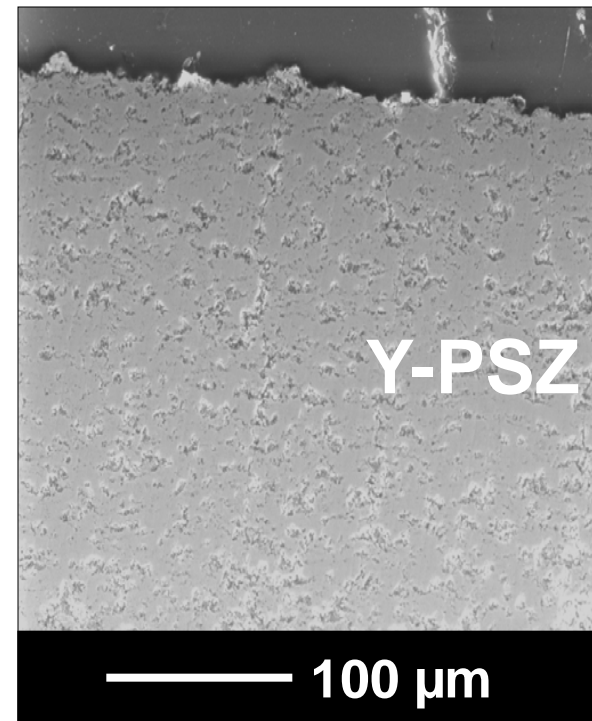


1. higher distance of re-oxidation of Ni under Ar / H₂ plasma flow
2. does oxidation occurs in-flight or once material deposited?

solution layer architectures (YSZ)



air cap atomizer
 $d_p > 25 \mu\text{m}$



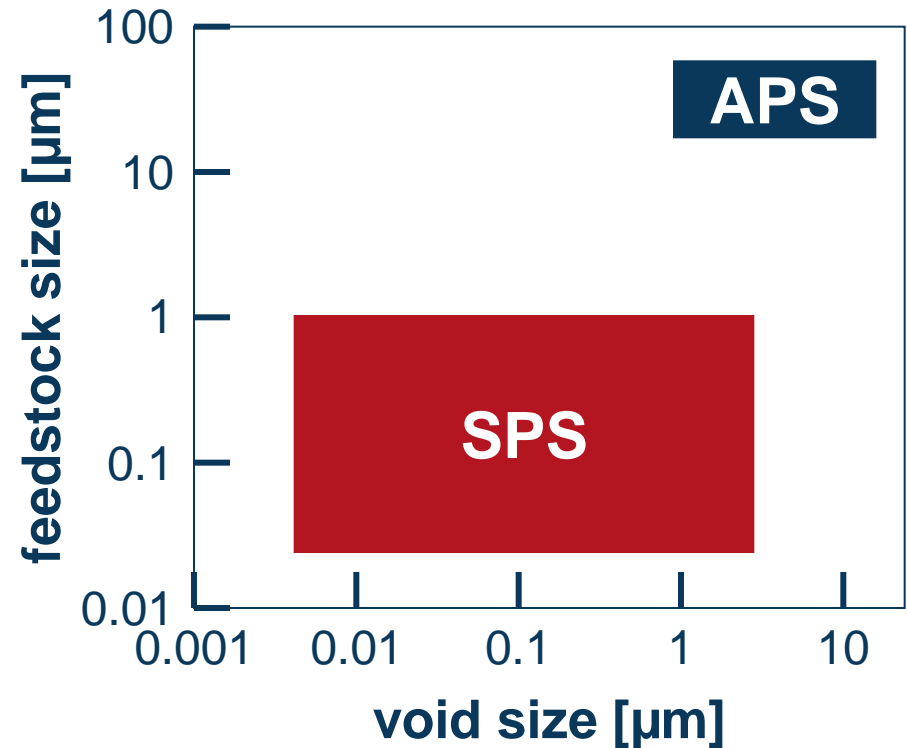
air cap atomizer
 $d_p < 25 \mu\text{m}$

Jordan ITSC 2007

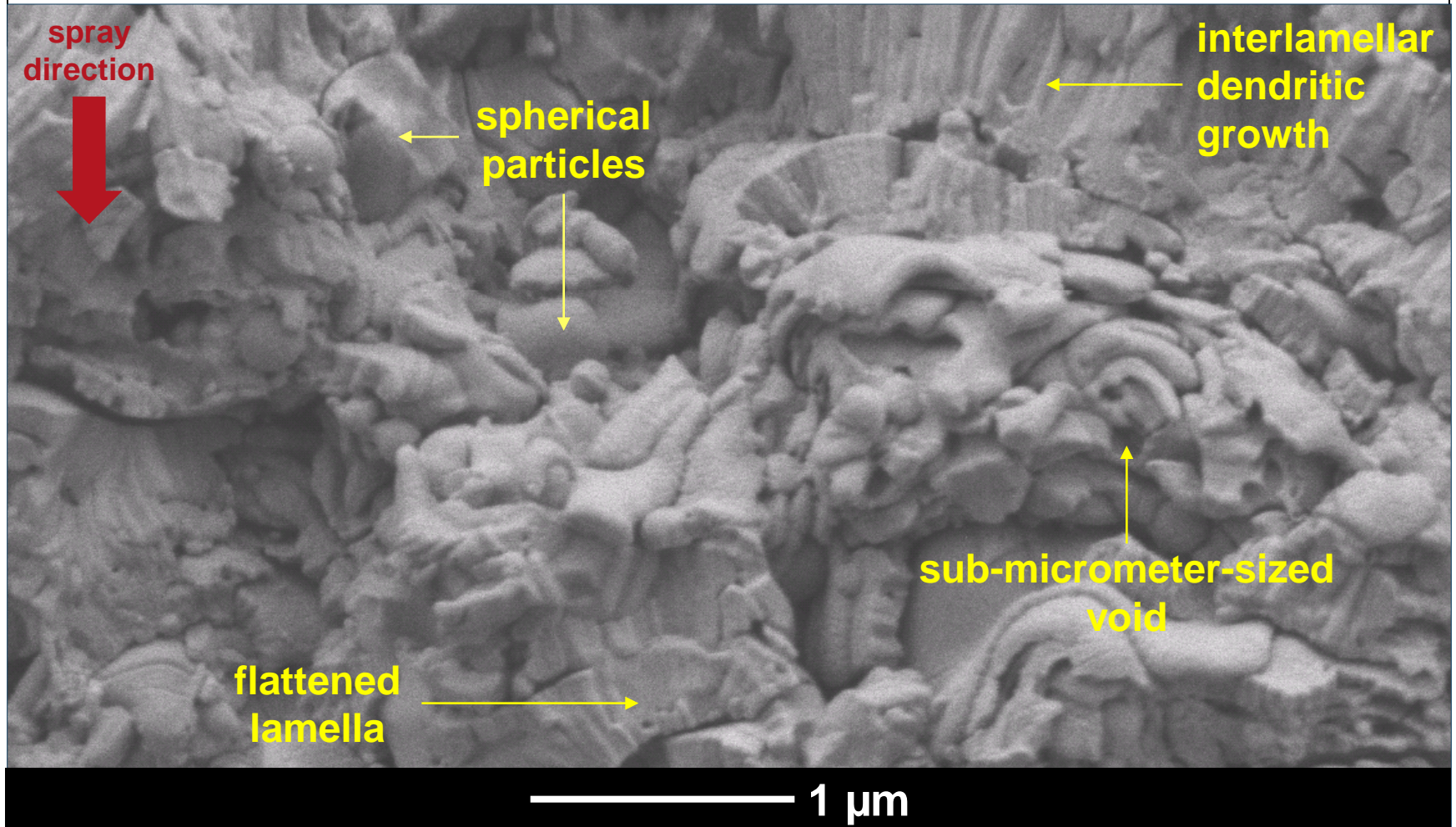
cracks → unpyrolized drops reheated by plasma heat flux

concluding remarks

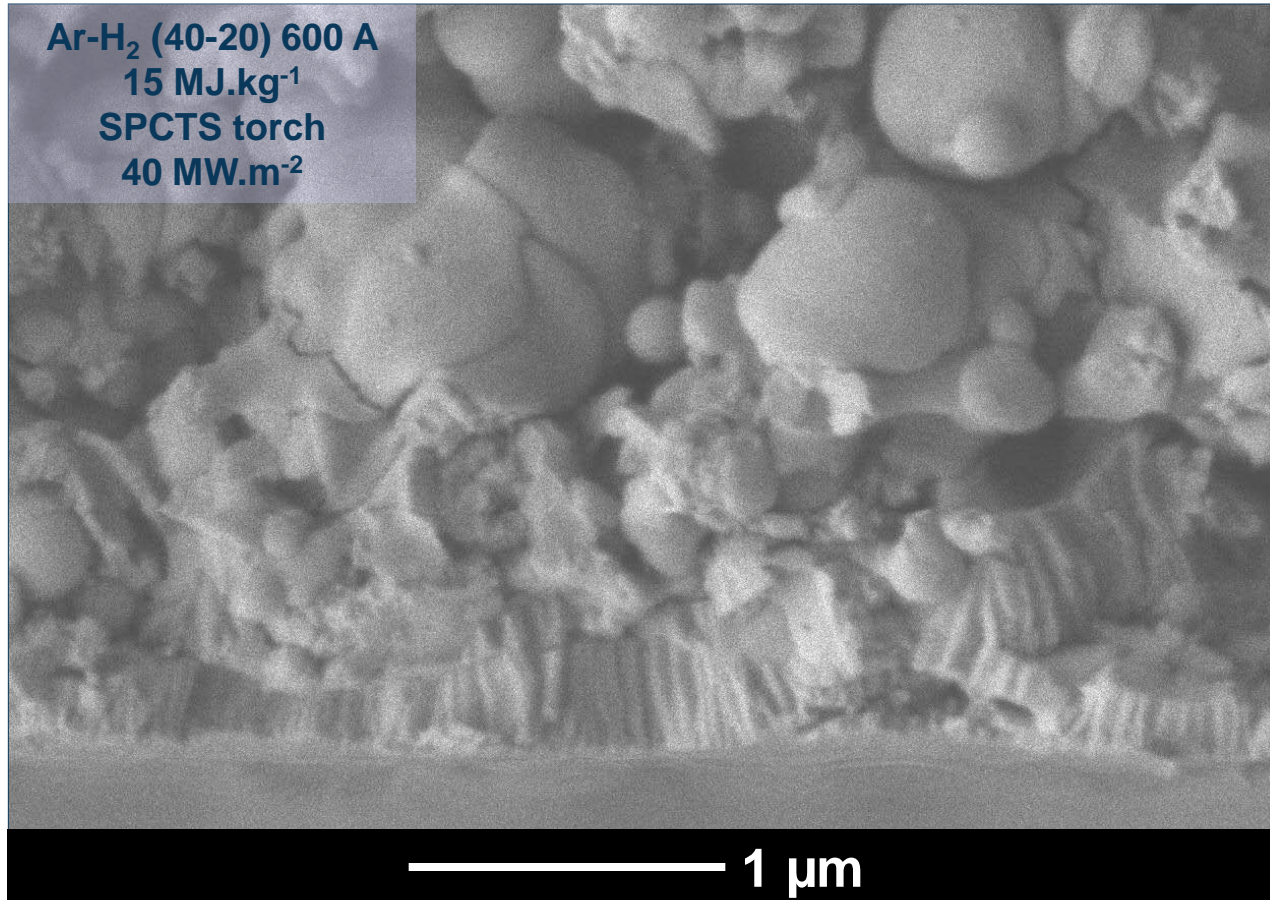
APS	SPS
globular cracks (normal to substrate) delaminations (parallel to substrate)	mostly globular
connectivity 60 to 80%	connectivity 10 to 30%

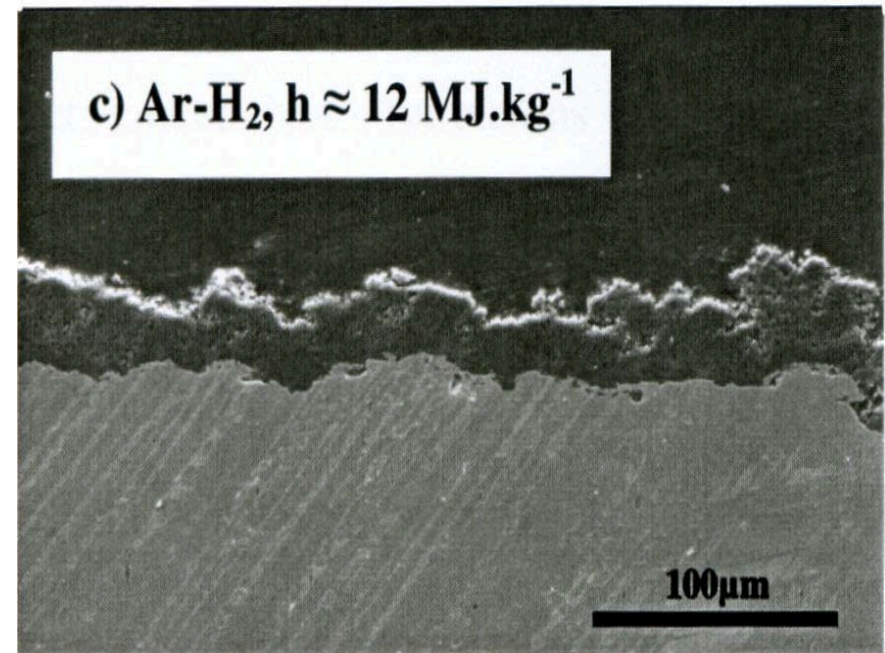
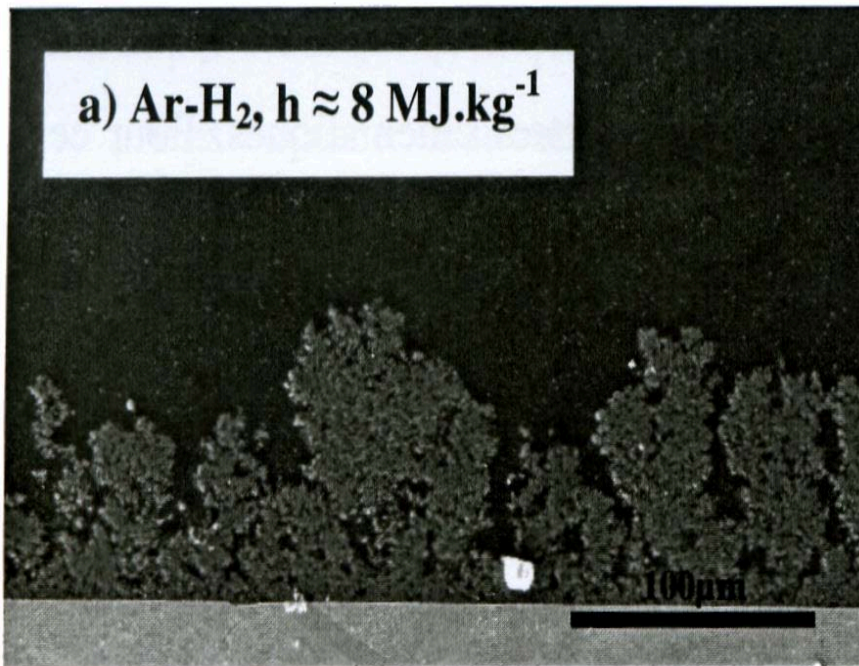


coating architecture

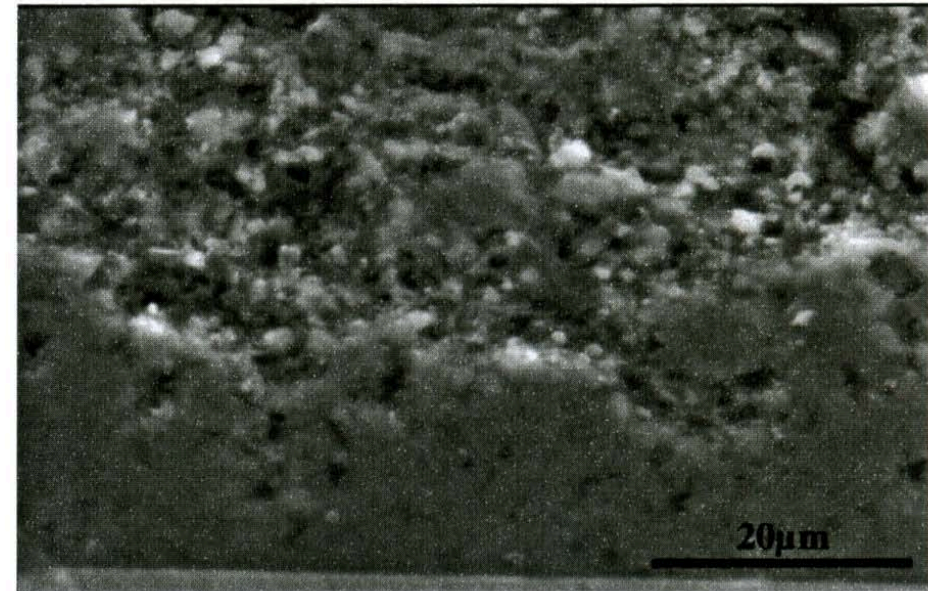
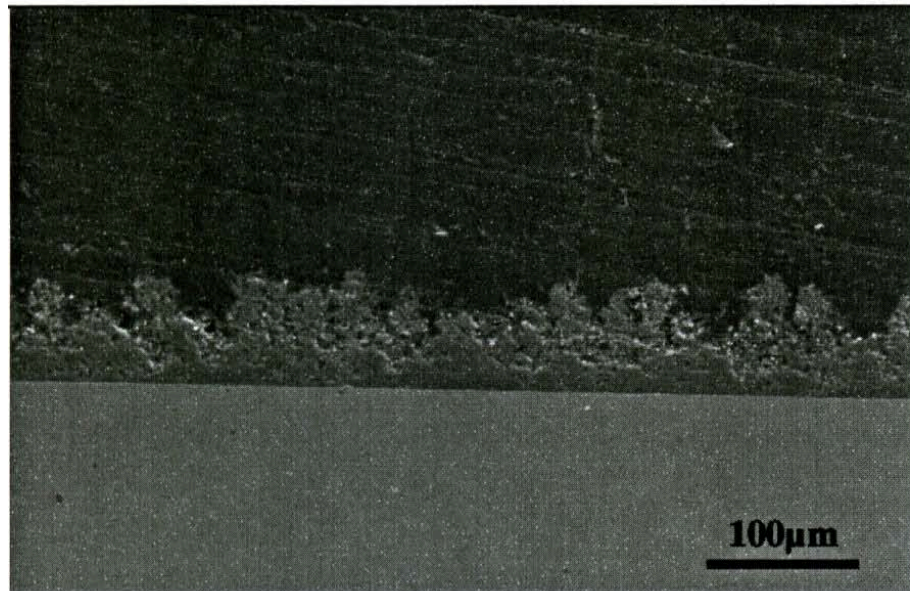


coating architecture

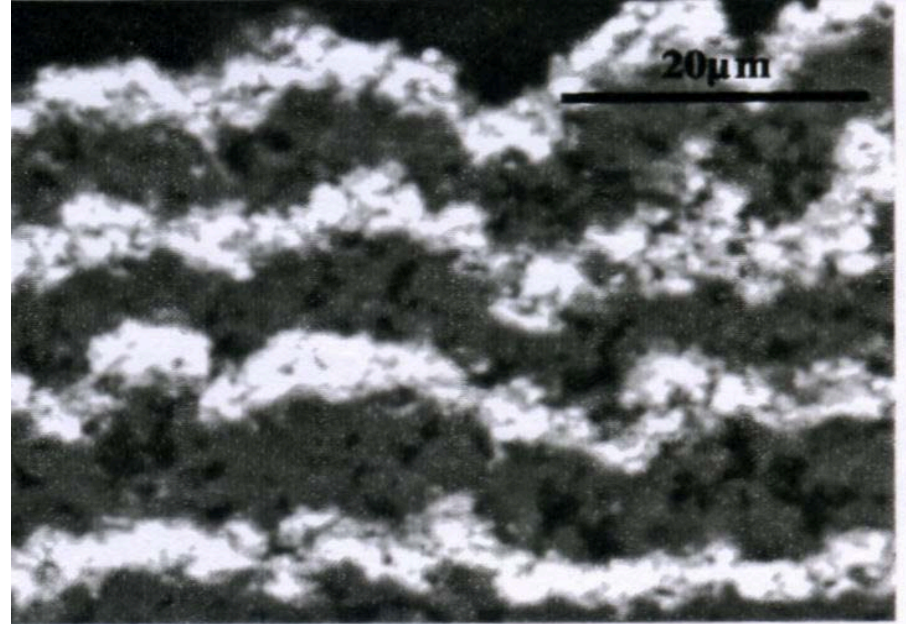
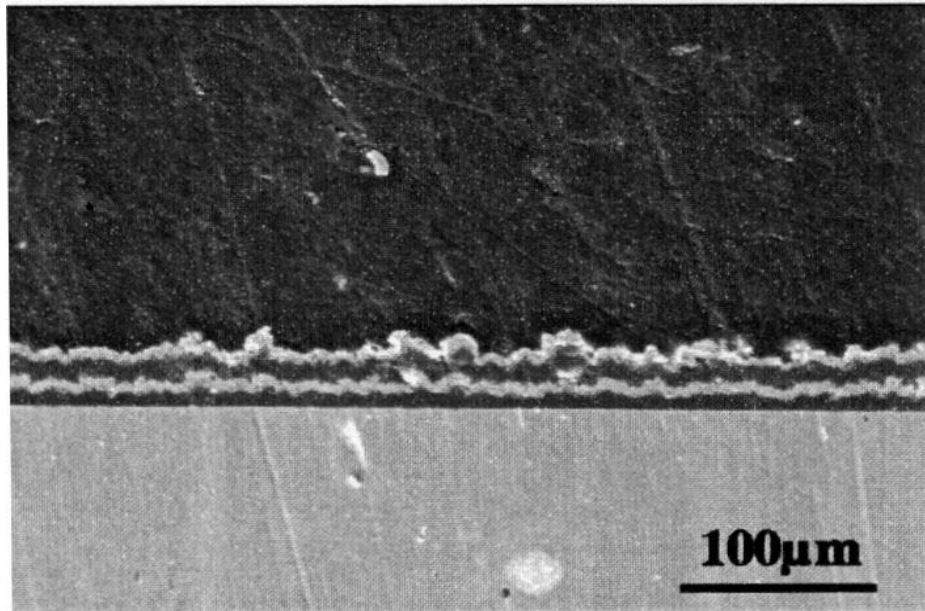




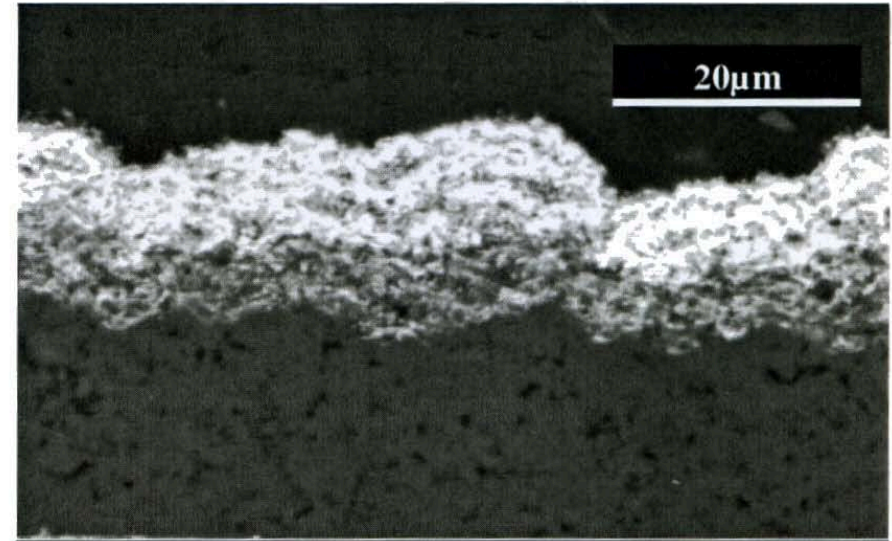
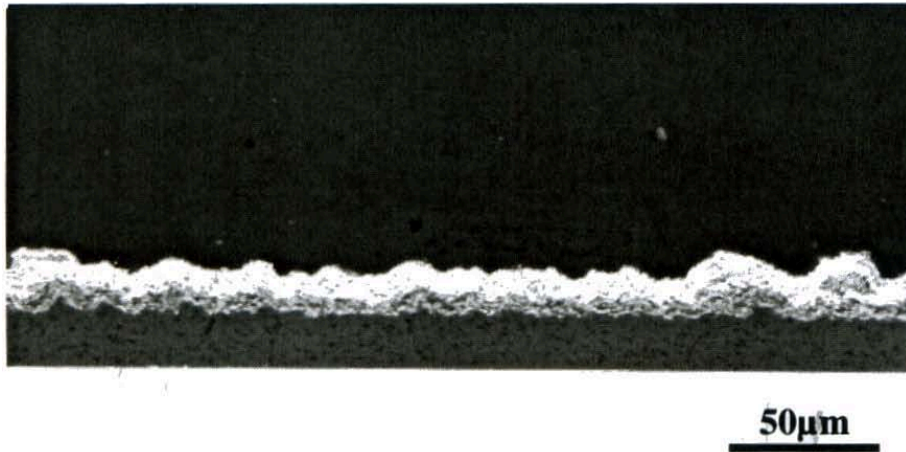
Gradient de porosité « nanostructuré »

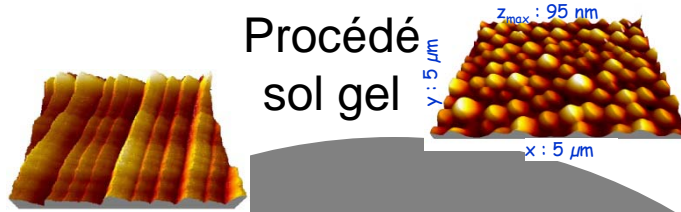


Multicouche « nanostructuré »



composite « nanostructuré »





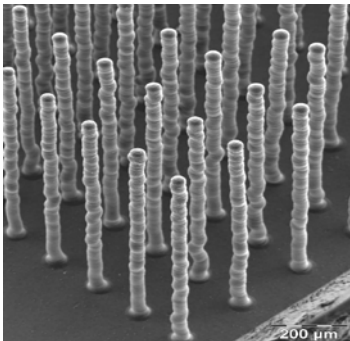
Procédé
sol gel

Organisation structurale multiéchelle des matériaux

Resp. : philippe.thomas@unilim.fr

SPCTS

Procédé
Injection
jet d'encre
céramique



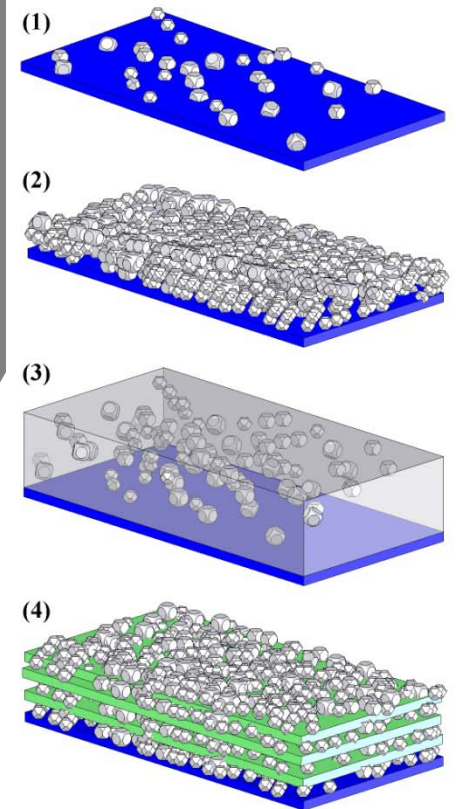
Procédés
Céramiques

Resp. : [fabrice.ros
signol@unilim.fr](mailto:fabrice.ros
signol@unilim.fr)

Procédés de
traitements
de surface

Resp. : [alain.de
noirjean@unilim.fr](mailto:alain.de
noirjean@unilim.fr)

Procédé
LECBD



JE VOUS REMERCIE POUR VOTRE ATTENTION

Je remercie également pour leur contribution aux résultats exposés

Stéphane valette

Elodie Brousse

Ghislain Montavon

Antoine Bacciochini

Pierre Fauchais

Fadel Ben Etouil

Pierre Lefort

Manon Nuzzo

Hélène Ageorges

Olivier Tingot

Alain Grimaud

Thibault Haure

Jean François Coudert

Vincent Rat

Pascal Tristant

Nicolas Lory

Quelques exemples de notre activité

1 - Les procédés céramiques

f_rossignol@ensci.fr



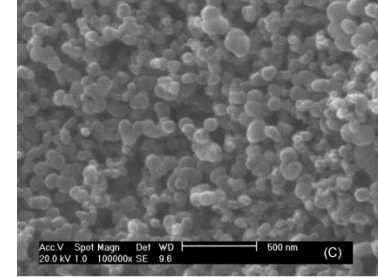
Matériaux de hautes performances

- **Systemes céramiques à microstructures et architectures contrôlées**
- **Nouveaux procédés d'élaboration**

Matériaux de hautes performances

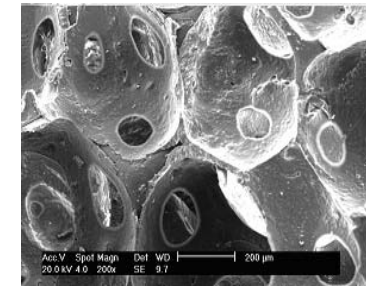
Hautes températures / Milieux agressifs

- Synthèse de nanopoudres (Si/C/N/O/Y/Al) par spray-pyrolyse à partir de précurseurs
- Frittage SiC (B_4C), ZrC(ZrB_2)
- Synthèse de poudres fines par SHS



Biocéramiques

Synthèse d'apatites phosphocalciques (HAP-TCP)



Semiperméabilité

Synthèse d'apatites ($La_9Sr_1Si_6O_{26,5}$) conducteurs ioniques

Optique / électro-optique

Matériaux polycristallins transparents

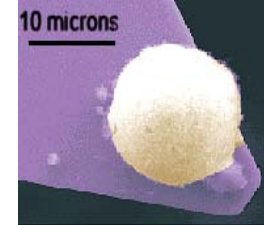
Mécanismes de frittage en vue de la maîtrise des microstructures (carbure, nitrure, borures, composites...) et de l'amélioration des propriétés

Mise en forme - Mécanismes fondamentaux

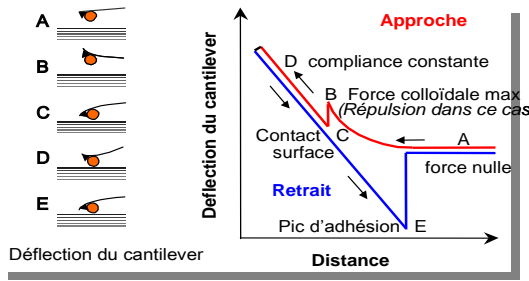
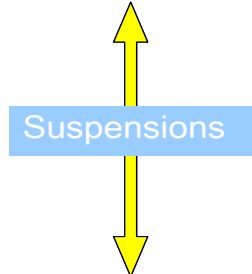
Interactions entre particules en suspension

Chimie de surface
Synthèse de nouvelles molécules
(FTIR, Raman, ESA, XPS...)

Mesure de force
(AFM)

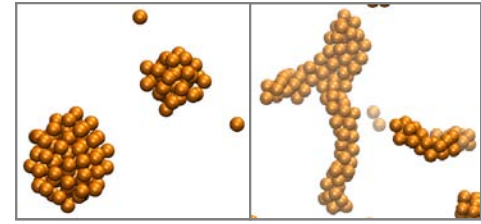


Mesure directe des forces colloïdales par AFM en milieu liquide



Structuration 3D
(MEB-Cryo,
Diffusion de la lumière...)

Modélisation



Modélisation (dynamique Brownienne) et caractérisation de la structure 3D de suspensions (cryo-FEG)

Rhéologie

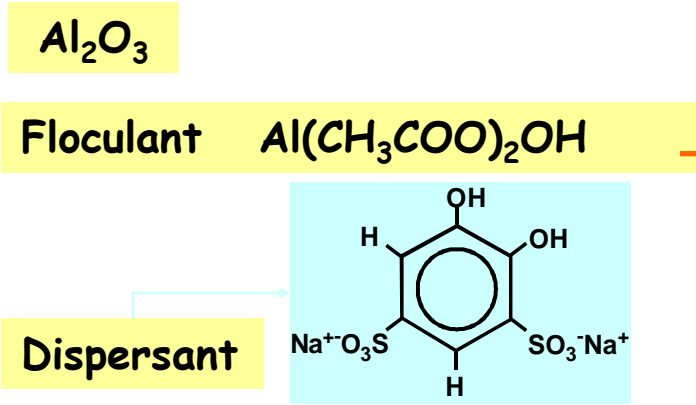
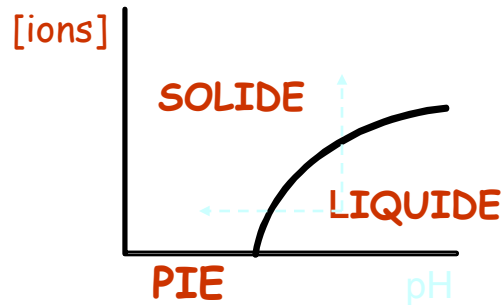
Compréhension et modélisation du comportement à l'écoulement de systèmes céramiques/auxiliaires de mise en forme

Mise en forme - Mécanismes fondamentaux

Procédés classiques

Injection, extrusion, pressage, coulage en bande, dépôt électrophorétique, déliantage

Coulage - Coagulation

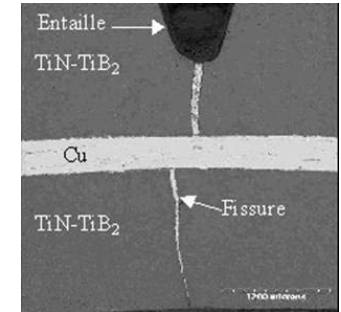
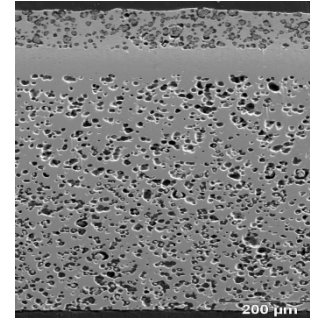


Design (Microstructure/Architecture) / Propriétés

Systemes multicouches et multimatériaux

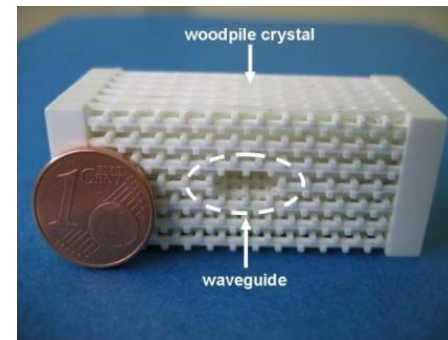
Elaboration de matériaux à gradients de propriétés (coulage en bande, HP, HIP)

SOFC, CMR, composites lamellaires...



Méthodes numériques

Stéréolithographie (structurales)



Impression jet-d'encre

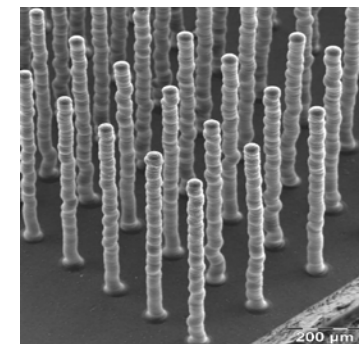
Microcomposants multifonctionnels
Microsystèmes (capteurs, actionneurs...)

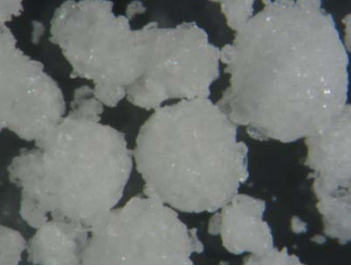


➔ Phénomène d'éjection

$$1 < \frac{Re}{\sqrt{We}} = \frac{\sqrt{\gamma \cdot \rho \cdot r}}{\eta} < 10$$

η , Viscosité, γ , Tension de surface,
 r , Diamètre de la buse
 ρ , Densité





Biomatériaux et fonctionnalisation



Formes pharmaceutiques solides - Biomatériaux

Formulation
principes actifs
excipients

**Procédé de mise en
forme**
broyage - mélange -
granulation - compression ...

**Gestion des
qualités d'usage**

Caractérisation des agglomérats
morphologie, microstructure, propriétés mécaniques,
distribution des phases, rhéologie...

Propriétés mécaniques
Libération des molécules
actives
Biodisponibilité

Structures biocéramiques à gradients de porosité

Mise en forme
de la matrice
biocéramique à porosité
contrôlée

**Fonctionnalisation
par des principes
actifs**

Propriétés mécaniques
Libération des agents
actifs
Repousse osseuse

Quelques exemples de notre activité

3. L'organisation structurale multiéchelle des matériaux

philippe.thomas@unilim.fr

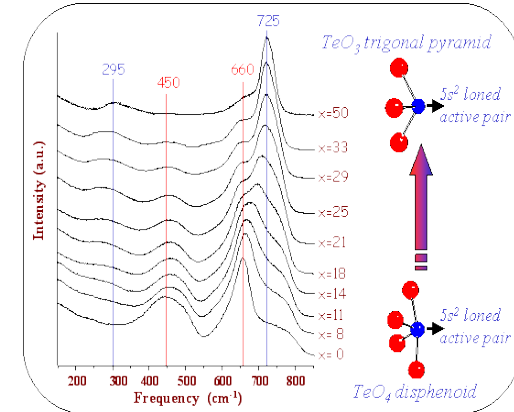
Verres et matériaux à base de TeO_2

Elaboration et étude structurale de matériaux pour l'optique non-linéaire (doublement de fréquence, remplacement de la silice : vitesse x 50)

Développement de nouvelles phases cristallines ou amorphes

Etude des corrélations entre la structure et la réponse en optique non-linéaire

Prédiction des propriétés diélectriques par calculs *ab initio* à partir des modèles structuraux



Spectres Raman de verres dans le système $x \text{Te}_2\text{O} - (100-x) \text{TeO}_2$

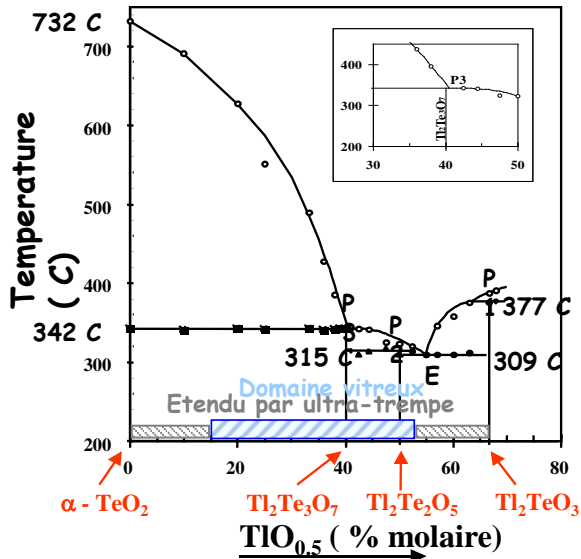
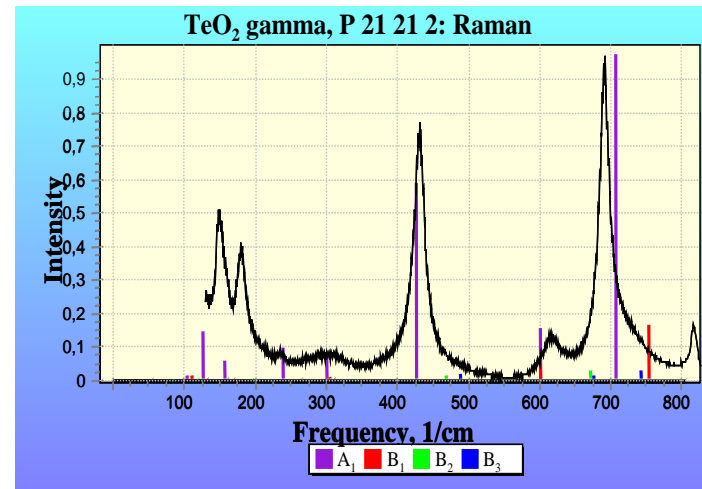
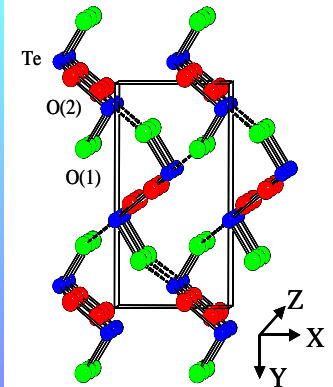


Diagramme de phase $\text{Tl}_2\text{O} - \text{TeO}_2$



Spectres expérimental et modélisé de diffusion Raman. Représentation de la structure de $\text{TeO}_2 \gamma$



Oxydes diélectriques complexes

Composés ferroélectriques / piézoélectriques sans plomb

- Phases d'Aurivillius : $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$, $\text{SrBi}_2\text{Nb}_2\text{O}_9$, $\text{SrBi}_2\text{Ta}_2\text{O}_9$...

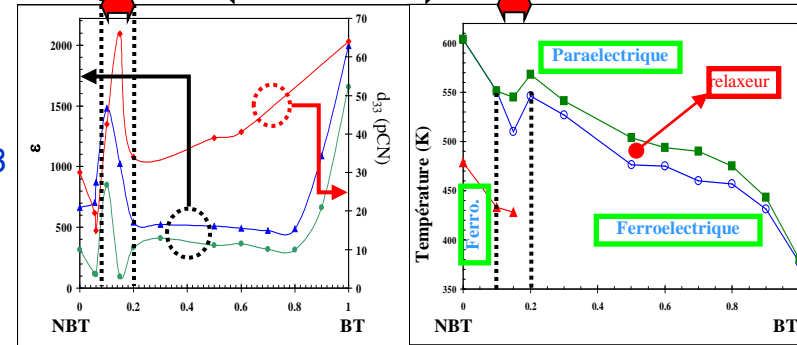
- Perovskite (relaxeur diélectrique) :

$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT)

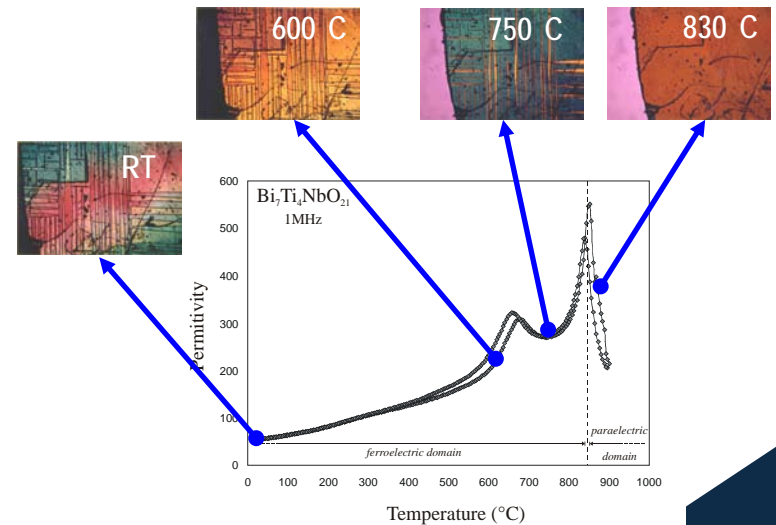
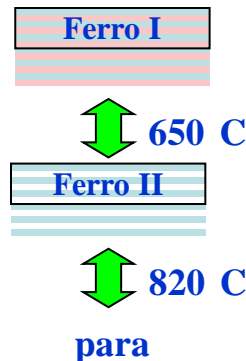
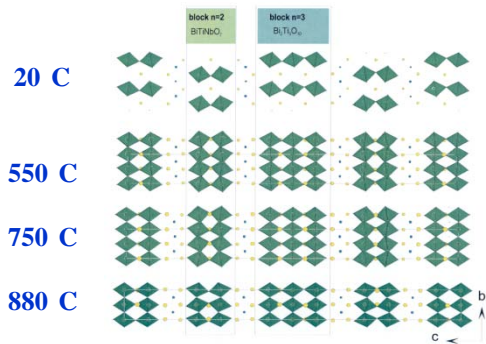
et solutions solides : NBT-BaTiO_3 , NBT-SrTiO_3

- Relation structure/propriétés piézoélectriques
- Etude structurale des transitions de phase

Etude du système $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ / BaTiO_3



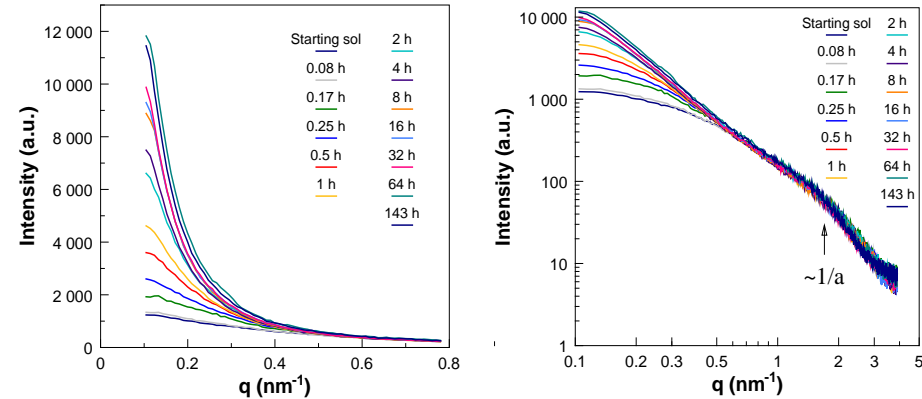
$\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$: étude structurale des transitions de phase



Précurseurs d'oxyde nanocristallisés

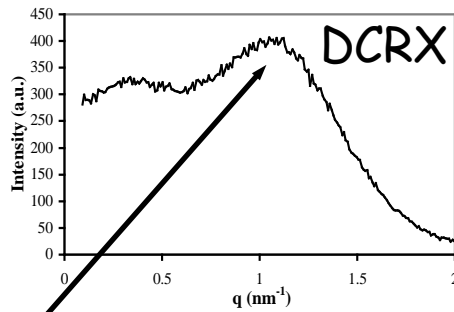
Elaboration par voie sol-gel

Etude de la transition sol-gel, des mécanismes d'agrégation et des structures fractales qui en résultent (diffusion centrale des rayons X)

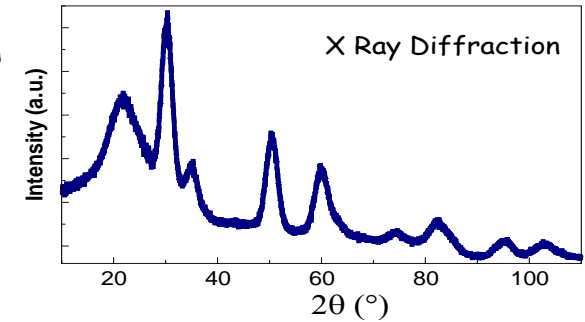
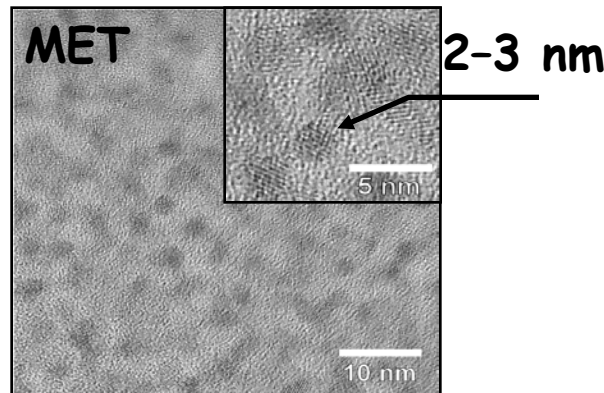


Etude des mécanismes d'agrégation durant la transition sol-gel dans des sols précurseurs d'oxyde de tellure

Elaboration de matériaux massifs nanostructurés par séparation de phase (diffusion centrale et diffraction des rayons X)



Distance entre les cristaux de zircon : 6 nm



Formation de nanocristaux de zircon dans une matrice amorphe de silice
Le mécanisme de séparation de phase induit une distribution non-aléatoire de la position des cristaux de zircon

Quelques exemples de notre activité

2. Les procédés de traitements de surface

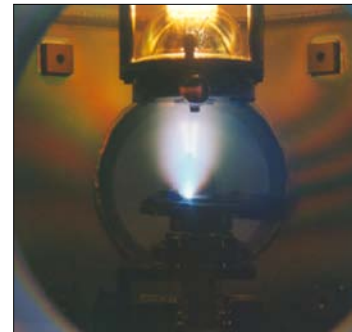
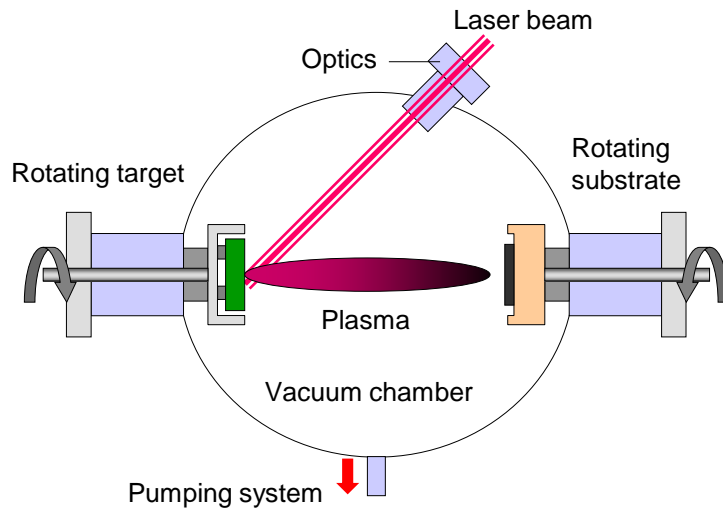
alain.denoirjean@unilim.fr

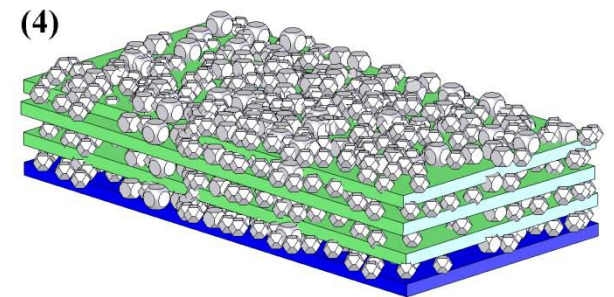
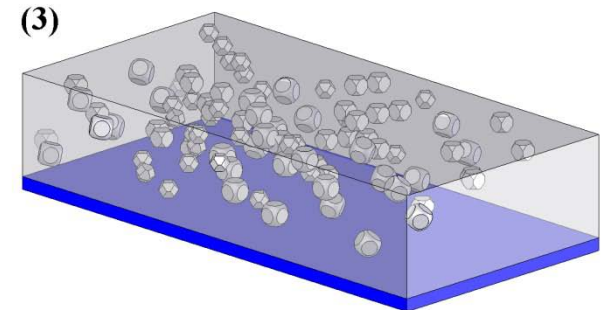
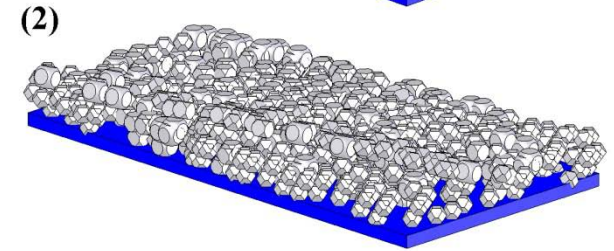
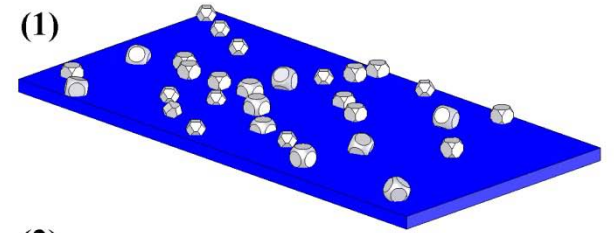
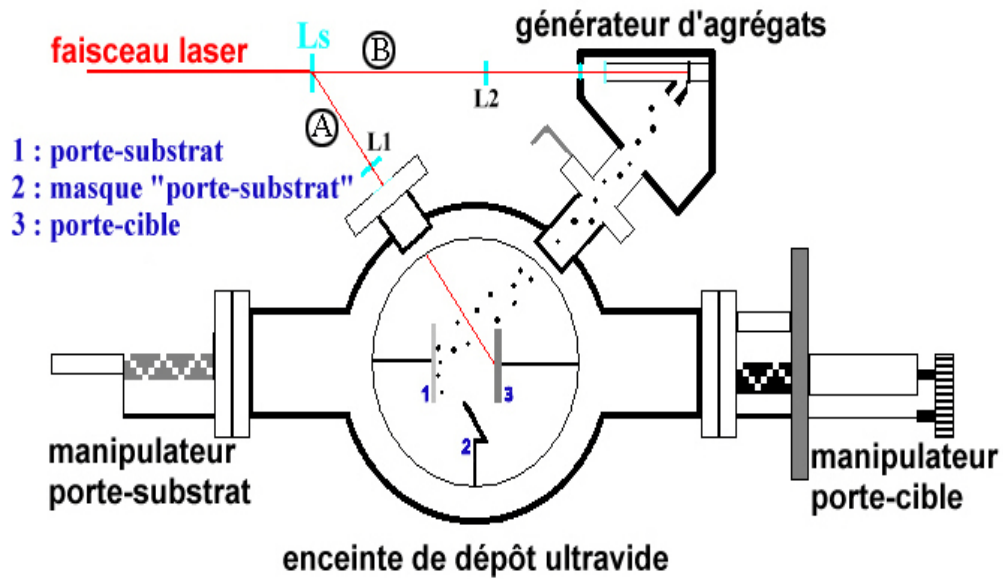
Low pressure plasma processes

Laser ablation (Pulsed Laser Deposition)
CVD (plasma, laser, microwaves-enhanced)

Thickness: Å - a few μm

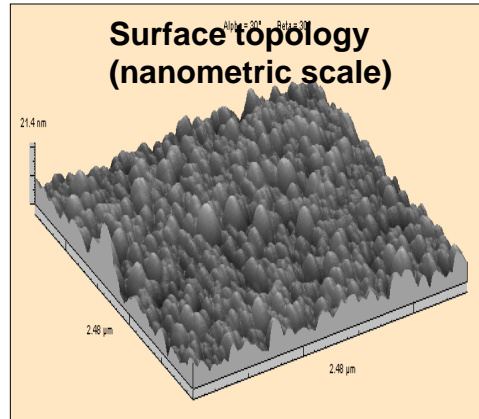
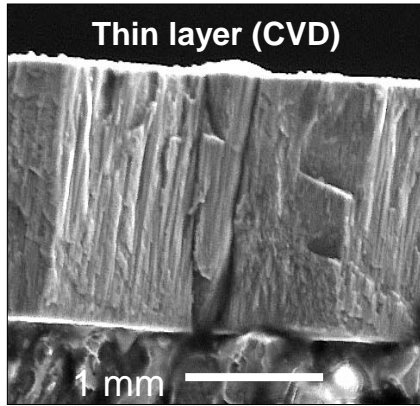
Diagnostics *in situ* (plasma, nature and velocity of reactive species...)
Reactional processes
Characterisation of microstructures (AFM, MFM, TEM...)
Evaluation of useful properties (optic, electric, mechanic)



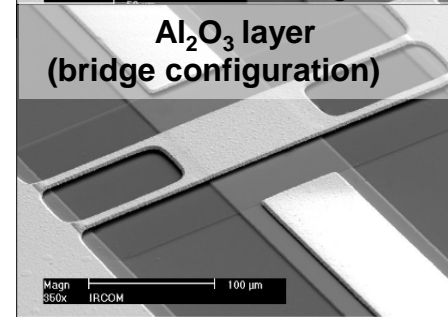
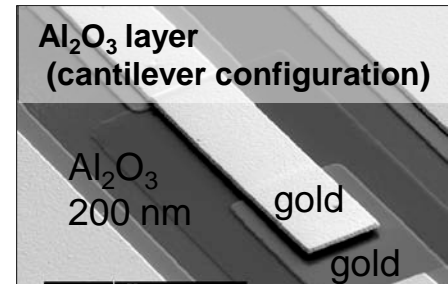


Domains of micro- and nanotechnologies

Microelectronic, optoelectronic, friction/wear (dry, high temperatures)
Functionally graded layers, diffusion barriers



Capacitor
Electrostatic actuation



Cobalt aggregates on Si(100) substrates

Composites: aggregates Co (2 nm) in amorphous Al₂O₃ matrix

