Injection synchrone de précurseurs liquides dans un plasma d'arc pulsé

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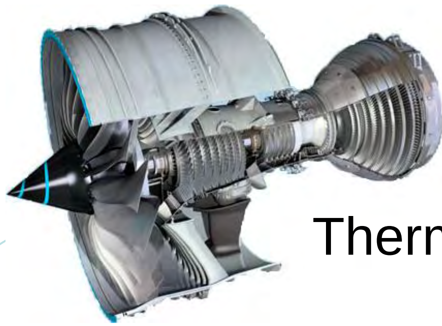
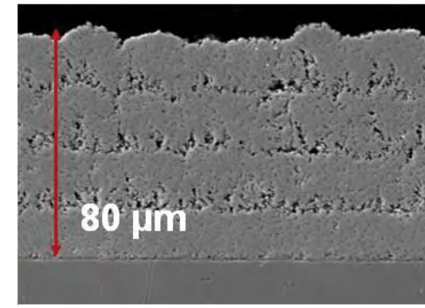
t_0: janvier 2014
Durée 24 mois
33 keuros HT pour équipement injection

LIVRABLES	
Avant	*Modifications proposées*
Tâche 1 : Etude du plasma pulsé sans injection	
- Etude des instabilités de l'arc dans la torche résonante - Diagnostic du plasma sans injection	- Etude de l'influence sur la stabilité de la torche de la superposition d'une variation de courant sinusoïdale à la composante continue du courant. (amplitude de courant variable faible par rapport à la composante continue). (mesure courant/tension et bilan énergétique sur torche) **Suppression de l'étude acoustique.** - Diagnostic spectroscopique • Identification des espèces et systèmes pour différentes distances et délai de déclenchement • Mesure de la température de rotation par simulation des spectres du premier système négatif de l'ion N_2^+ pour différentes distances et délais de déclenchement.
Tâche 2 : Etude du plasma pulsé avec injection synchrone	
- Mise en œuvre d'une injection piézo-électrique monobuse - Diagnostics (spectroscopie d'émission, émission acoustique)	- Mise en œuvre d'une injection piézo-électrique monobuse - Identification des espèces et des systèmes pour différentes distances et délais de déclenchement. - Comparaison avec le cas sans injection **Suppression de l'étude acoustique.**
	Tâche 3: Collecte/dépôt
	- Collecte/dépôt en point fixe et rotation (formation de cordons) – mise en place cinématique dépôt - Corrélation entre microstructure/structure et distances/délais de déclenchement (analyse MEB, DRX et optique)

Plasma spraying of liquid feedstock (suspensions/solutions)

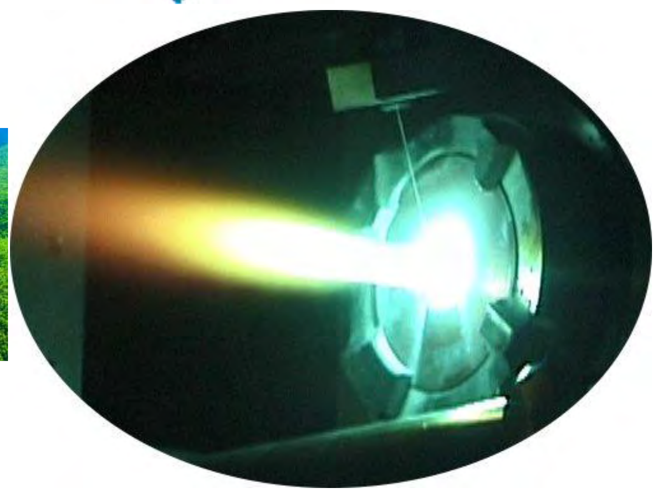


Thermal barrier coatings



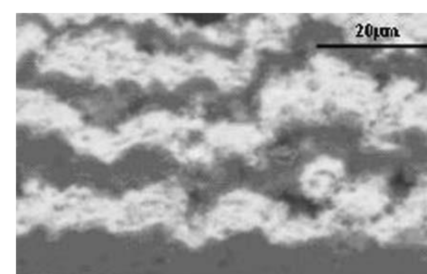
Control of coating microstructures, structures, chemical composition

Photocatalytic coatings



Biomaterials

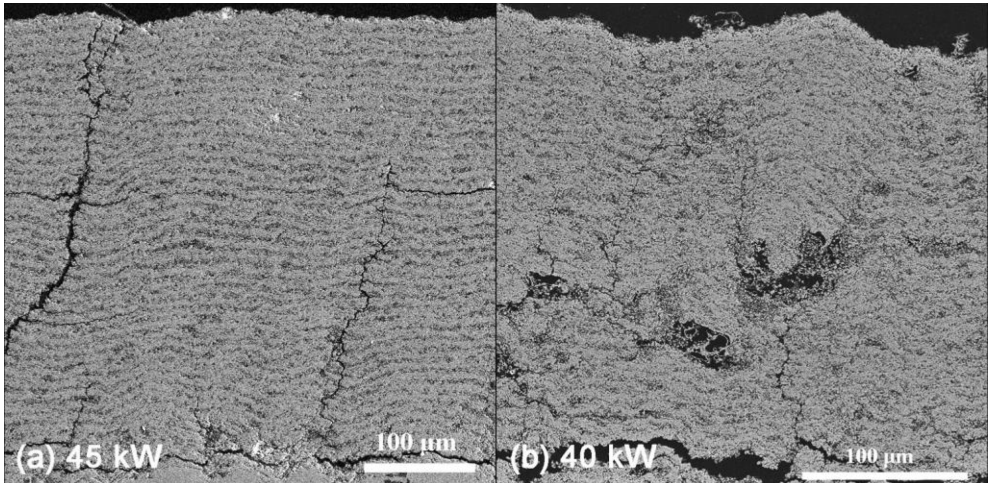
Wear resistance



O. Tingaud *et al.*, J. Thermal Spray Technol. (2010)

Coating properties depend on plasma jet stability :

Dependence of in-flight processes affecting liquid and submicron powders



Thermal Barrier Coatings
YSZ deposition by Solution Precursor Plasma Spraying SPPS
Jordan et al. , J. Thermal Spray Technol. 16, 2014

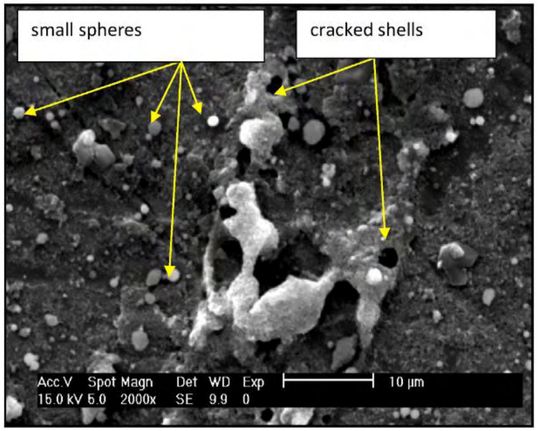
Thermal decomposition of perovksites

Suspension pérovskite $LaMnO_3$

↓

$La_2O_3 + La(OH)_3 + La_4MnO_{11} + LaMnO_3$

C. Monterrubio-Badillo et al., Surf. Coat. Technol. (200), 2006.

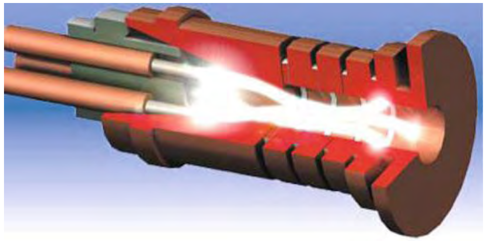


HA coatings for biomaterials
SPPS deposition

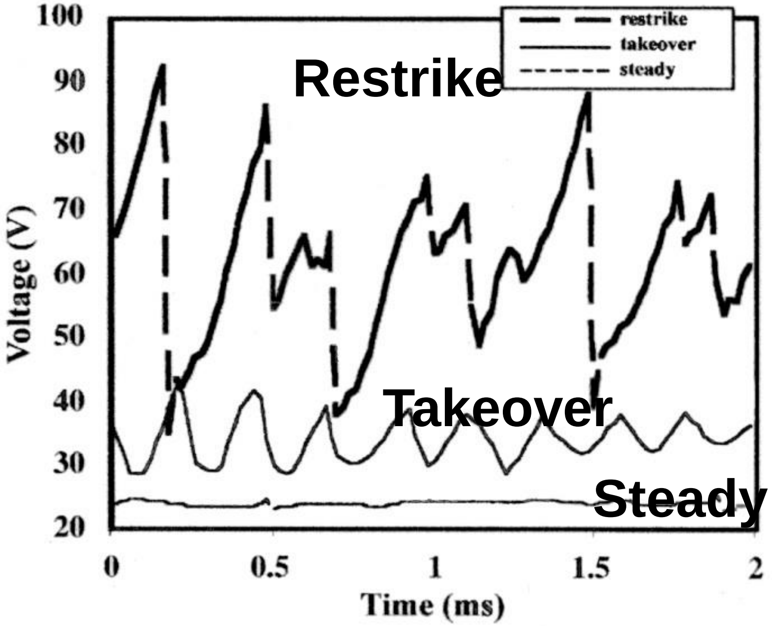
R. Candidato et al., Surf. Coat. Technol. (277), 2015.

- Problem of arc instabilities in dc torches
    - Different modes of arc instabilities
    - Each torch geometry has its own signature
    - Difficult to predict

- How to stabilize the arc ?
    - ⇨ Cascaded dc torches



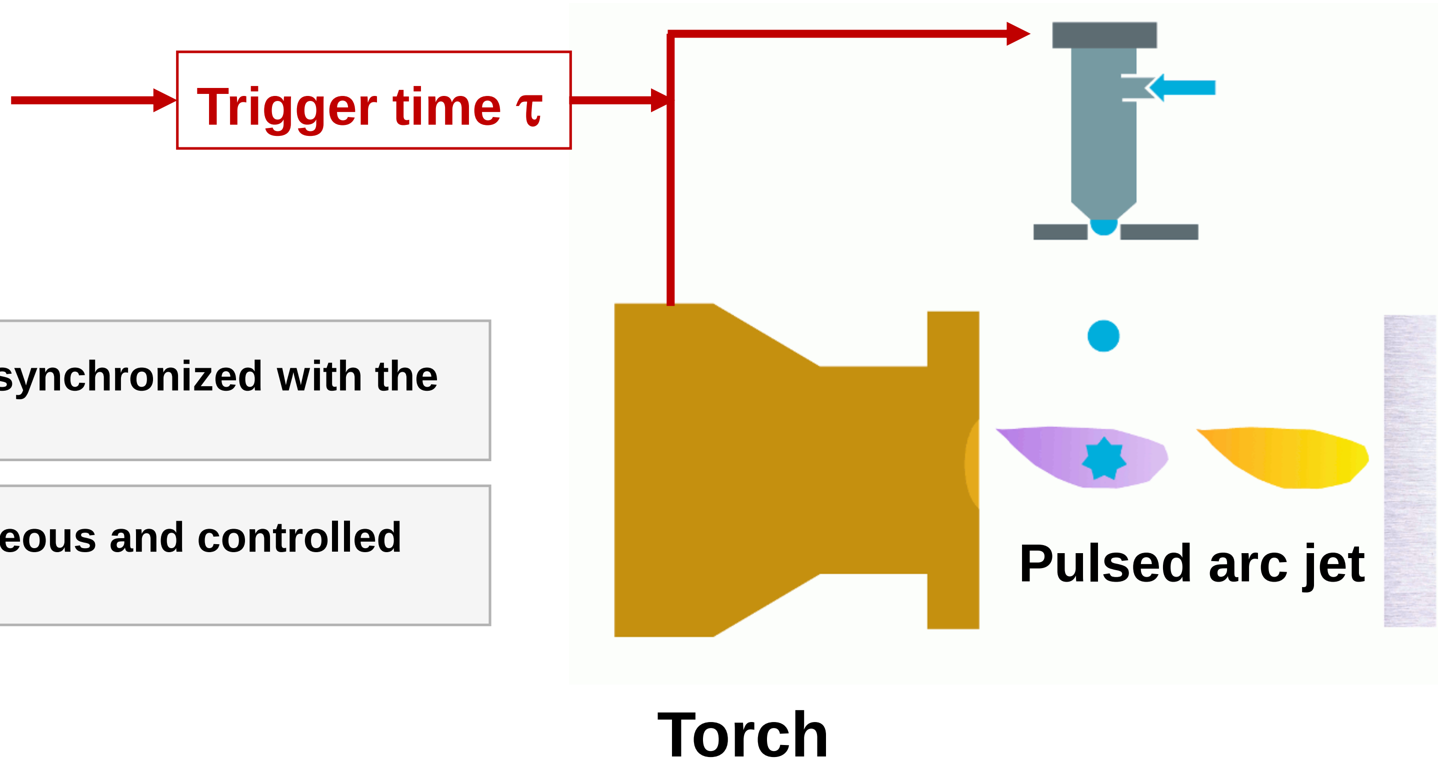
Z. Duan, J. Heberlein J. Thermal Spray Technol. (2002)



How to control the arc to improve heat and momentum transfers ?

⇨ Pulsed plasma jet with a synchronized drop-on demand injection of droplets

Basic idea of pulsed plasma spraying with synchronized injection of droplets



Injection synchronized with the plasma

Homogeneous and controlled treatment

Dc torch ⟺ Injection technology

OUTLINE

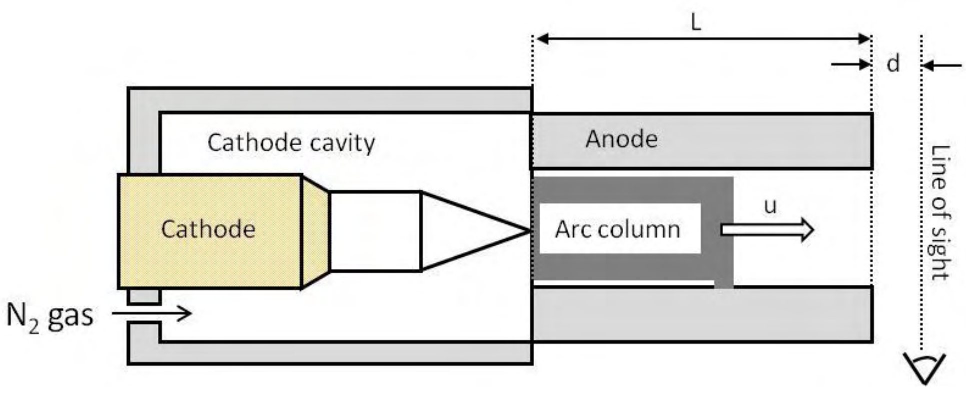
1- Direct current pulsed arc: restrike mode, properties

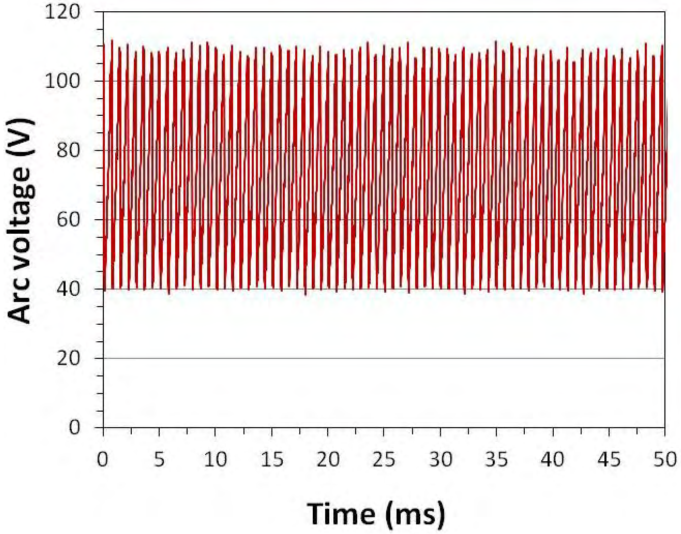
2- Modulation of arc current
- stabilizing the pulsed mode
- dynamics of the arc

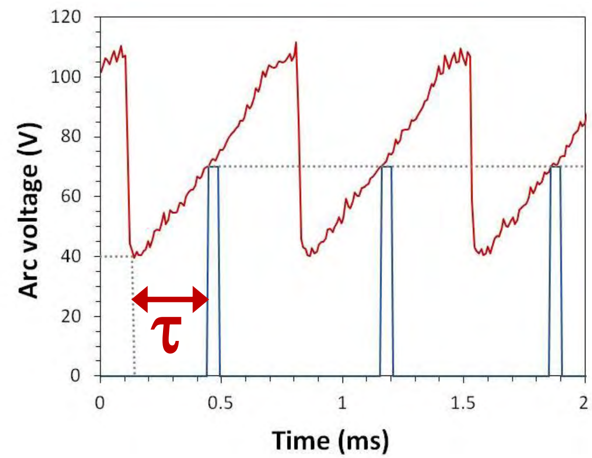
3- Plasma spraying of solution precursor in pulsed mode
- liquid injection
- dependence of in-flight processes on injection timing
- coating features

Self-sustained pulsed arc

➢ **Direct Current I = 15 A – N_2 – Atmospheric pressure**



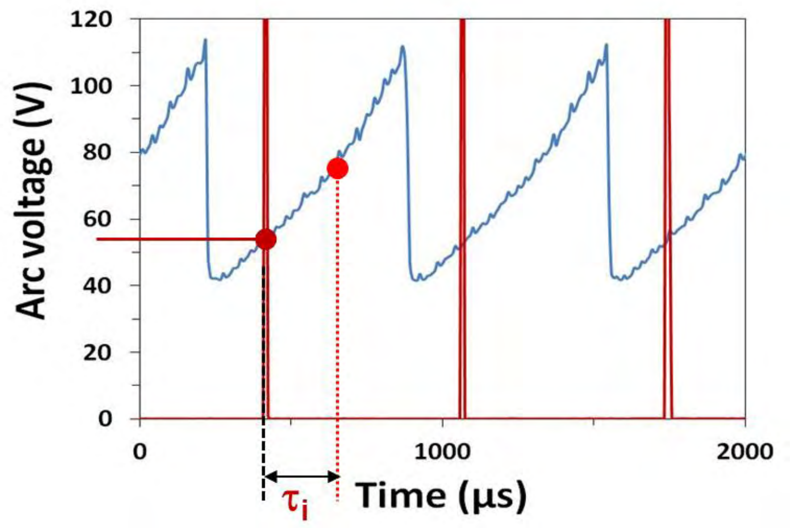


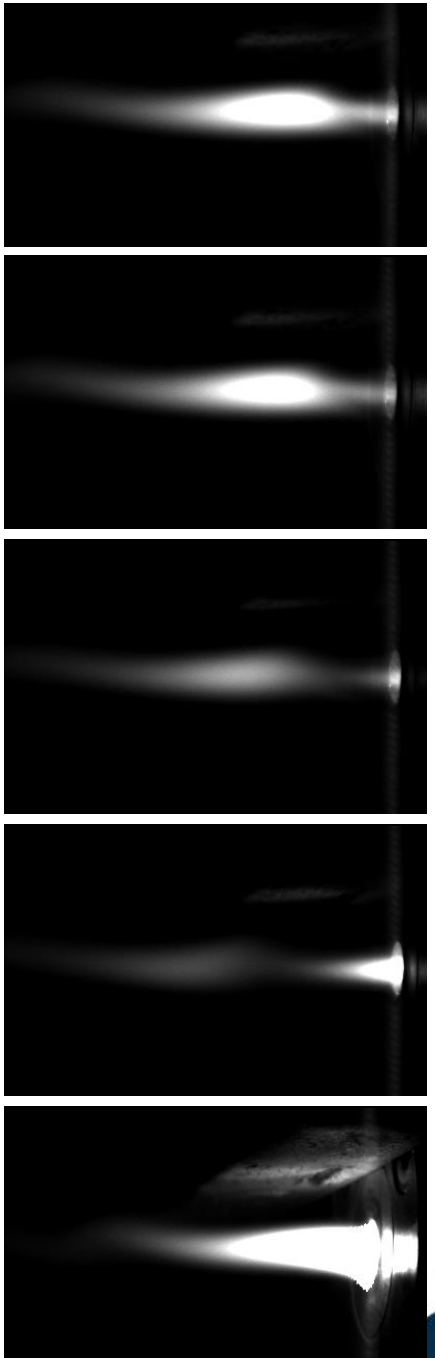


- **Natural frequency of the torch: f_m ~ 1.4 kHz**
- **h_{moy}= 13 MJ.kg^{-1}**
- **Pulsed mode: Restrike mode promoted**

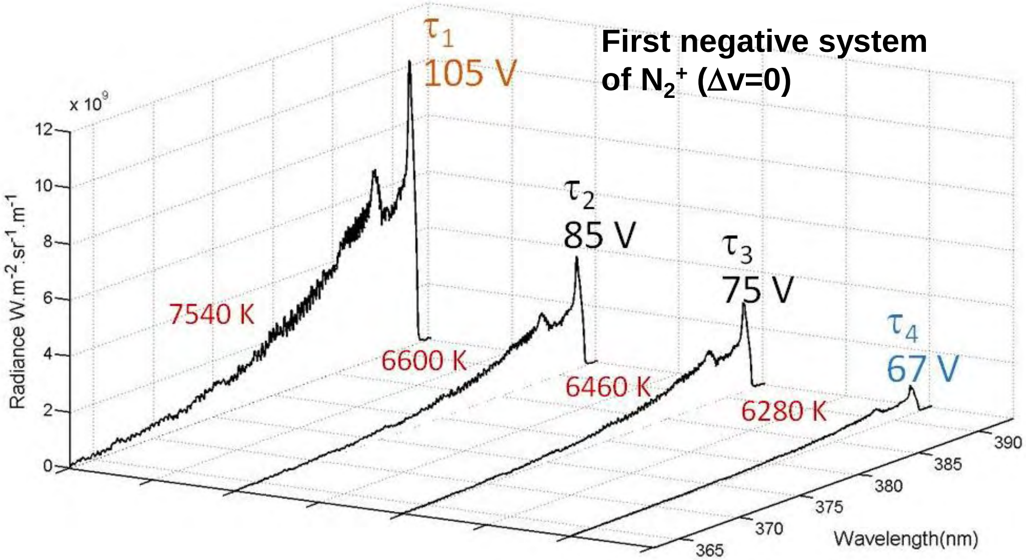
➢ **Trigger time τ_i**

Laminar pulsed arc jet





Time-resolved temperature measurements



Influence of arc current modulation

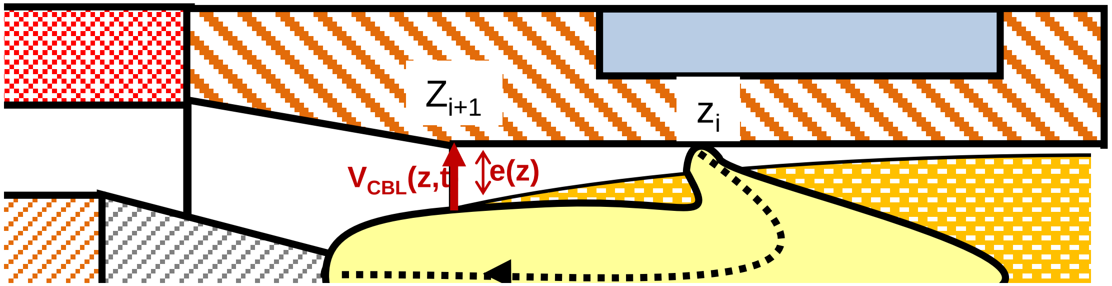
- Motivations : increase the life time of pulsed mode to satisfy plasma spraying conditions

- How to influence the restrike mode ?

⇨ arc current influences the arc reattachment through boundary layer in the arc channel

⇨ restrike model

Breakdown voltage V_b



Rearcing in $z = z_i+1$ if $V_{CBL}(z_{i+1},t) \geq V_C$

$$V_c = e_{CBL}(z_{i+1}, t_i)\overline{E}c$$

$$V_{CBL}(z_{i+1}, t_i) = V_{col}(z_i, t_i) - V_{col}(z_{i+1}, t_i) + V_\ell(z_i, t_i) + U_a$$

⇨ Criterion for restrike :

$$(z_i - z_{i+1})\, E_{col}(t_i) + U_a \geq (r_0 - r_{arc}(t_i))\,\overline{E}c$$

⇨ Restrike depends on arc radius and the electric field strength

Expected influence of arc current modulation on restrike

- Electric field strength
- Boundary layer thickness

$$I(t) = 2\pi E_{col}(t)\int_0^{r_{arc}} r\sigma(r,t)\,dr$$

Characteristic frequency for heat transfer f_{th} in the arc column is higher than the excitation frequency $f_{th} > f_0$

- Magnetic forces

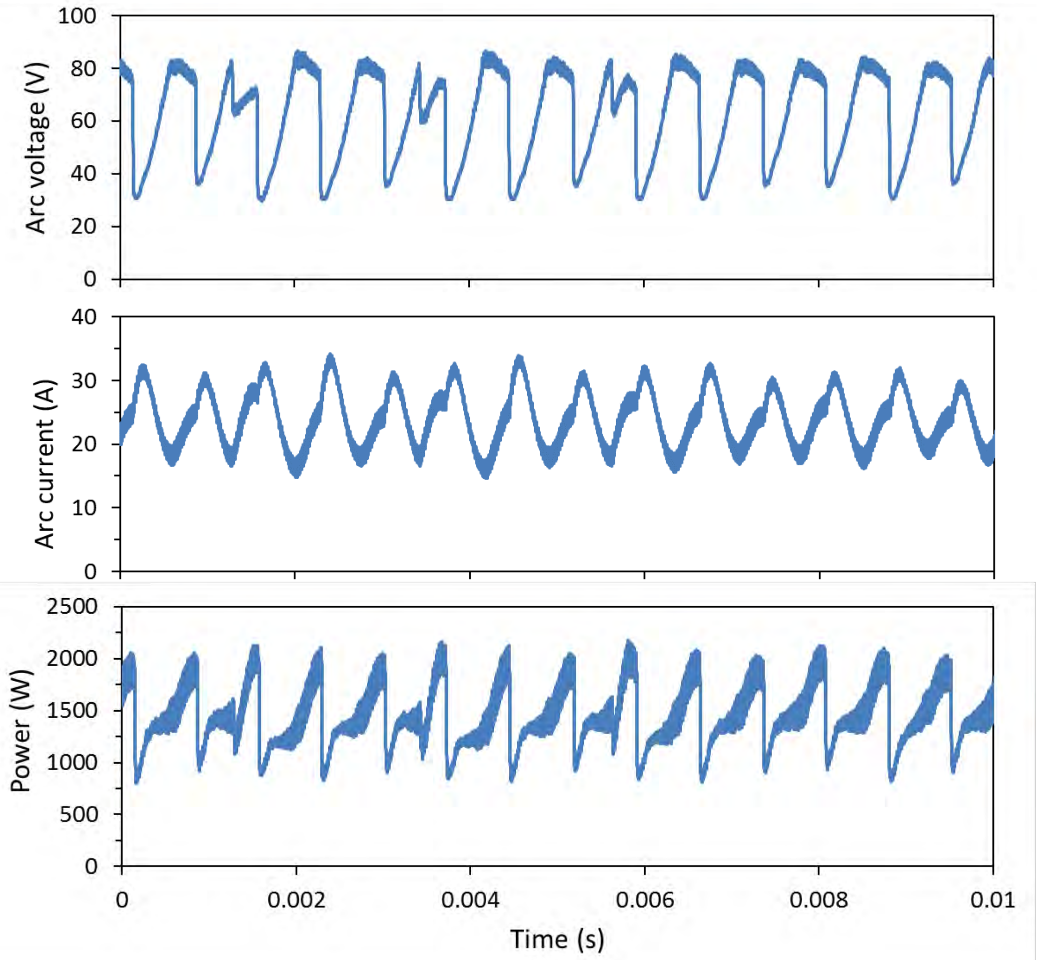
- *What kind of current modulation ?*

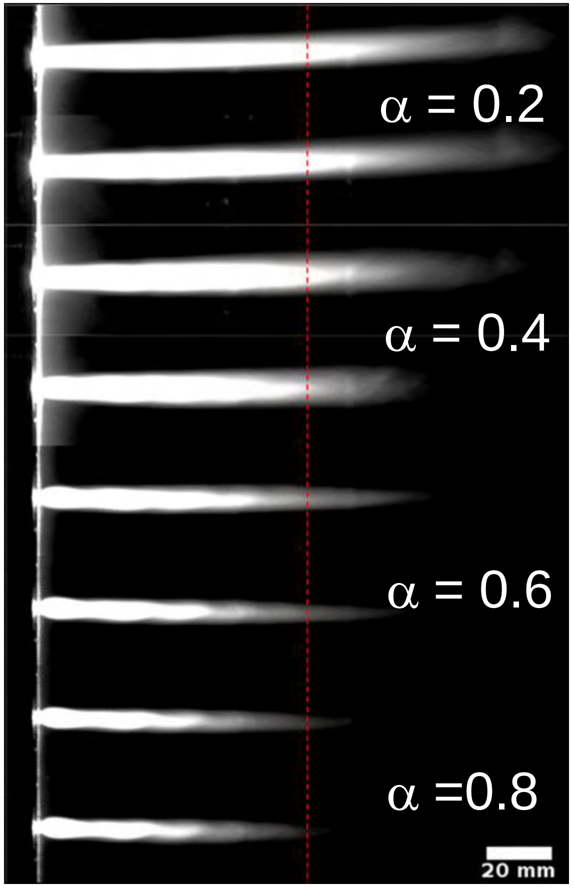
$$I(t) = I_0\left(1 + \alpha \sin\left(2\pi f_0 t\right)\right)$$

- α : amplification coefficient (<1)
- f_0: excitation frequency close the natural frequency f_m

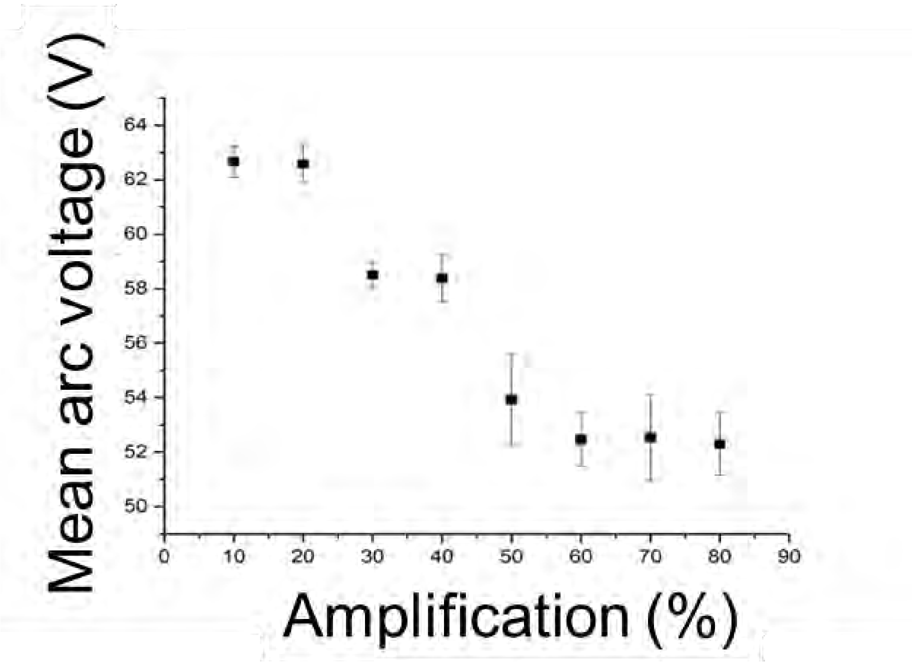
Typical signals

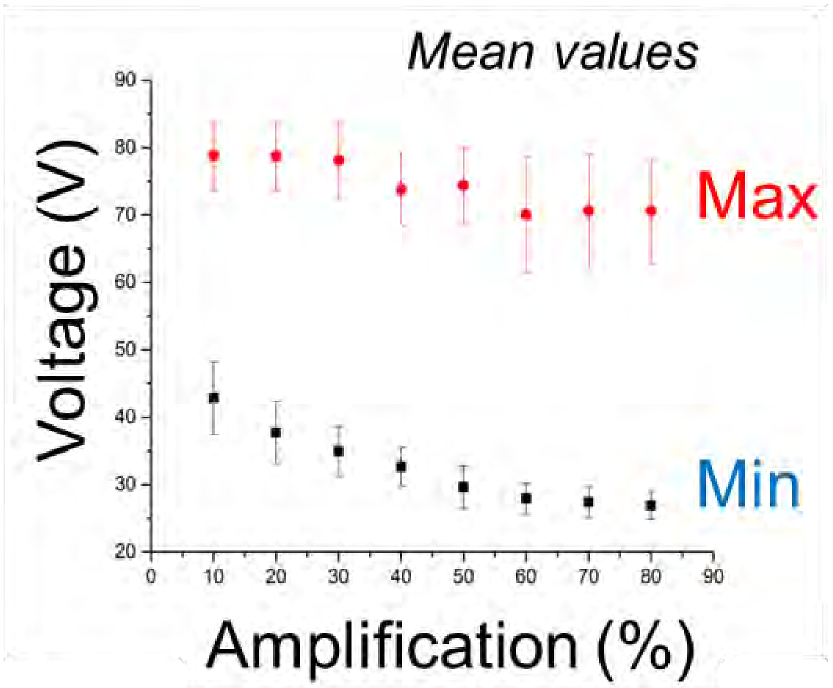
I_0 = 25 A, α = 0.4 and $f_0 = f_m$= 1.4 kHz



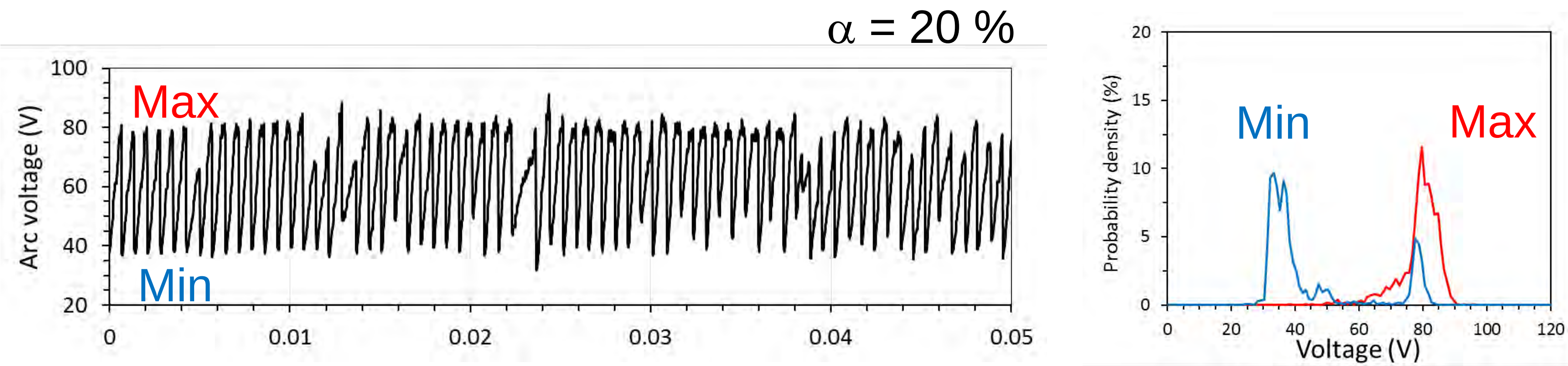


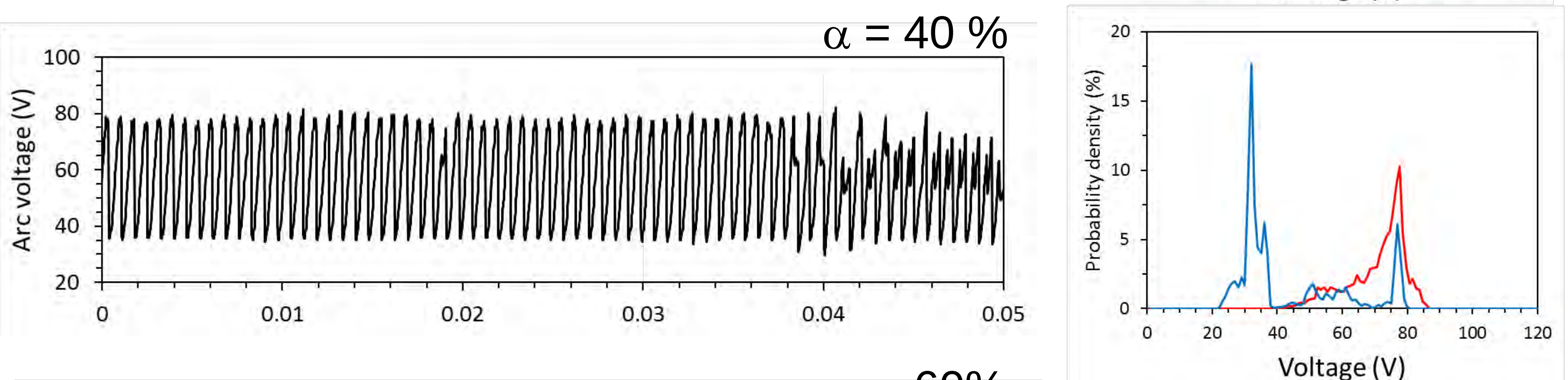
Influence of amplification coefficient α - $f_0 = f_m$

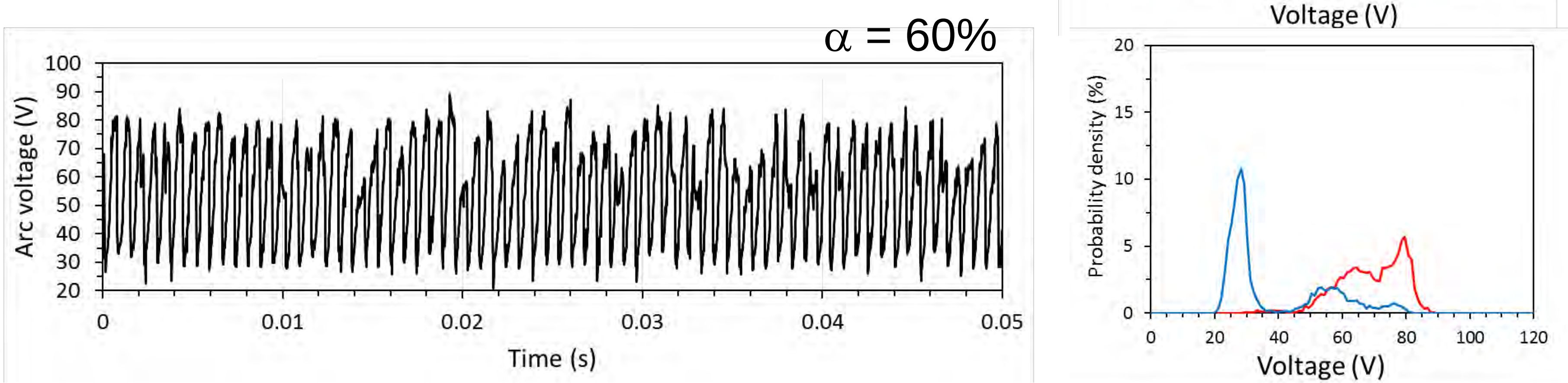




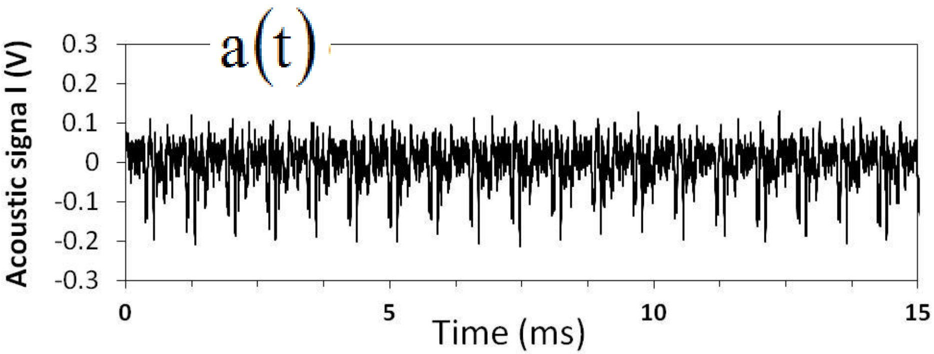
N=4000-6000 samples

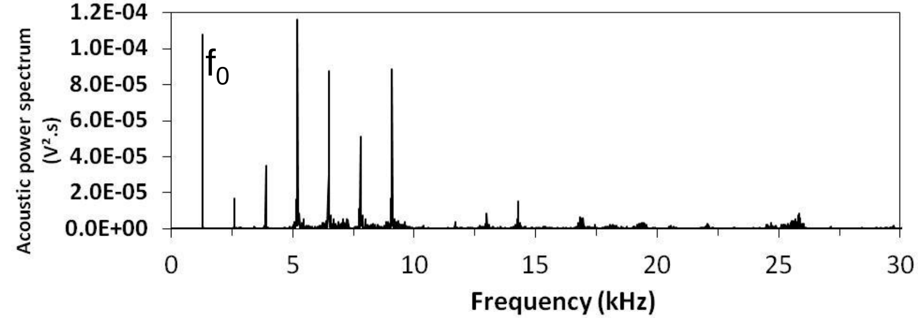


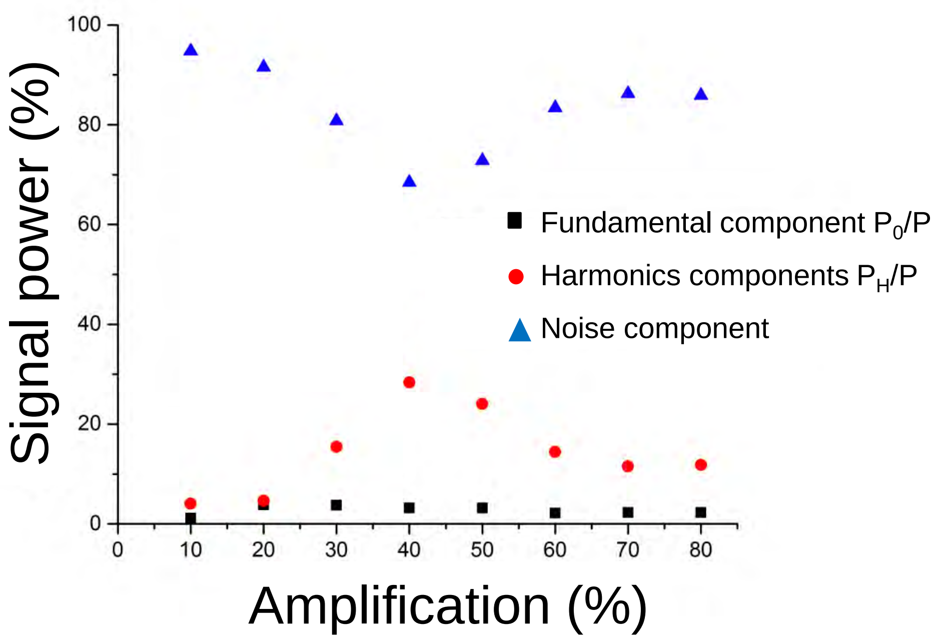




Acoustic study







Acoustic emission: Fitaire law

$$a(t) \propto \frac{dP_{elec}}{dt}$$

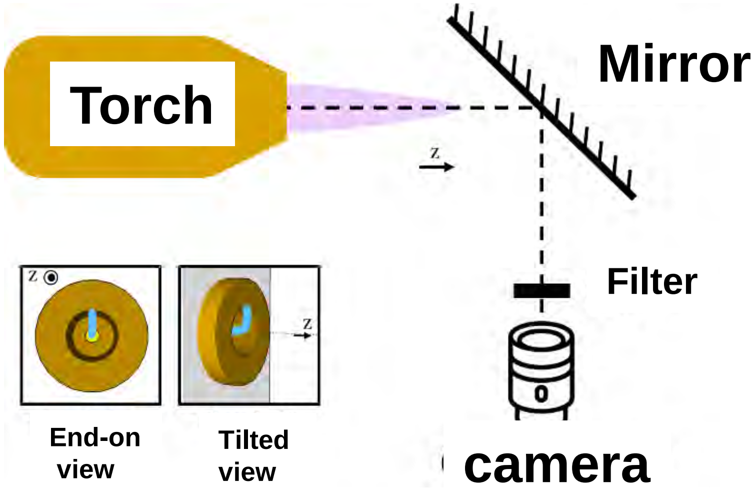
- Reduction of noise

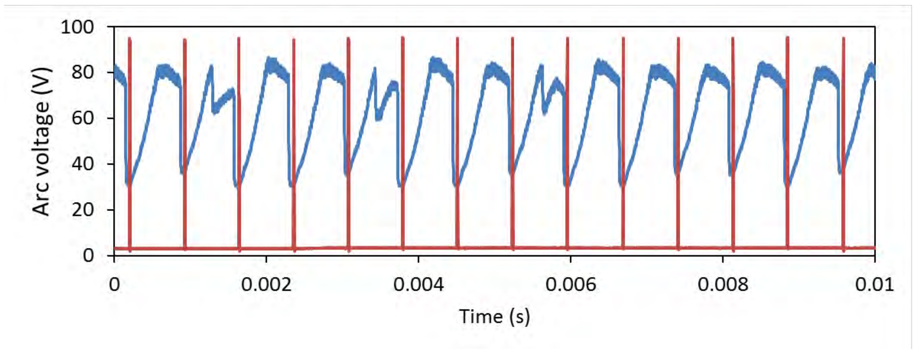
Stabilizing effect of arc current on restrike

F. Mavier et al. IEEE Trans. Plasma Sci. 45, 7776957 (2017)

Dynamics of the arc

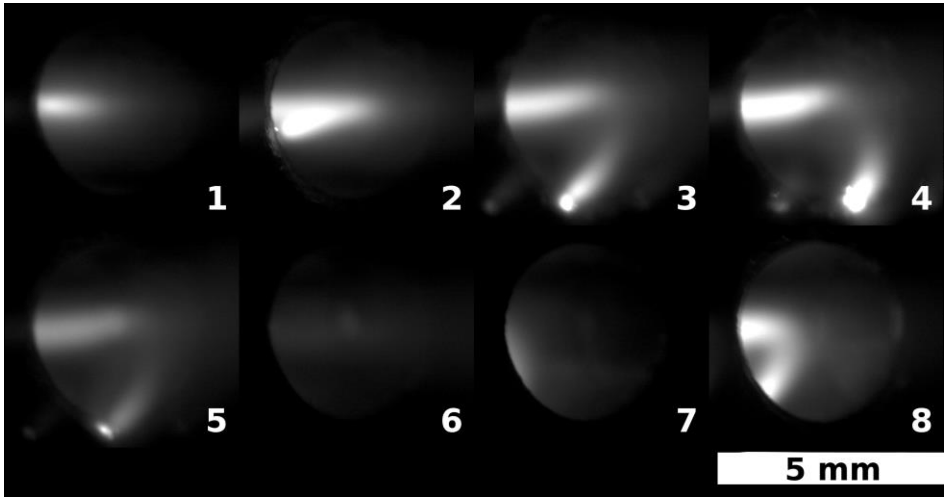
Time-resolved end-on imaging of the arc channel – $\alpha = 0.4$ - $f_0 = 1.4$kHz



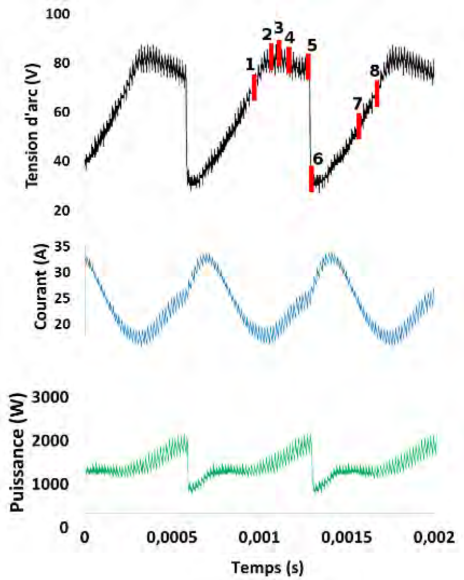


➢ **Trigger time** τ

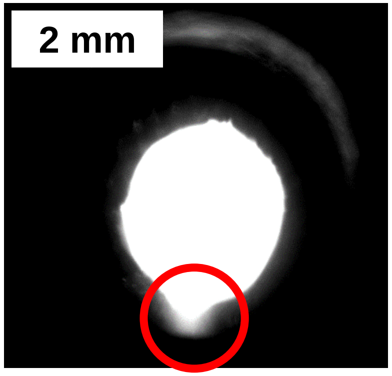
Arc dynamics : single restrike

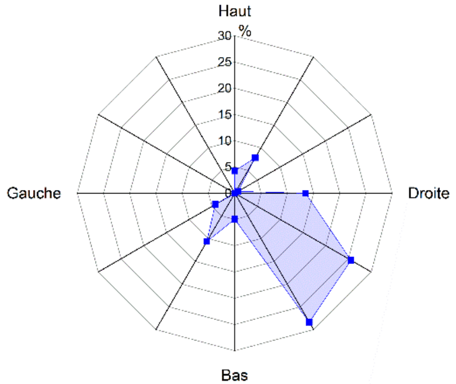


Time-resolved imaging, exposure time 50 µs



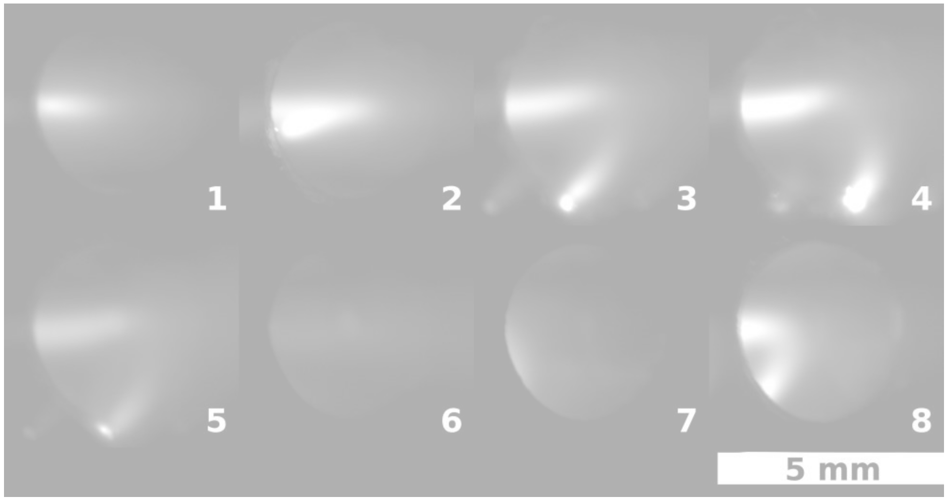
Distribution of arc root positions



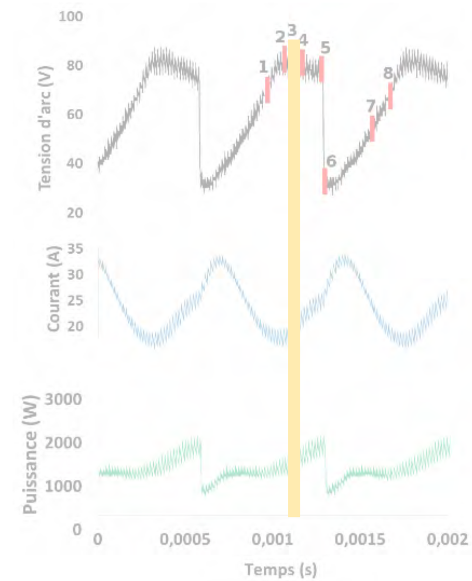


Before rearcing

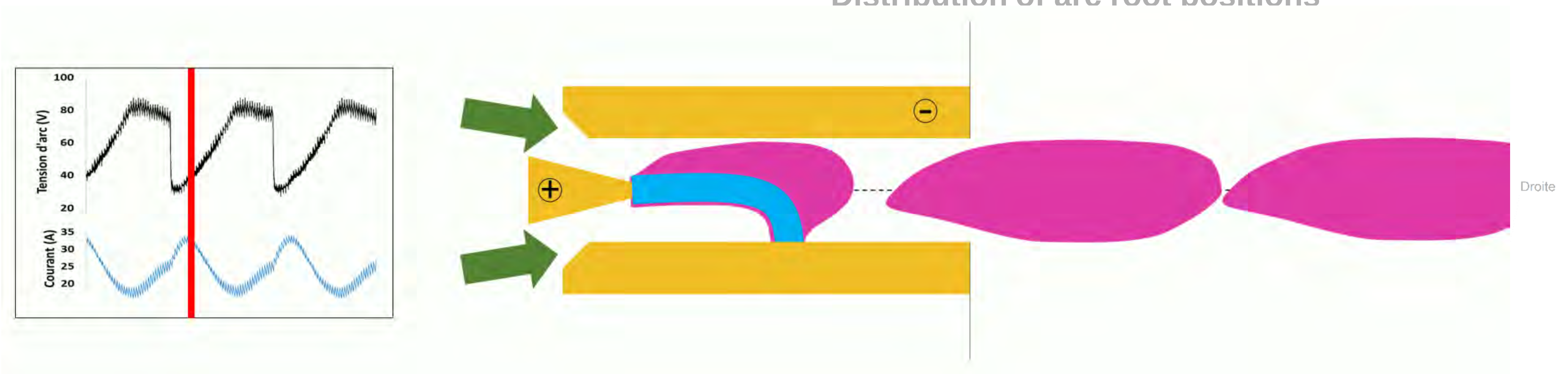
Arc dynamics : single restrike



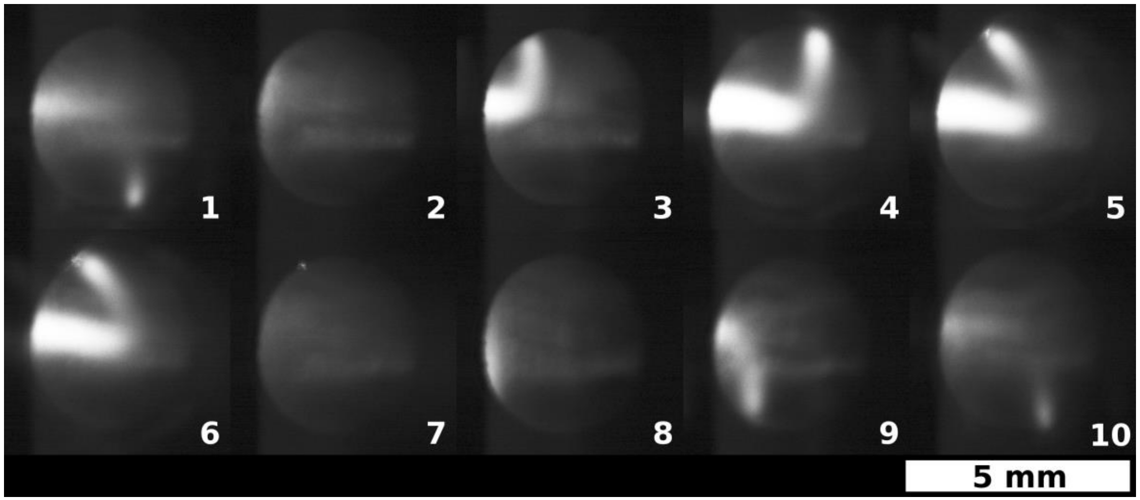
Time-resolved imaging, exposure time 50 µs

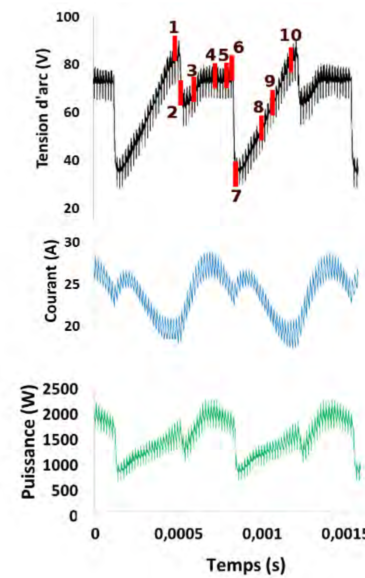


Distribution of arc root positions

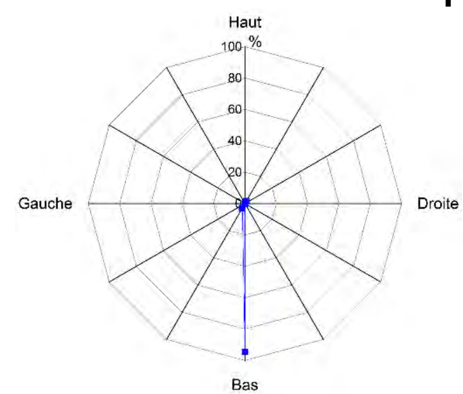


Arc dynamics : double restrike

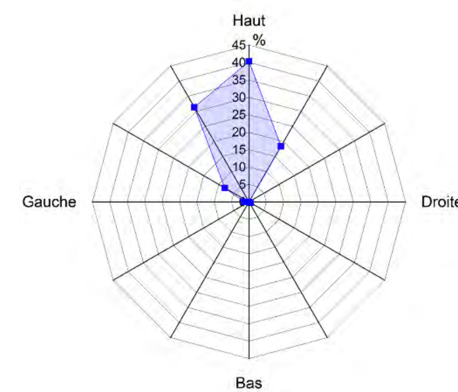




Distribution of arc root positions

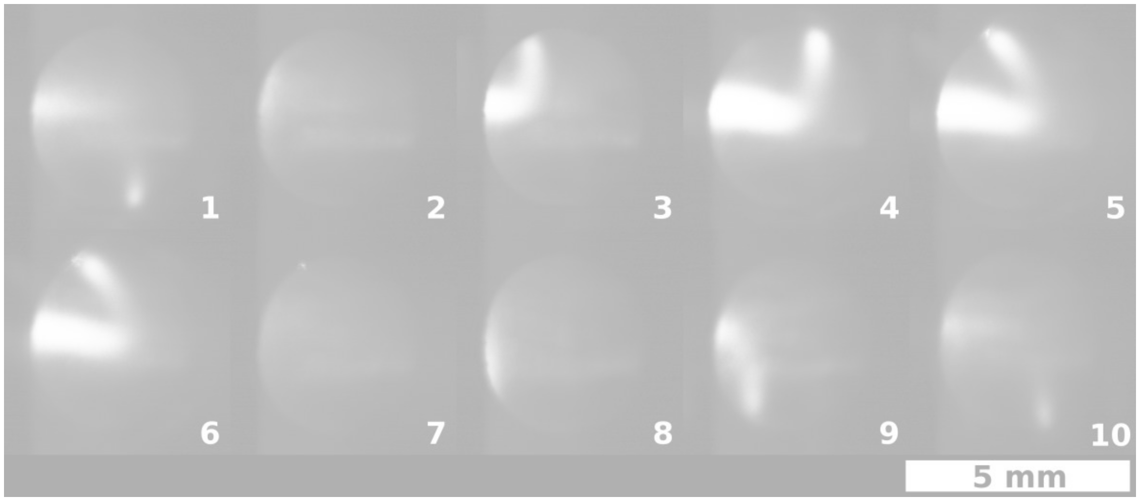


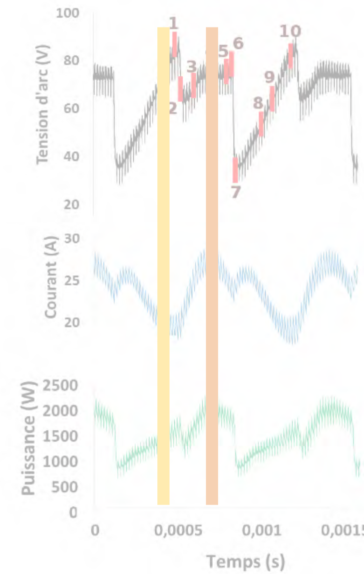
Before minor restrike

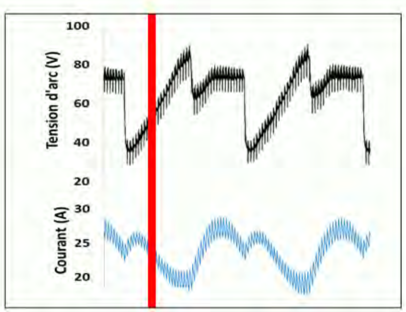


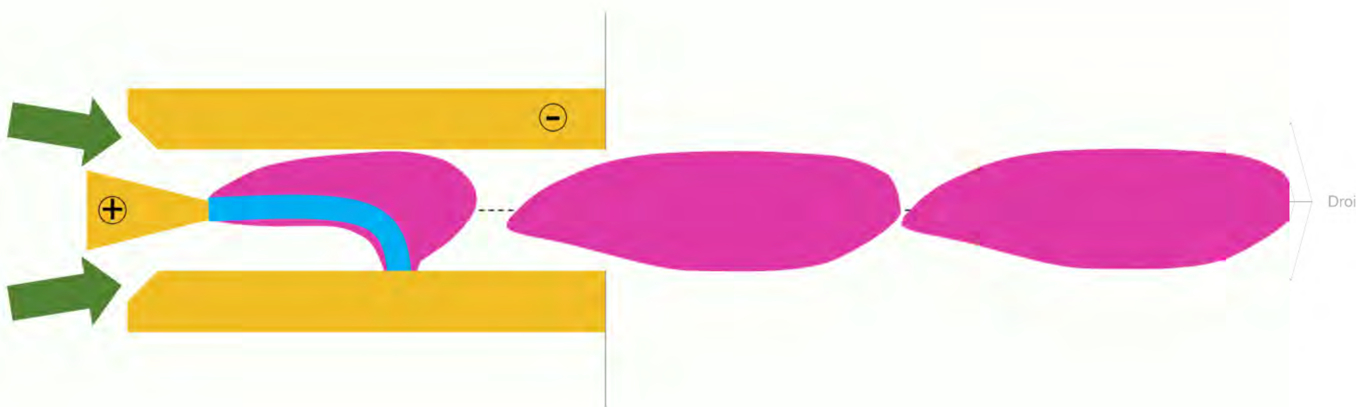
Before major restrike

Arc dynamics : double restrike



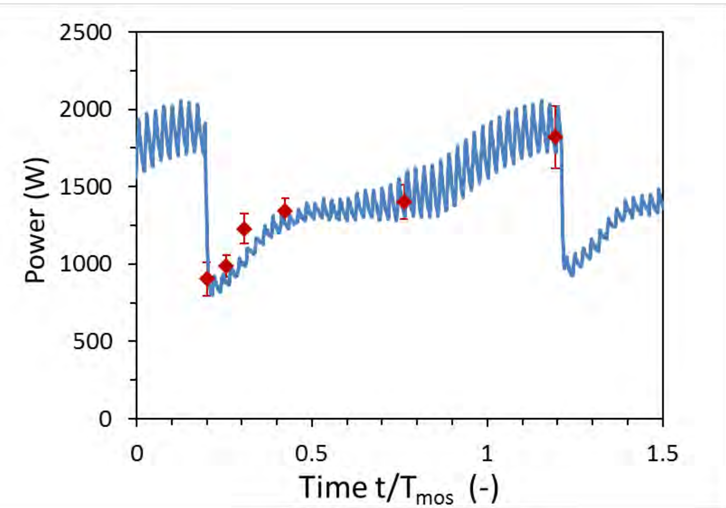


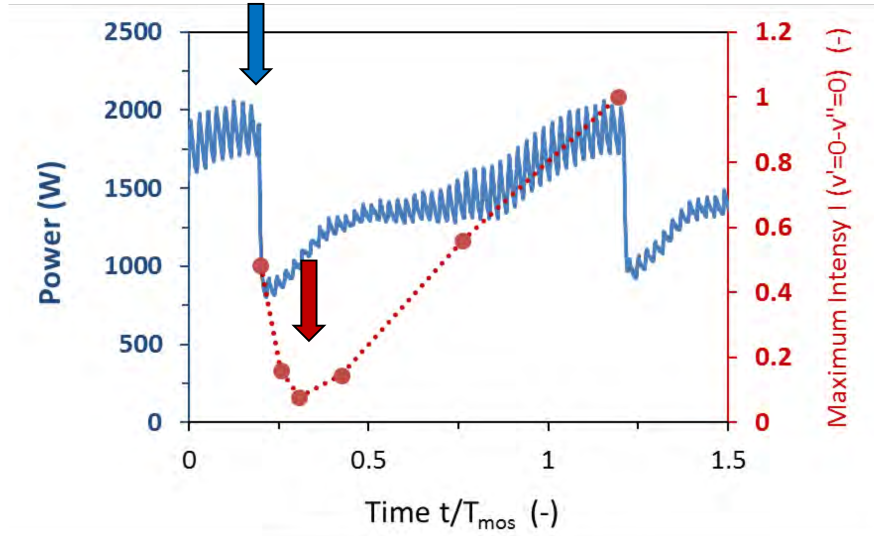


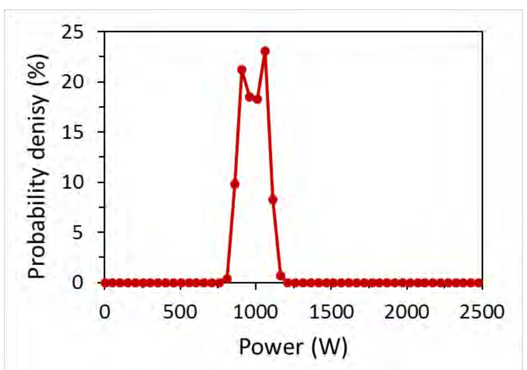


Time-resolved temperature measurements (z = 1 mm) $\alpha = 0.4$ - $f_0 = 1.4$kHz

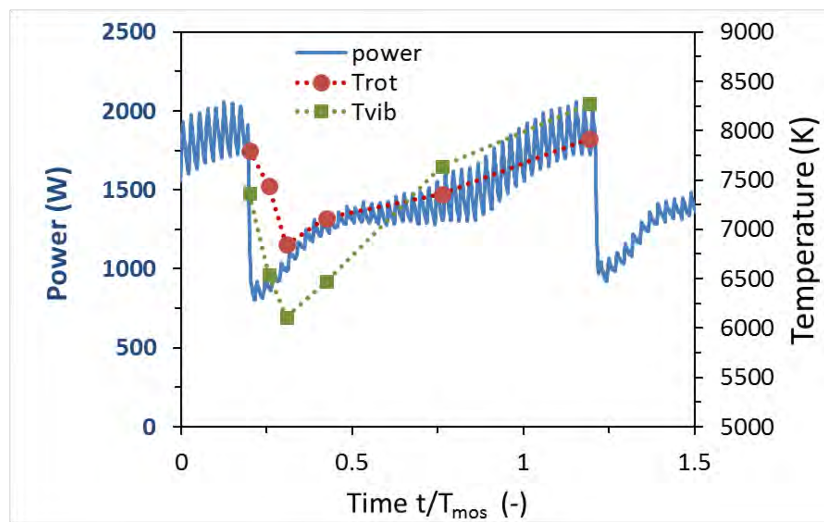
Measurements over one period



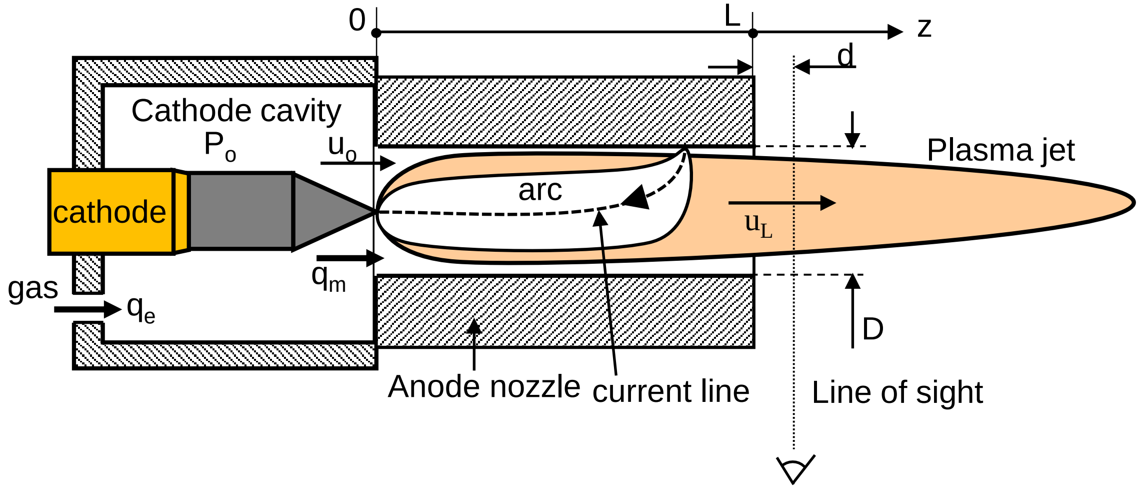




Reproducibility of triggering
example : P_{elec}(trigger) = 1 kW



Parameter coupling in a dc plasma torch



- *Input parameters*: torch geometry, plasma forming gases, arc current
  Arc voltage
- *Output parameters*: plasma specific enthalpy and speed
  mass flow rate, gas pressure inside the cathode cavity
- Properties averaged over the channel cross at nozzle exit
- 0D, transient, linear, analytical model

Integrating 1-D time dependent conservation equations over the axial distance z
L : nozzle length

Energy equation

$$m_p \frac{dh_L}{dt} + q_m (h_L - h_0) = -\alpha_{cr} L h_L \qquad q_m h_0 = (V_{arc} - V_{elec}).I$$

Momentum equation

$$L \frac{dq_m}{dt} + (u_L - u_0) q_m = -S(P_L - P_0) - \frac{L q_m}{\tau_f}$$

Mass balance in the cathode cavity

$$q_e - q_m = V_{cav} \left(\frac{\partial \rho}{\partial P} \right)_{cav} \frac{dP_0}{dt}$$

Fundamental frequency

$$\omega_0^2 = \left(\frac{\partial \rho}{\partial P} \right) \frac{S}{L V_{cav}}$$

Linearizing conservation equations

$$x = \bar{x} + x' \qquad x = \{\, p_i \quad i \quad q_m \quad u_L \quad P_0 \quad \rho_L \quad h_L \,\}$$

Non-dimensional fluctuating components

$$h = -\rho \qquad u = q - \rho = q + h$$

Conservation equations

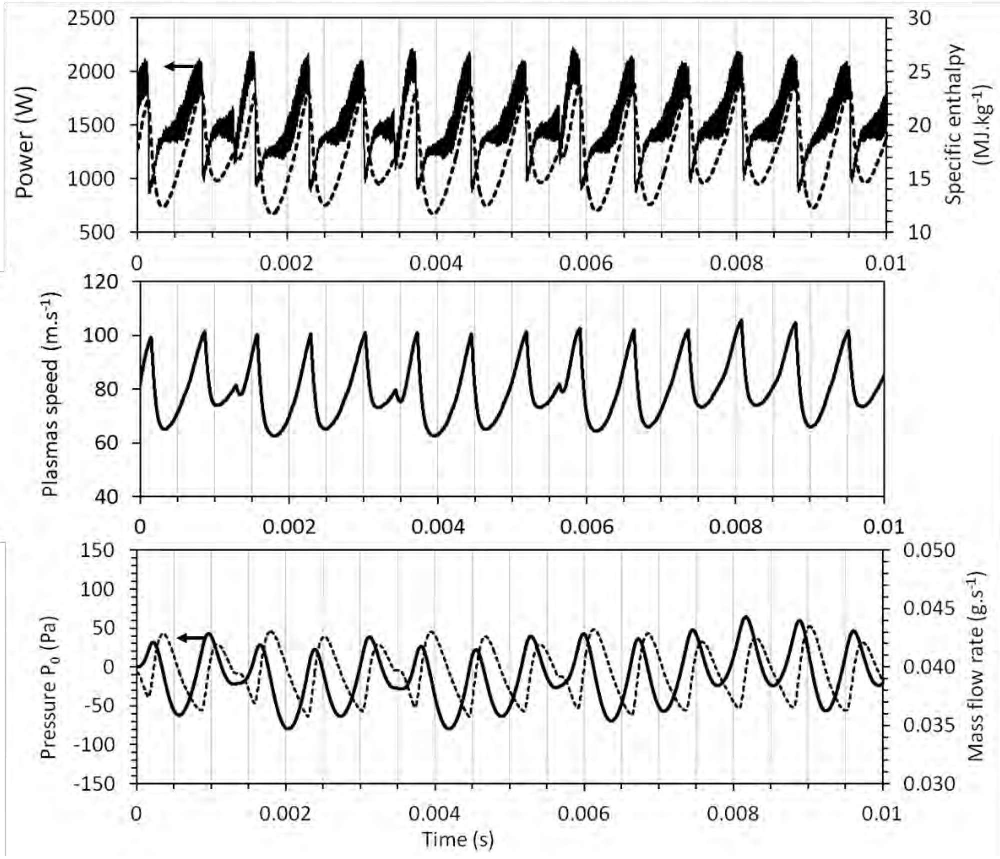
$$\dot{h} + \frac{h}{\tau} = \frac{p_i}{\tau} - \delta \frac{i}{\tau} - \frac{q}{\tau_{res}} \qquad \ddot{q} + \frac{\dot{q}}{\tau_{cav}} + \omega_0^2 q = -\frac{\dot{h}}{\tau_{res}}$$

Characteristic times:

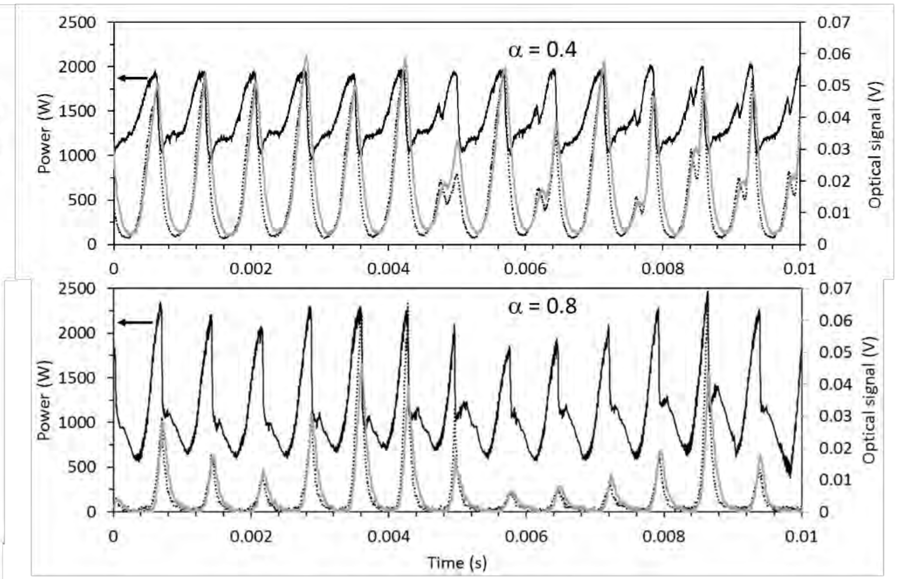
$$\frac{1}{\tau} = \frac{1}{\tau_{res}} + \frac{1}{\tau_{tr}} \qquad \frac{1}{\tau_{cav}} = \frac{2}{\tau_{res}} + \frac{1}{\tau_f}$$

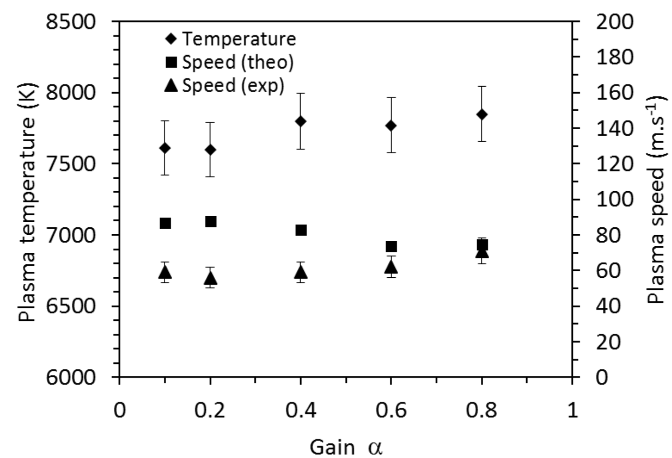
Residence time (τ_{res}) — Heat transfer time (τ_{tr}) — Viscosity effect (τ_f)

Calculated enthalpy and plasma speed



Plasma speed measurement

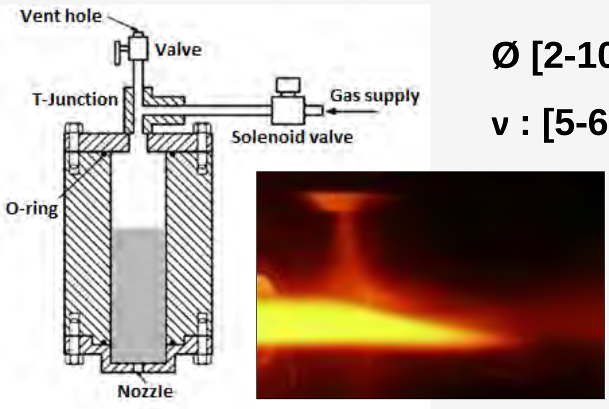




F. Mavier *et al.* J. Phys. D: Appl. Phys.51, 405201 (2018)

Liquid injection technology

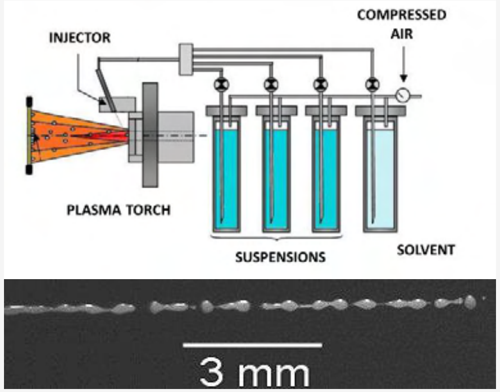
Atomization



Ø [2-100 µm]

ν : [5-60 m.s^{-1}]

Mechanical injection



Ø 300 µm

ν : 20 m.s^{-1}

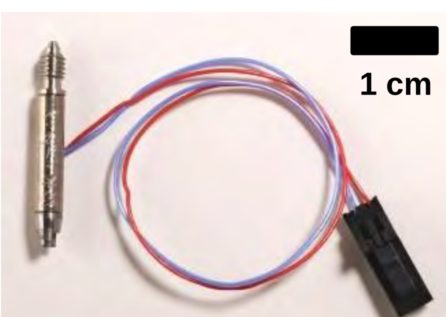
f : ~30 kHz

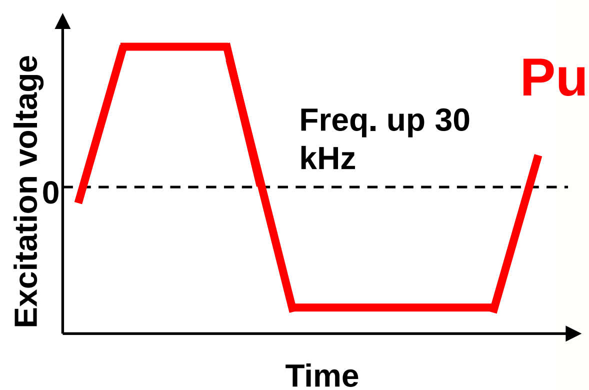
Ink-jet microdispenser

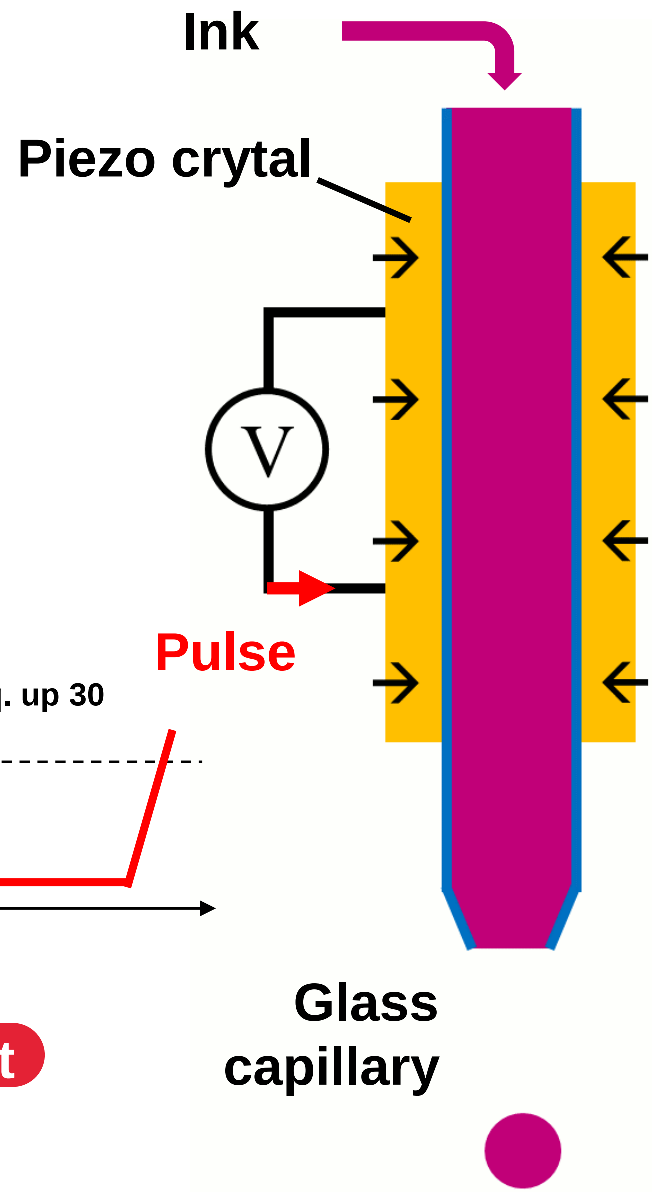
Ink-jet on demand

Specifications

- Individual droplet emision
- Injection frequency 1400 Hz
- Repeatable droplet emission



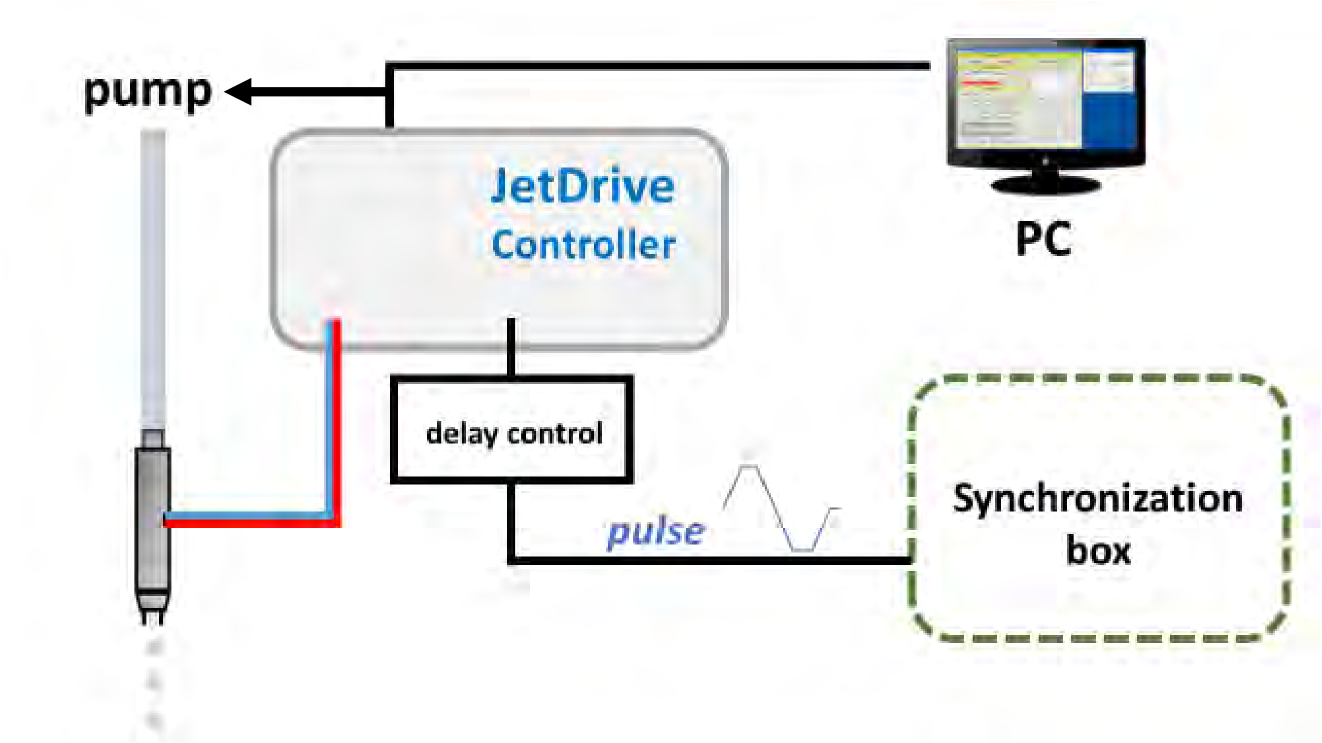




1 pulse = 1 droplet

Ø 80 µm, 3,2 m.s^{-1}

Ink-jet microdispenser



Materials

Aqueous inks

Al_2O_3

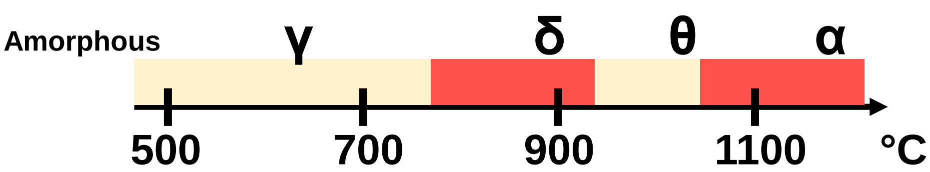
Aqueous solution
Aluminium nitrate
$Al(NO_3)_3$

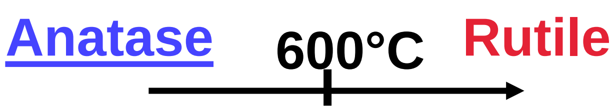
69 g/100 mL - 41%m

TiO_2

Nano-suspension
Anatase

6±2 nm - 20%m





Mechanical, chemical thermal, electrical resistance

- Thermal Barrier Caotings[1]
- MEMS substrate[2]
- Wear resistant coatings[3]

Photocatalytic cotaings and Super-hydrophobicity

- Pollutants degradation[4]
- Self-cleaning surfaces[5]

1 : L. Pawlowski, Surf. Coat. Technol. (35),1988.
2 : C. J. Li et al., Wear, (260), 2006.
3 : C. C. Stahr et al., J. Therm. Spray Technol. (16), 2007.
4 : K. Nakata et A Fujishima, J. Photochem. Photobiol. C Photochem. Rev., (13), 2012.
5 : N. Sharifi et al., Surf. Coat. Technol. (289), 2016.

Inks formulation

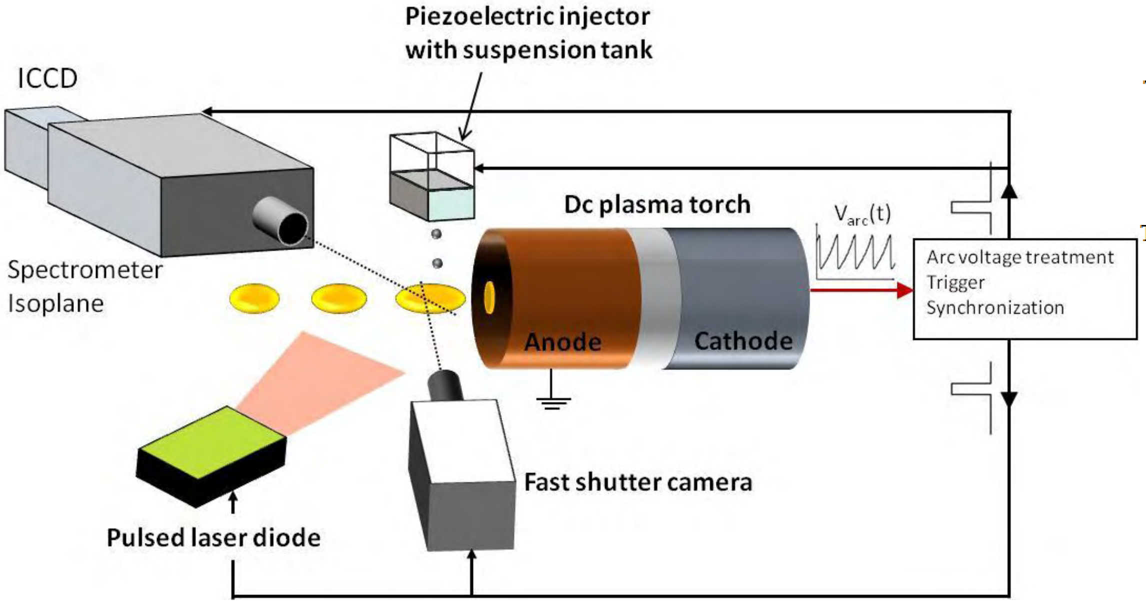
				Nano-suspension TiO_2 Anatase	Aqueous solution Aluminium nitrate $Al(NO_3)_3$
pH	↗	**[2-11]**	Ammoniac	2	1 → 2
Viscosity η (mPa.s)	↗	**4-8**	Glycerol	1 → 5	1 → 7
Surface tension γ (mN.m^{-1})	↘	**20-70**	Surfactant	74 → 39	74 → 41
Ejection ratio Z*		**[1-10]****	$Z = \frac{Re}{\sqrt{We}} = \frac{\sqrt{\rho \gamma r}}{\eta}$	59 → 8	57 → 6

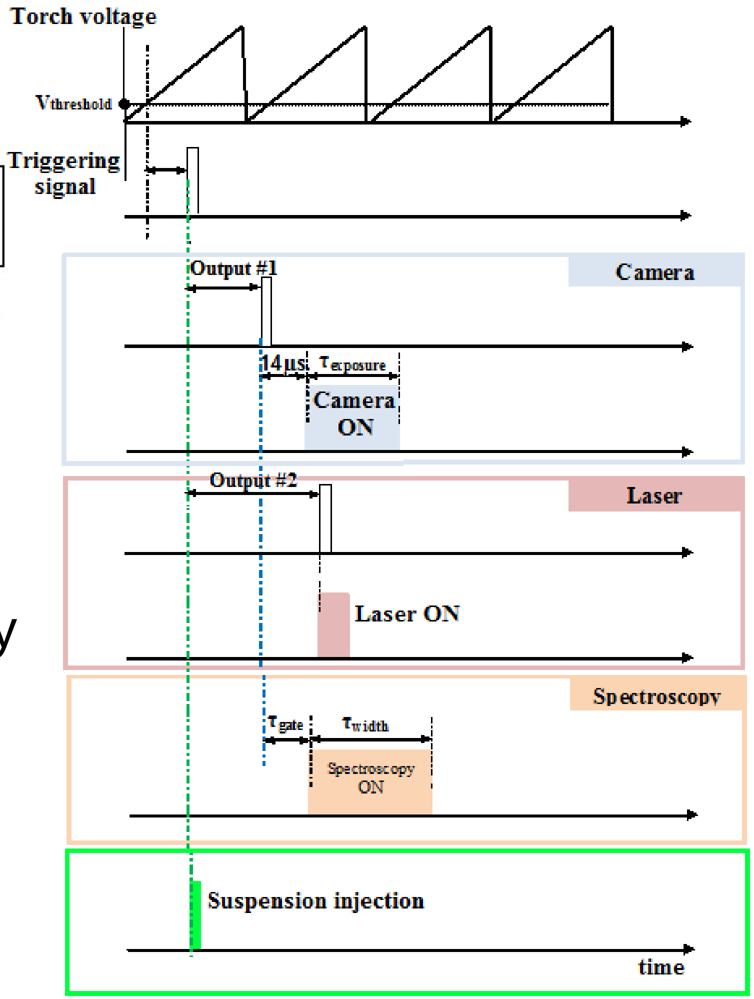
Inks formulation

				Nano-suspension TiO_2 Anatase	Aqueous solution Aluminium Nitrate $Al(NO_3)_3$
				Suspension 58%m Glycerol 41%m BRIJ58 <1%m	Nitrate Al 27%m Water 41%m Glycerol 30%m Ammoniac 2%m BRIJ58 <1%m
pH	↗	**[2-11]**	Ammoniac	2	1 → 2
Viscosity η (mPa.s)	↗	**4-8**	Glycerol	1 → 5	1 → 7
Surface tension γ (mN.m^{-1})	↘	**20-70**	Surfactant	74 → 39	74 → 41
Ejection ratio Z*		**[1-10]****	$Z = \frac{Re}{\sqrt{We}} = \frac{\sqrt{\rho \gamma r}}{\eta}$	59 → 8	57 → 6

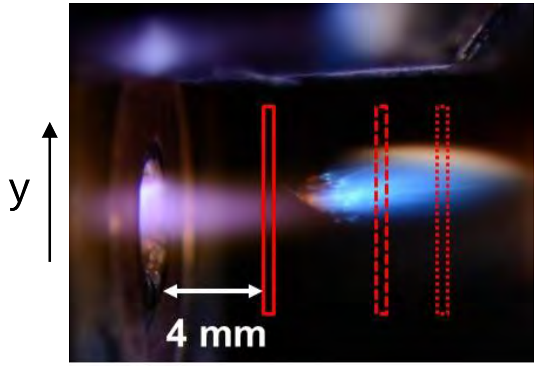
*** : J. Fromm, IBM J. Res. Dev., 1984, 28, 322-333. ** : N. Reis and B. Derby, Materials Research Society Symposium Proceedings, Vol 625, pp. 117-122, 2000**

Experimental set-up



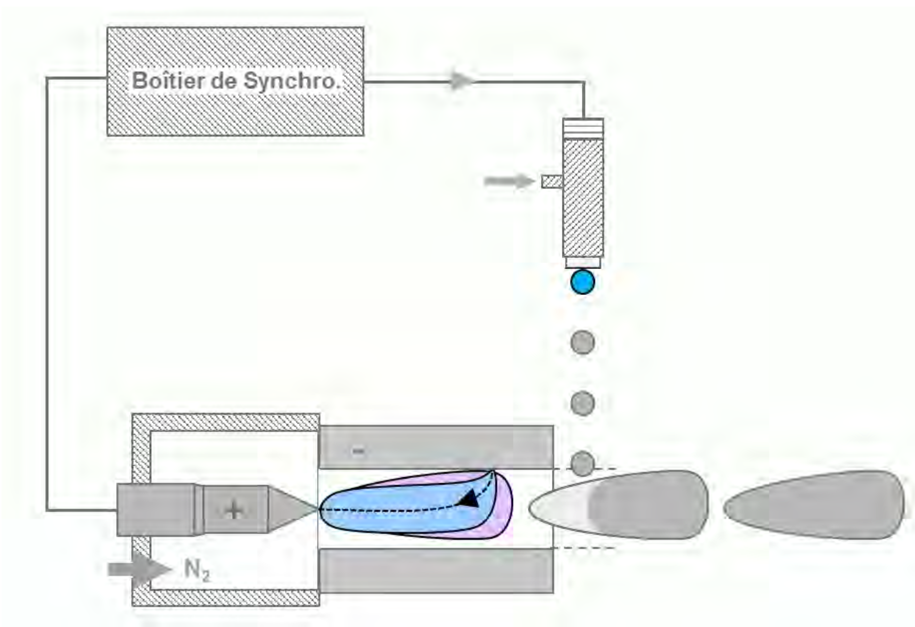


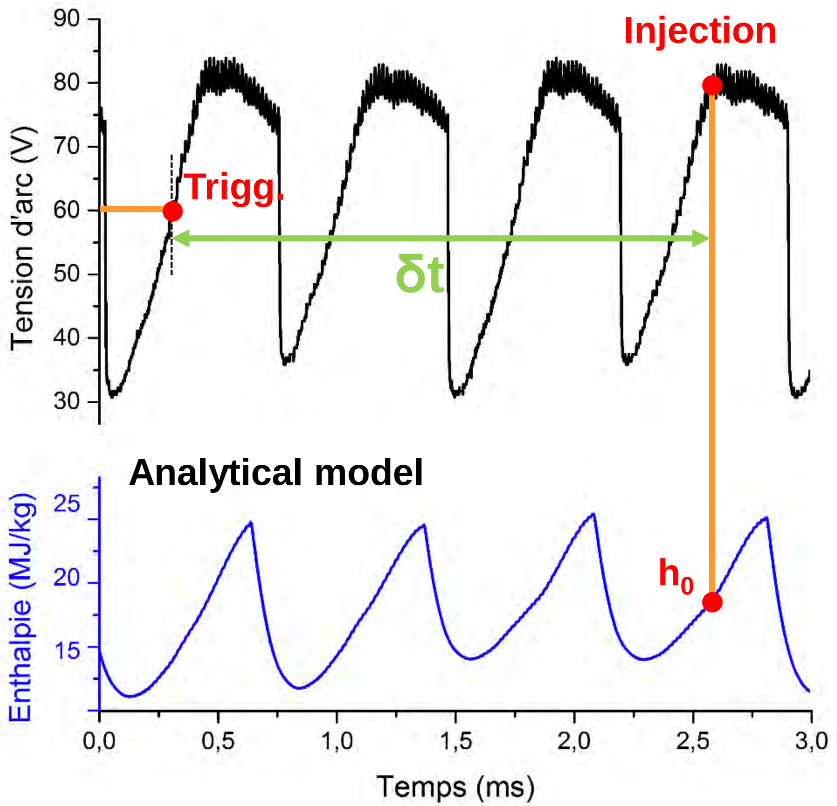
- Time-resolved optical emission spectroscopy observations



Droplets emission and injection

Plasma : 60 $m.s^{-1}$ > droplets : 1-3 $m.s^{-1}$





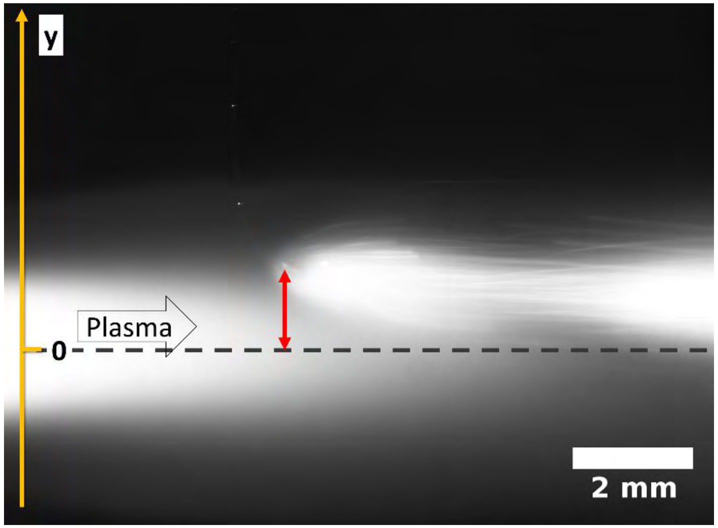
Distribution of interception heights by plasma

Anatase suspension

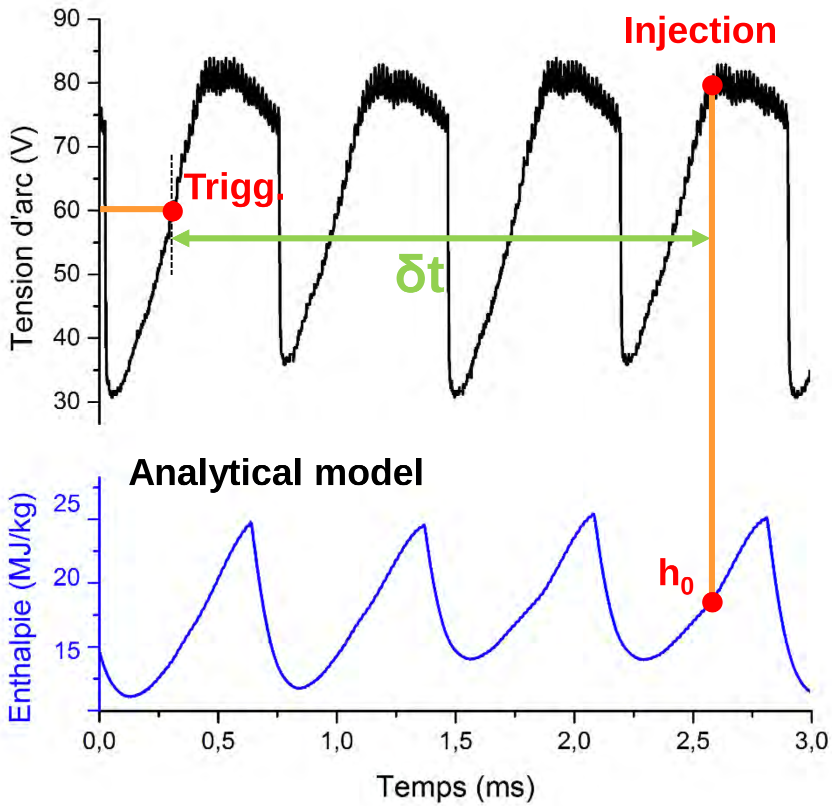
Voltage trigger 60 V

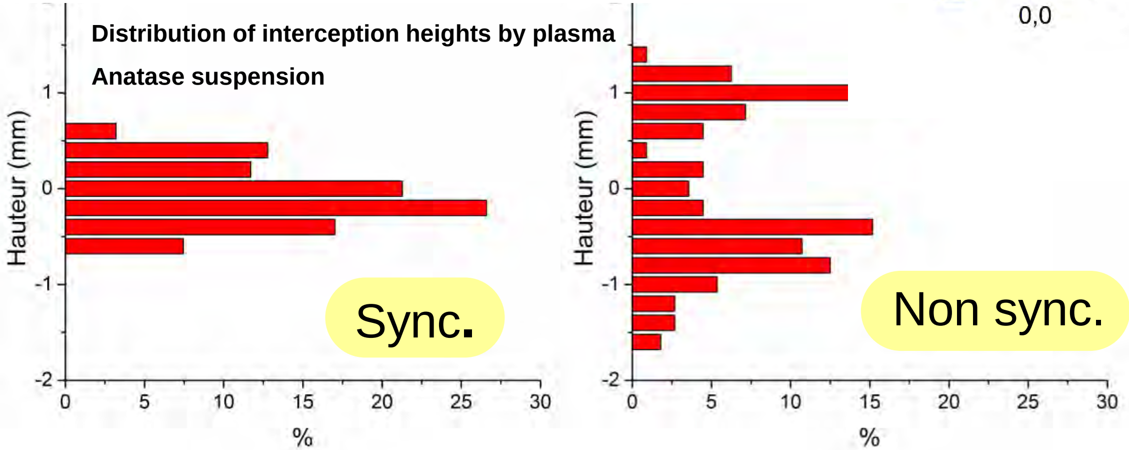
Droplets emission and injection

Plasma : 60 m.s-1 > droplets : 1-3 m.s-1



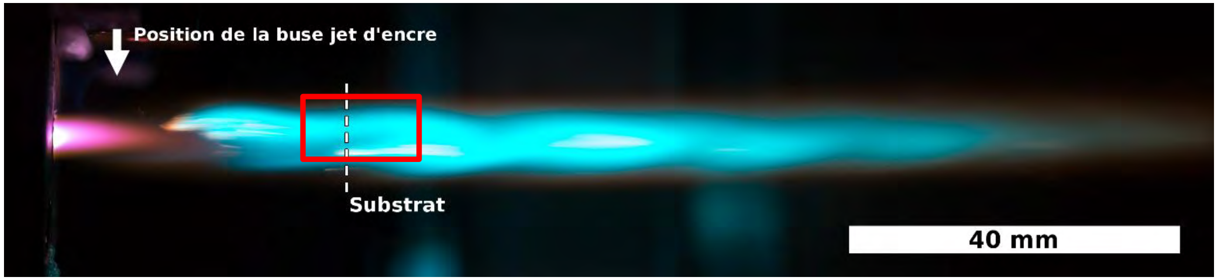
Exposure time : 50 µs





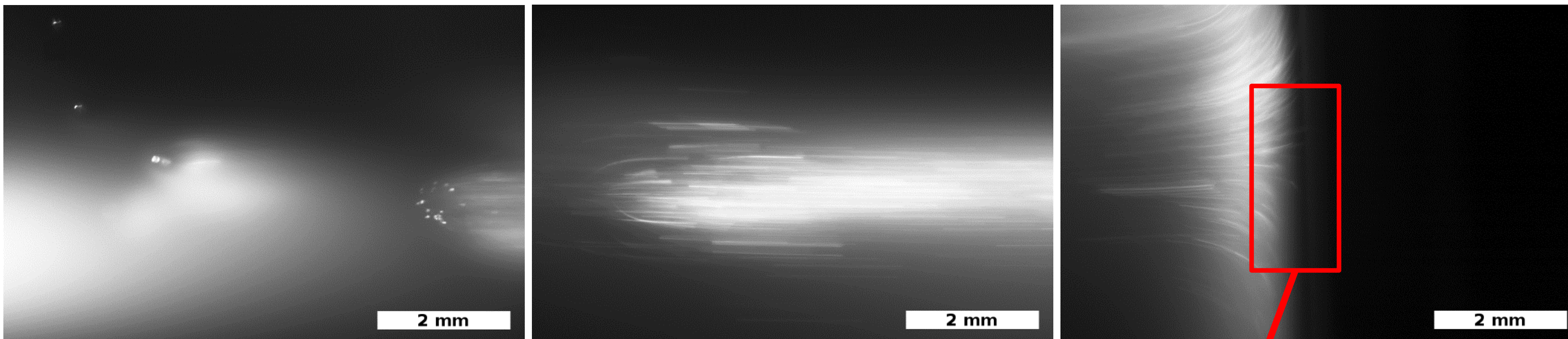
Voltage trigger 60 V

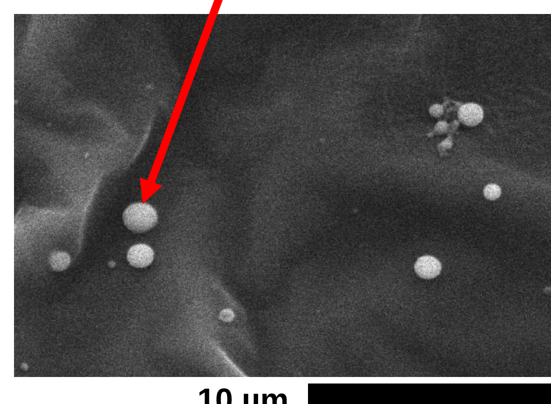
SPPS – Aluminium nitrate solution



Exposure time 200 µs

Stokes number 0,7





Weber number < 1

No mechanical fragmentation

Acceleration time $\tau_{acc} = \frac{\rho_l . d_g^{\,2}}{18\eta}$ 2,3 ms

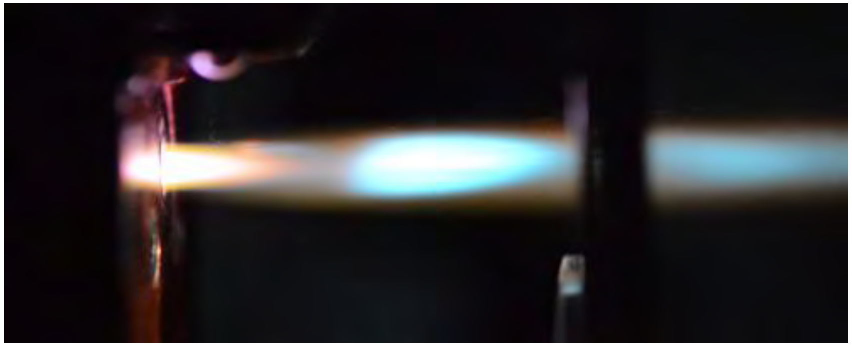
Vaporization time of solvent $\tau_{vap} = \frac{\rho_l . L_v}{4Nu . a_\varphi}\left(\frac{d_g^{\,2}}{h_p}\right)\left[1 - \left(\frac{d_s}{d_g}\right)^2\right]$

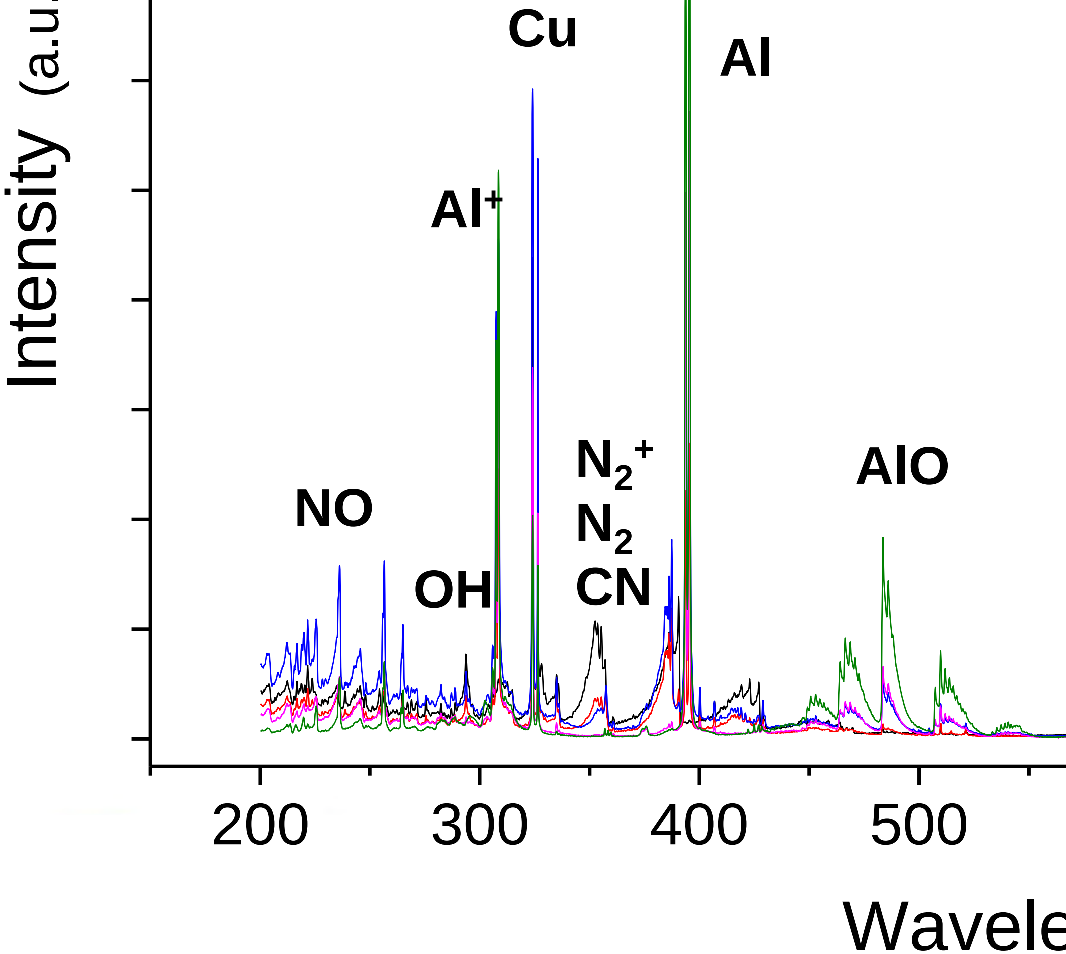
110 µs

F. Mavier et al. Surf. Coat. Technol. 318 18-27 (2017)

- **Solution Precursor Plasma Spraying**

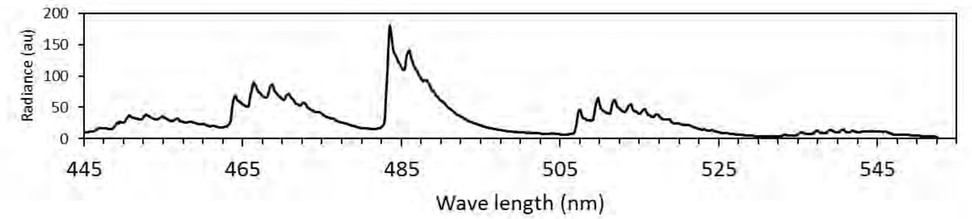
Aluminum nitrate ink : $Al(NO_3)_3 + H_2O$

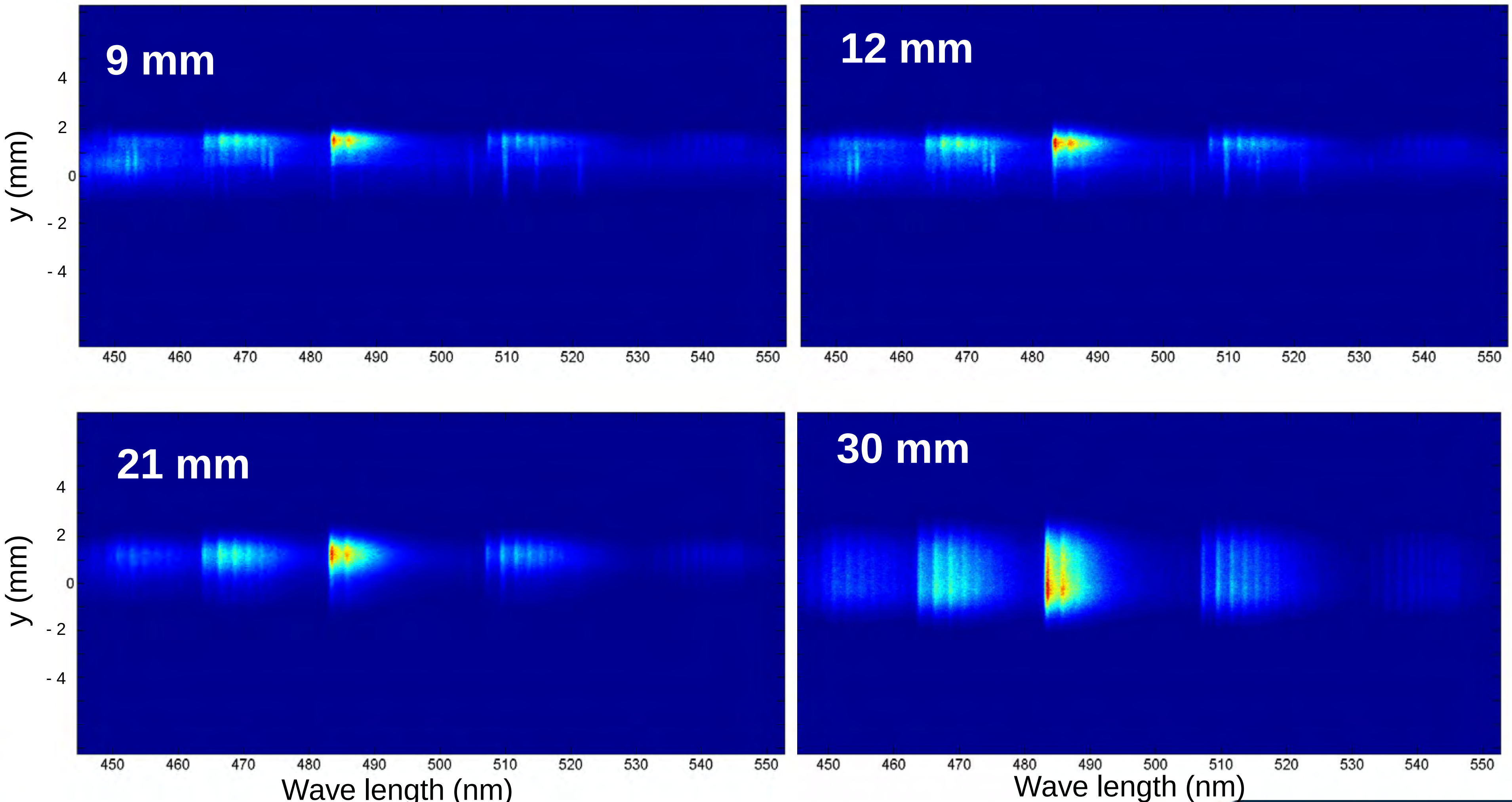




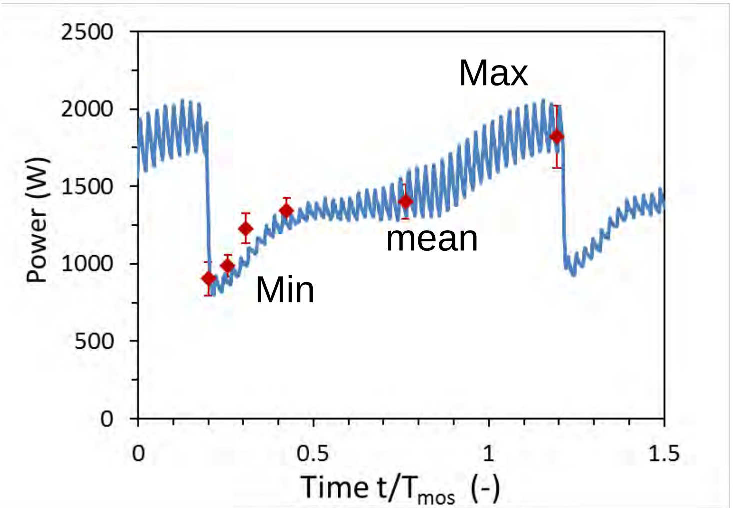
Time-averaged trajectories of AlO emission

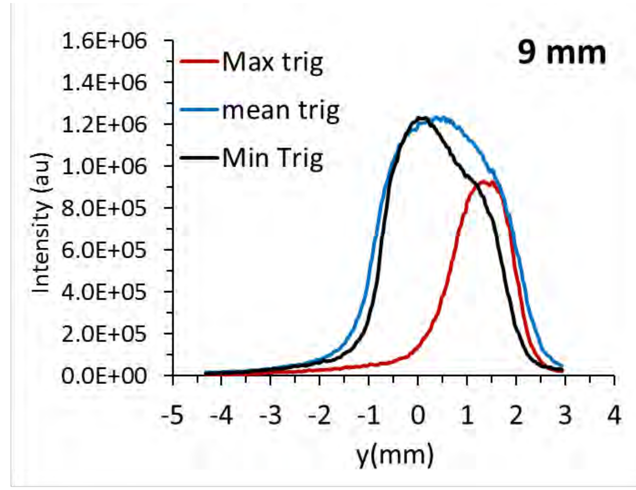
AlO ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$)



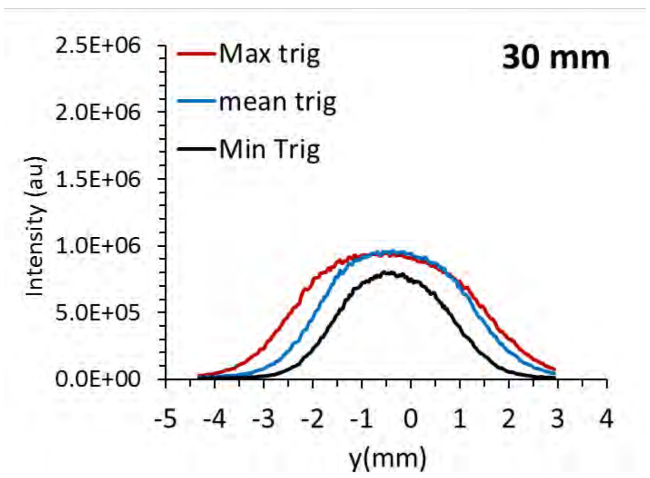


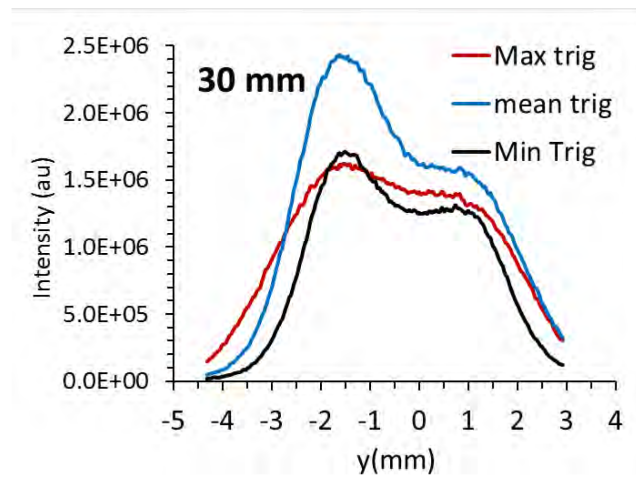
Time-resolved emission y-profiles of Al and AlO





Al (II)
308 nm

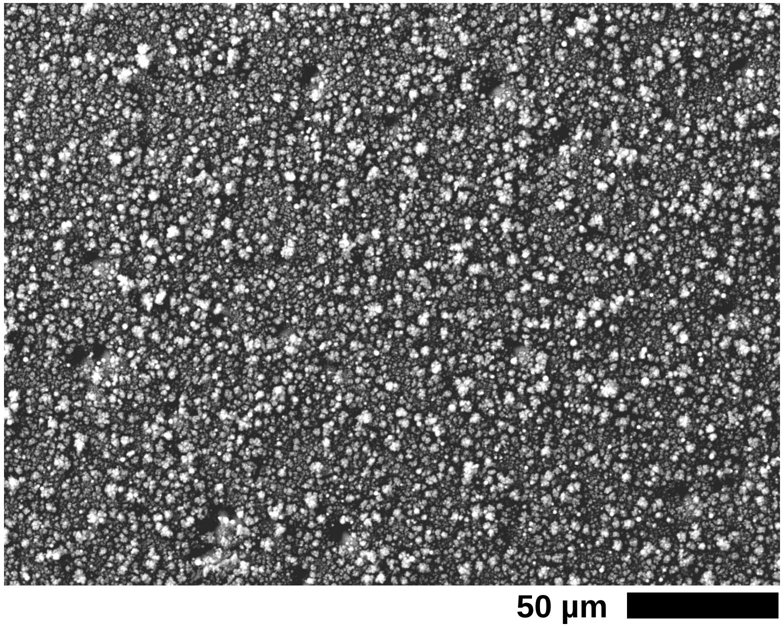


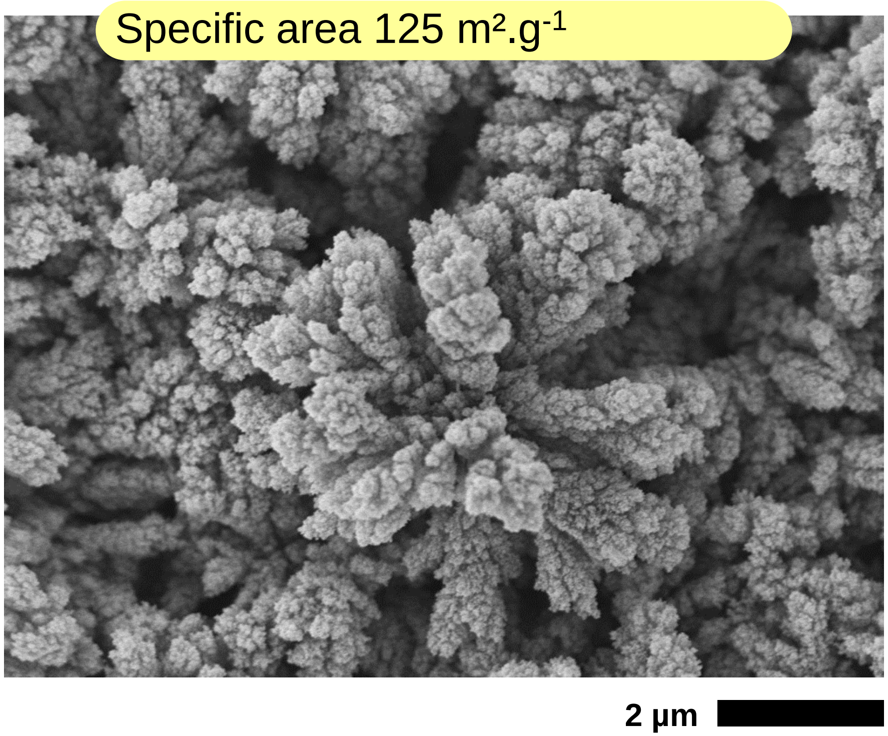


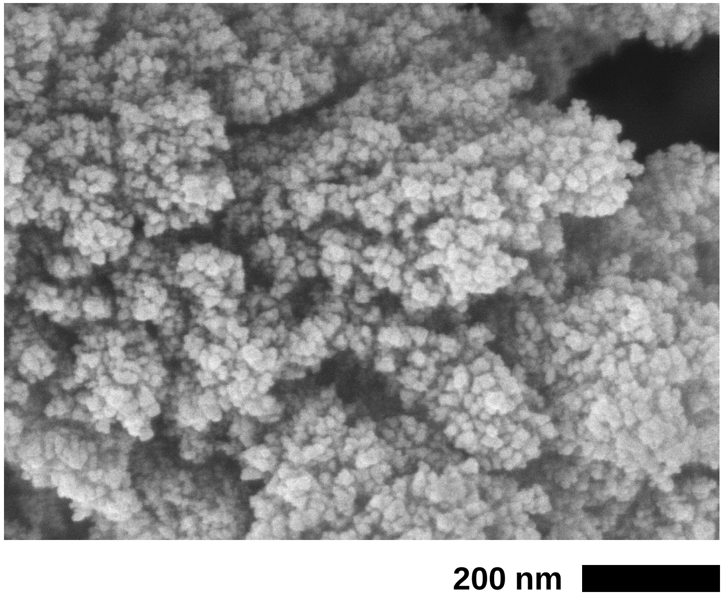
Al (II)
308 nm

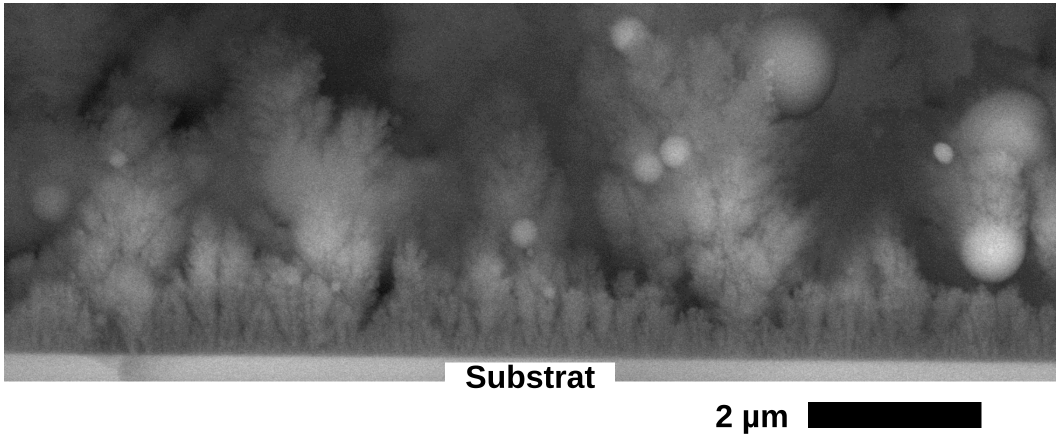
AlO
($B^2\Sigma^+ \rightarrow X^2\Sigma^+$)

SPPS – Aluminium nitrate solution

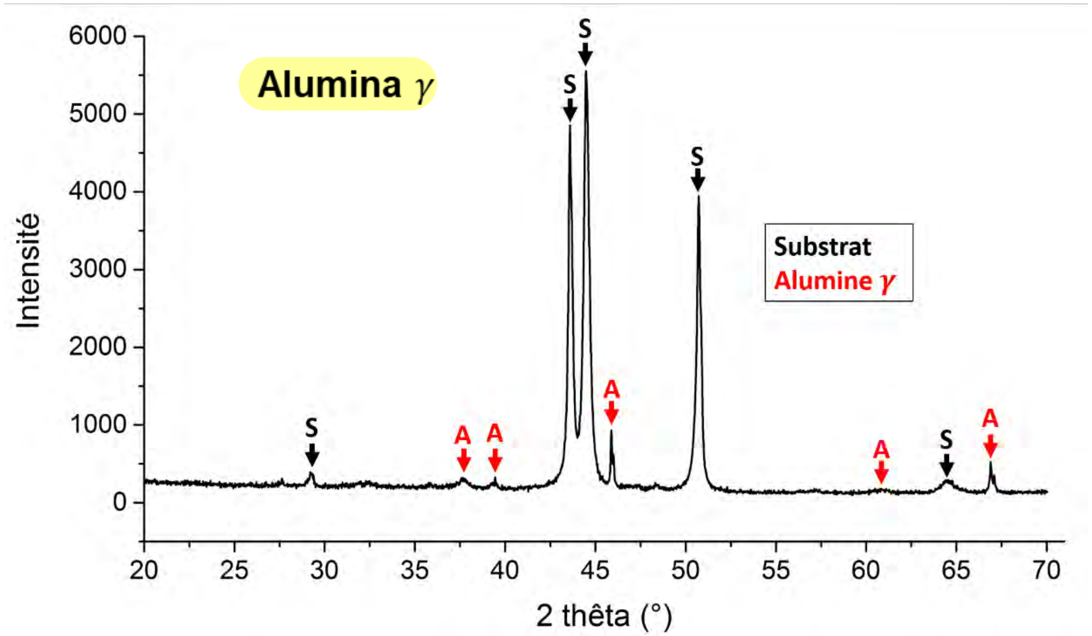






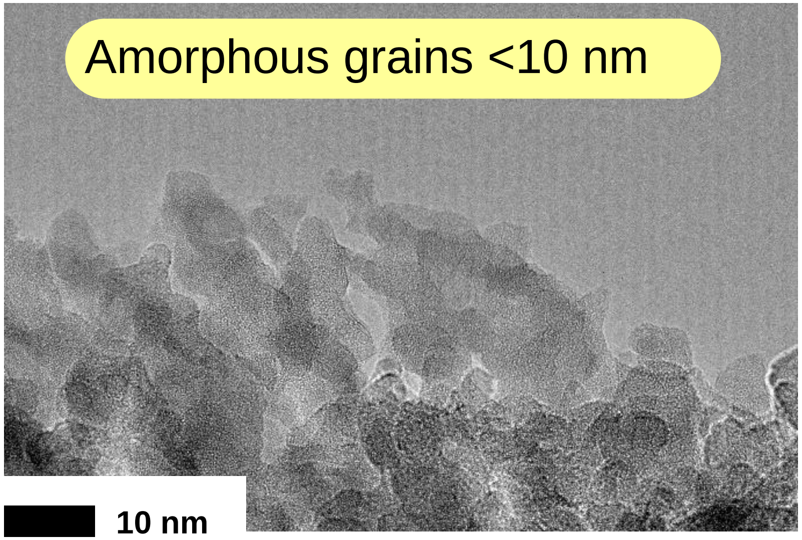


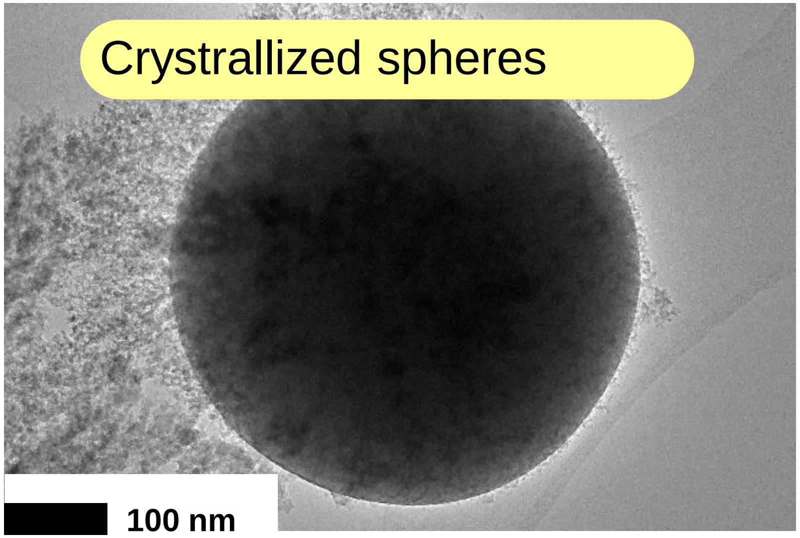
SPPS – Aluminium nitrate solution



Al et O ratio $\frac{2}{3}$

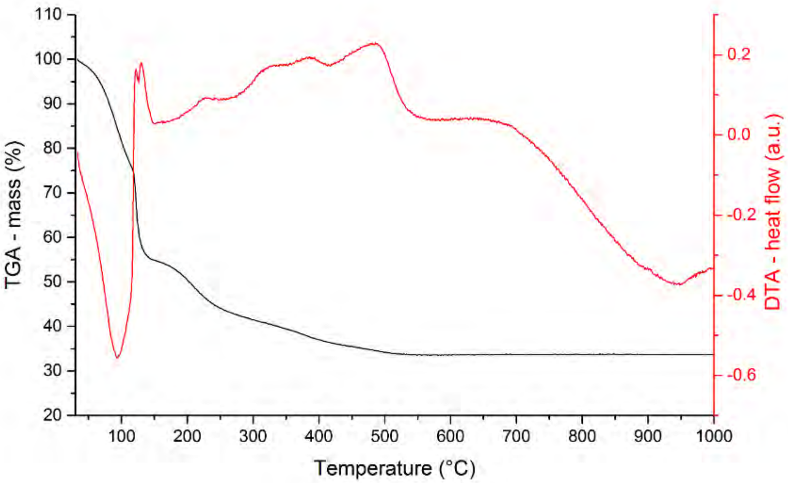
Cohesive coatings but low adherence



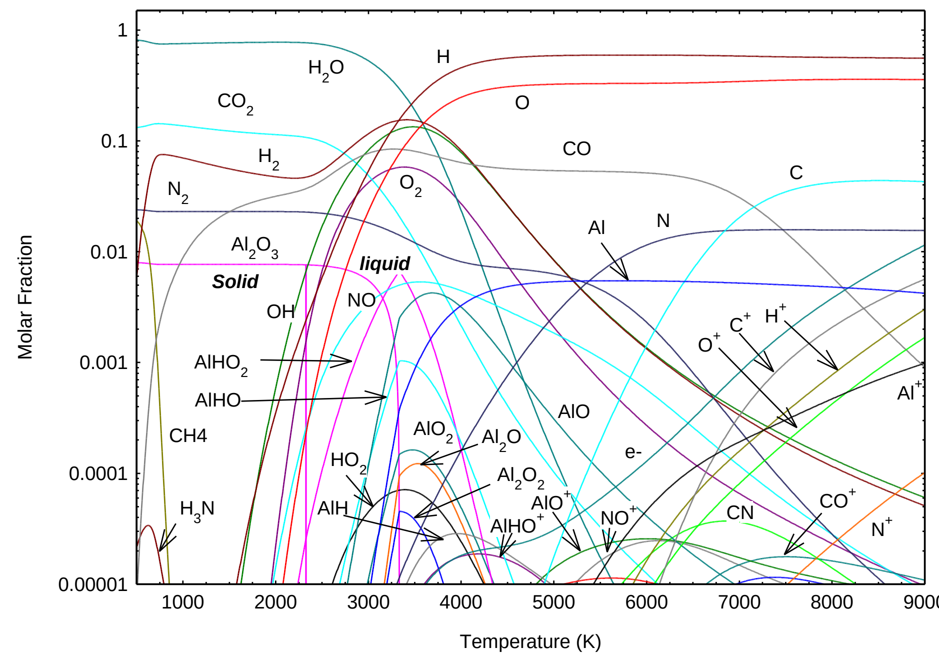


SPPS – Aluminium nitrate solution

TGA/DTA analysis



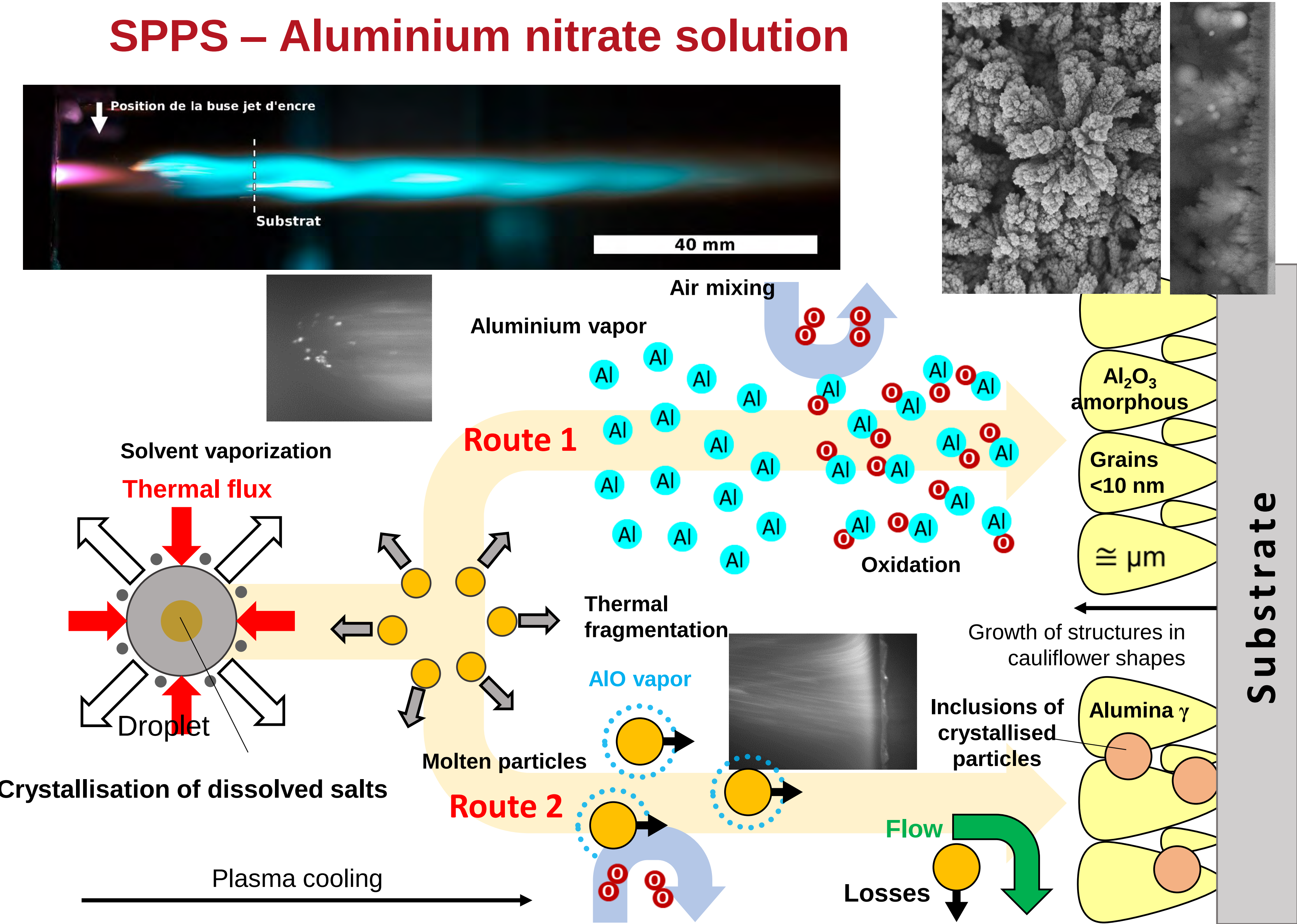
Thermodynamic calculations



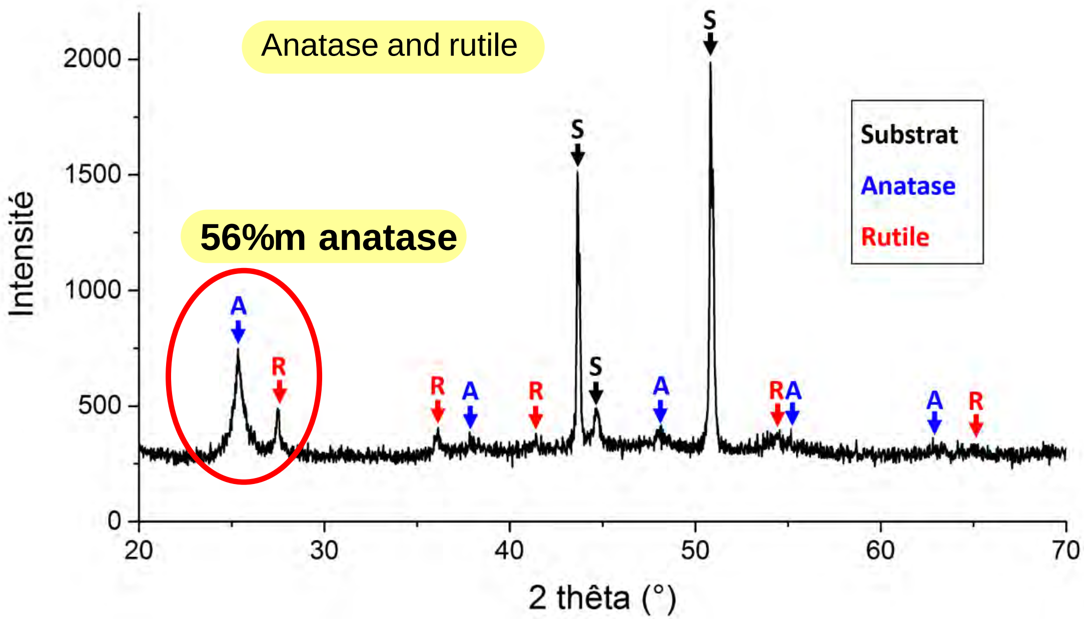
P. André

F. Mavier et al. Plasma Chem. Plasma Process. 38 657-682 (2018)

SPPS – Aluminium nitrate solution



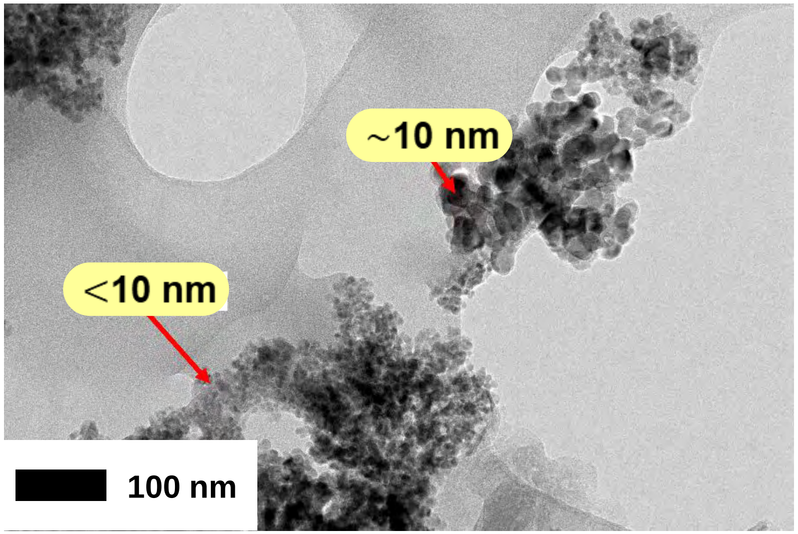
SPS – Anatase suspension

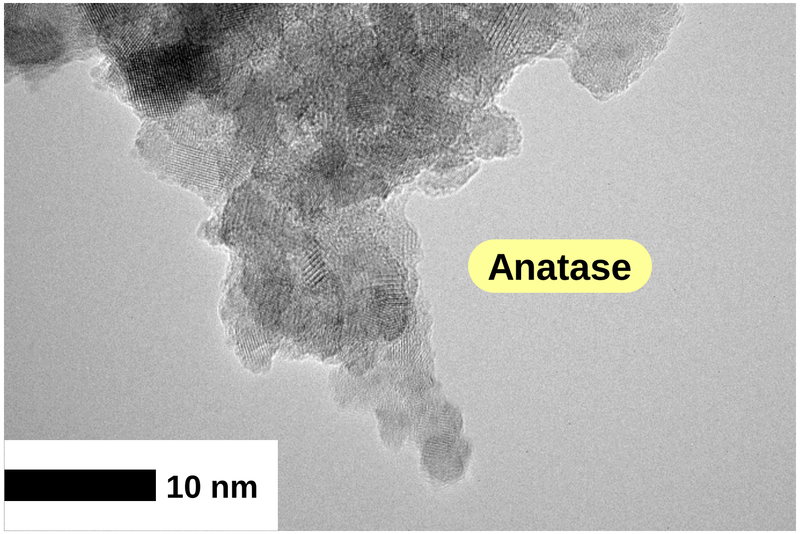


(Suspension of nanoparticles 6 nm)

Ti et O ratio ½

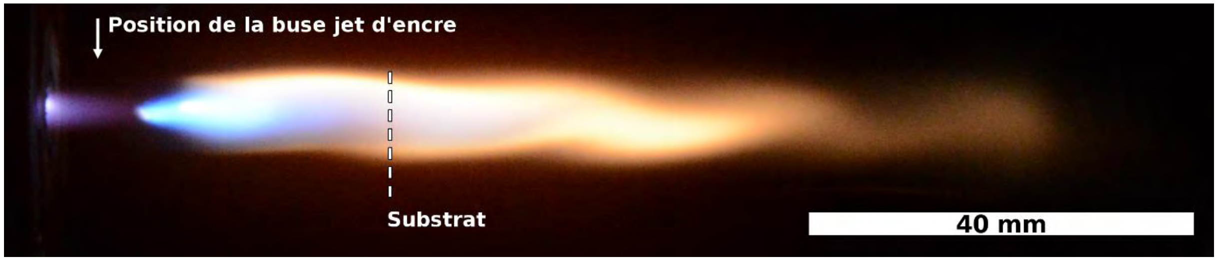
Weak adherence of coatings on silicon wafer

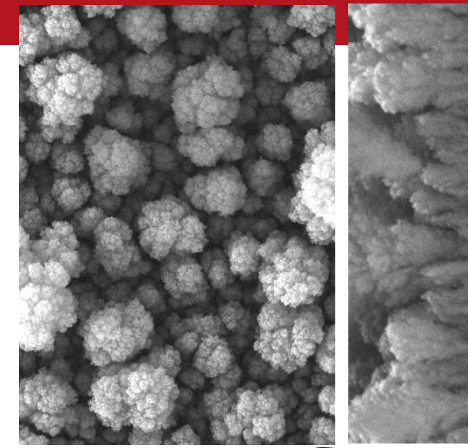


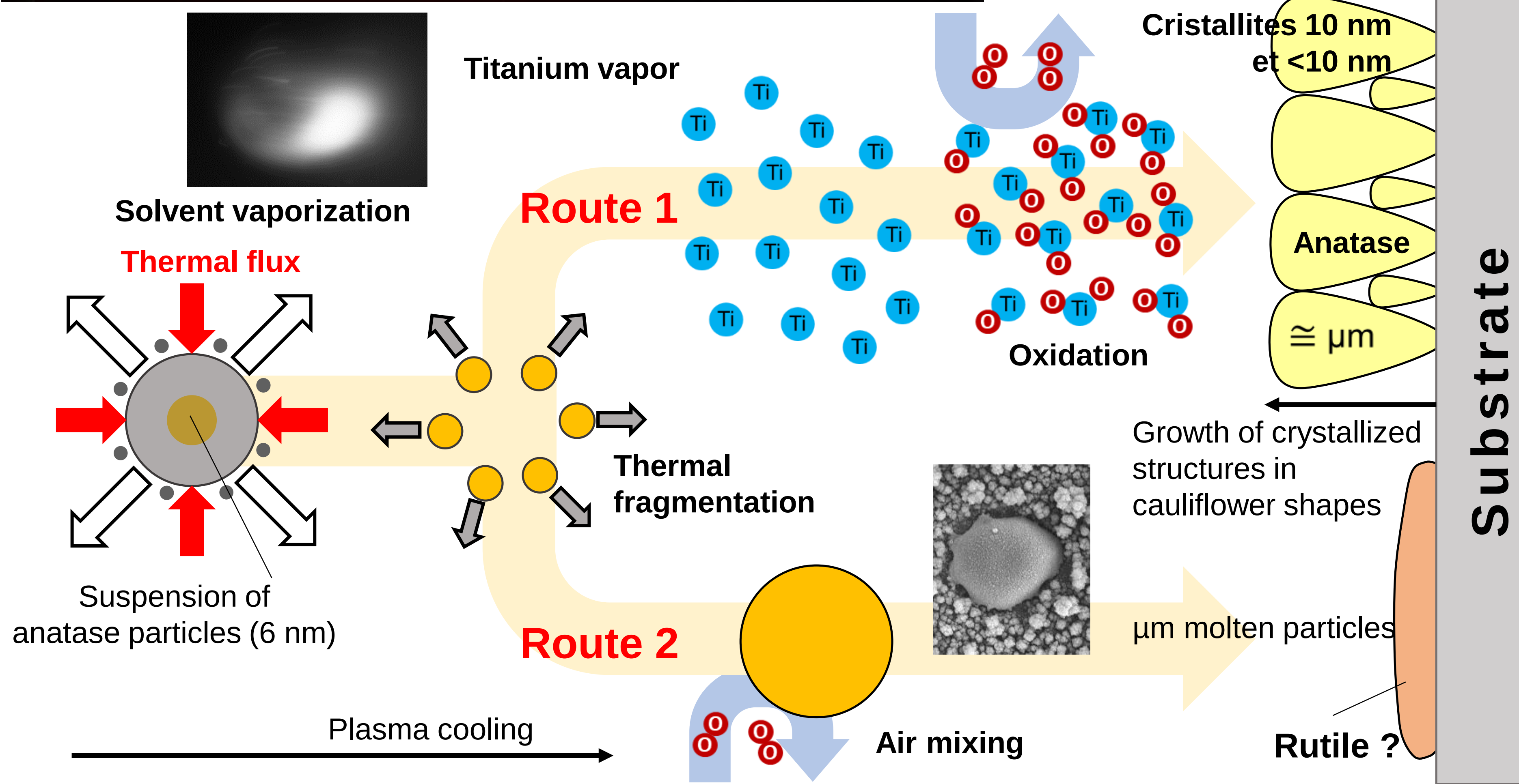


F. Mavier et al. J, Thermal Spray Technol. 27, 1041-1055 (2018)

SPS – Anatase suspension

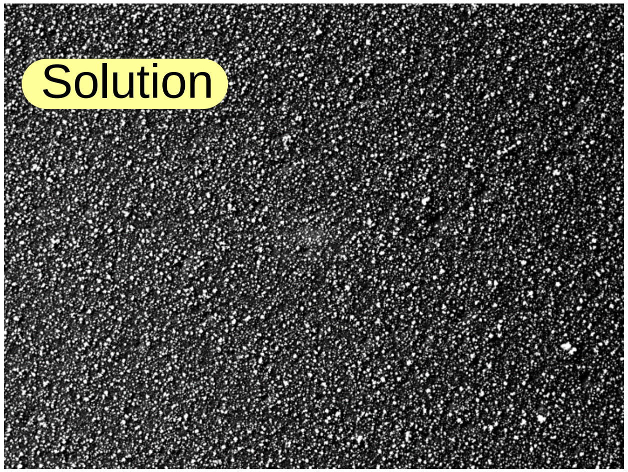




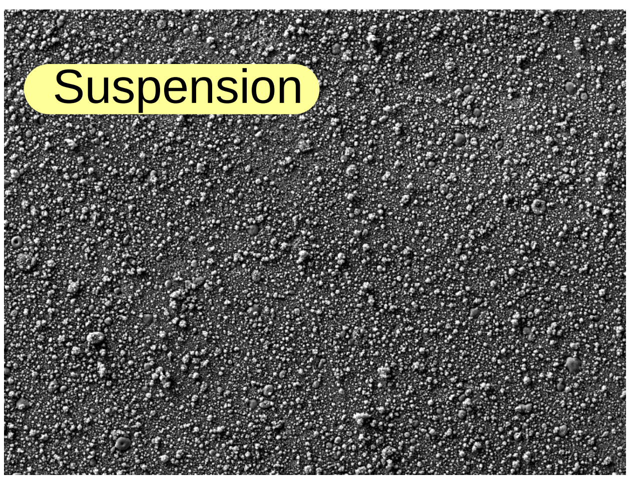


Influence of the synchronisation

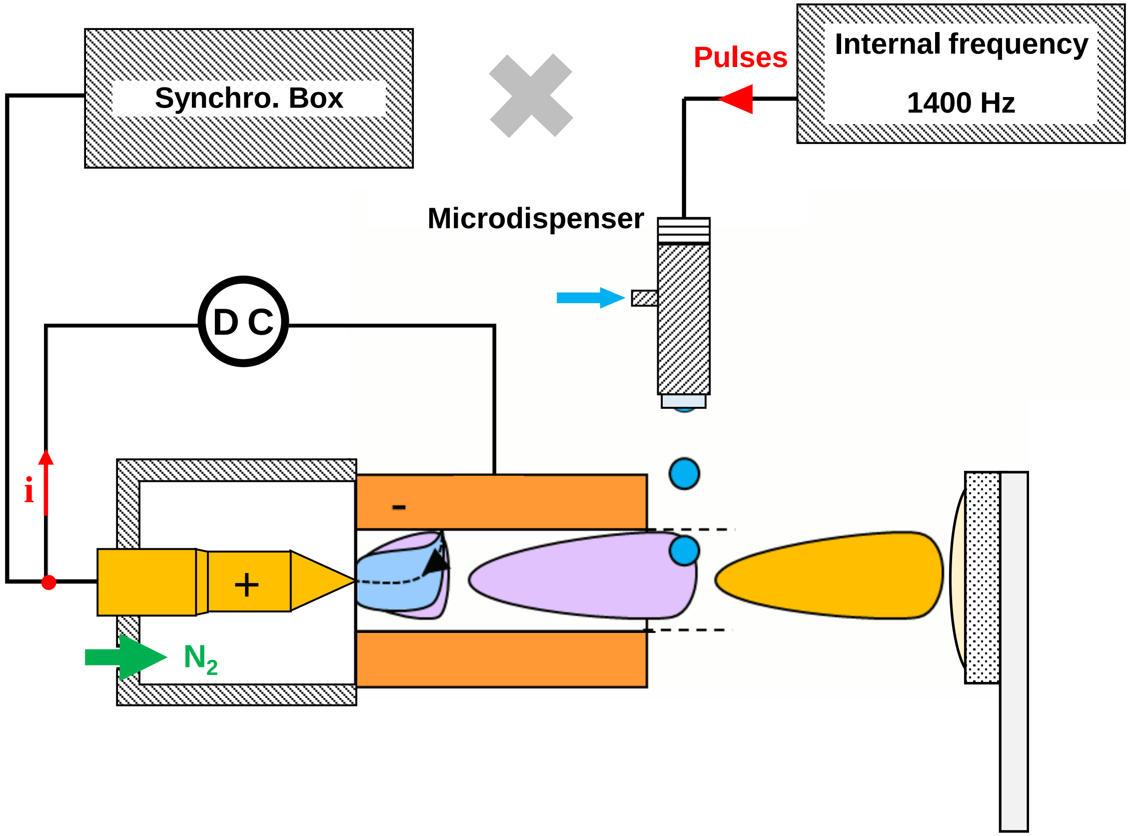
Sync



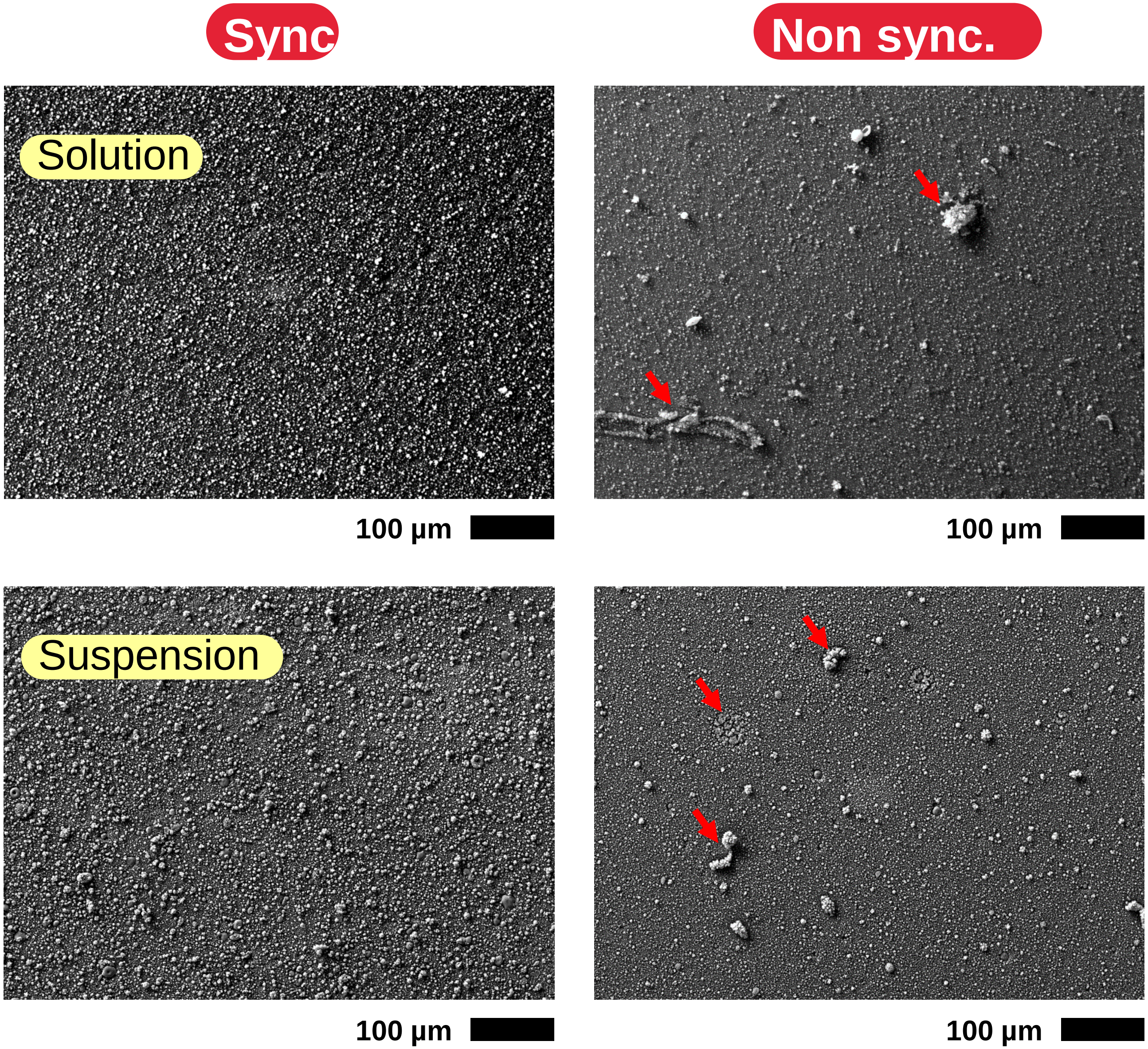
100 µm



100 µm

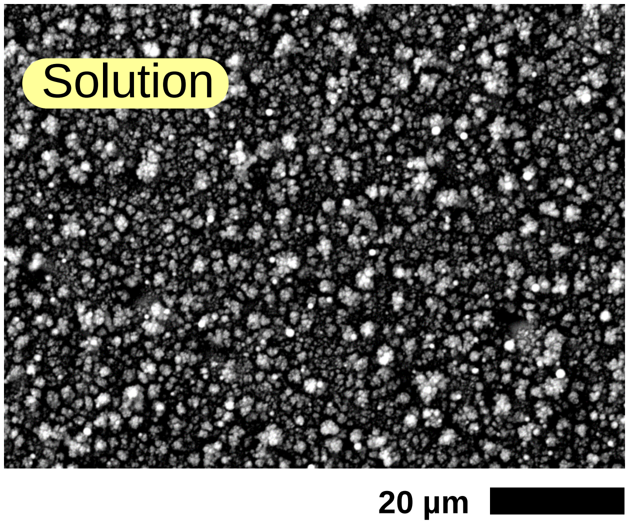


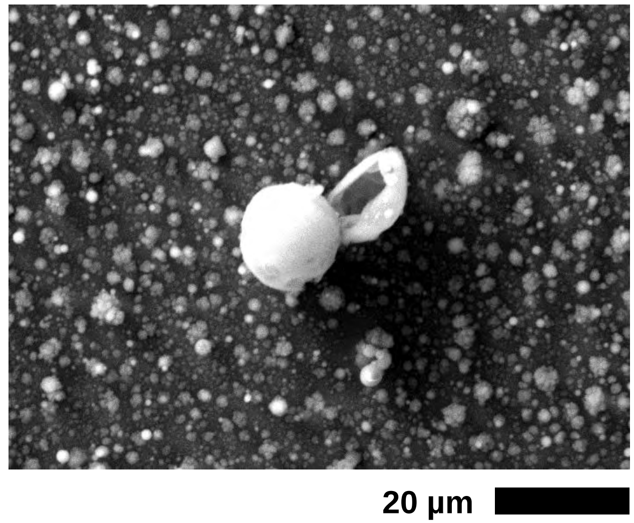
Influence of the synchronisation

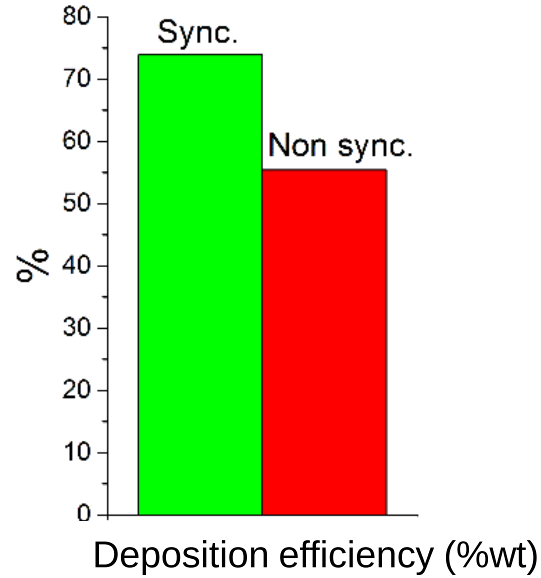


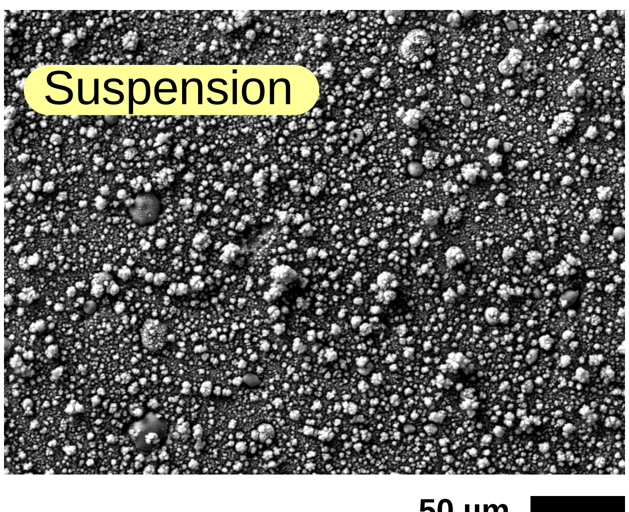
Influence of the synchronisation

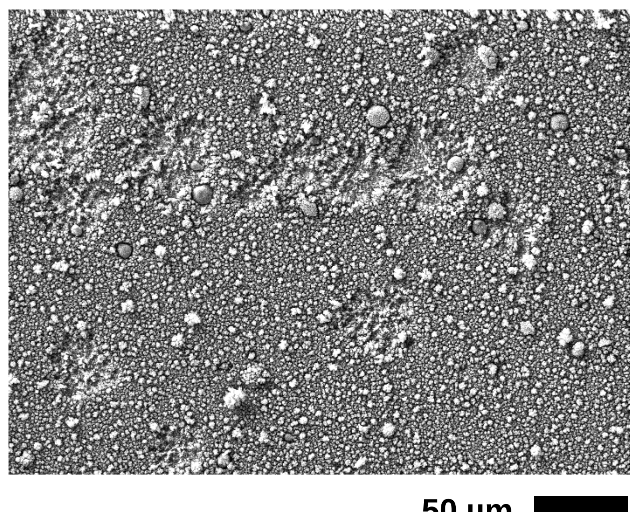
Sync. | Non sync.

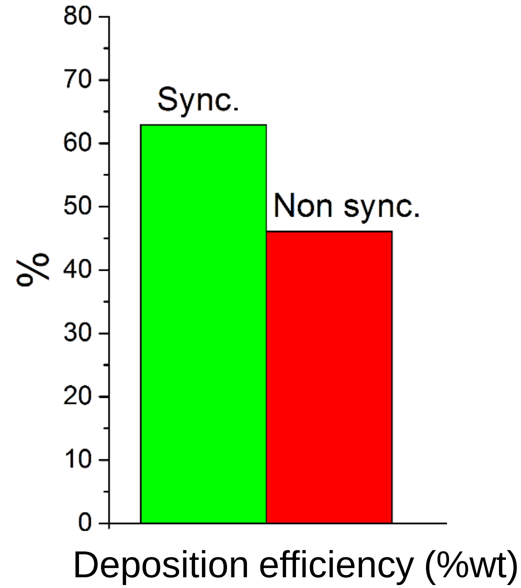












Conclusions

Arc current modulation

Stabilization effect of restrike mode
Modulation of plasma properties.

Modulation of plasma properties

Synchronized ink-jet

Pulsed ink jet – Injection control

Microdispenser – On-demand injection
Triggering of injection following the arc voltage periods

Coatings deposition

Oxide formations
Nanostructured porous microstructures
in cauliflower shapes
Depositon efficiency improved with synchronisation

Growth mechanisms