

ISPC Conference

ISPC 24

24TH INTERNATIONAL SYMPOSIUM ON PLASMA CHEMISTRY
NAPLES (ITALY) JUNE 9-14, 2019

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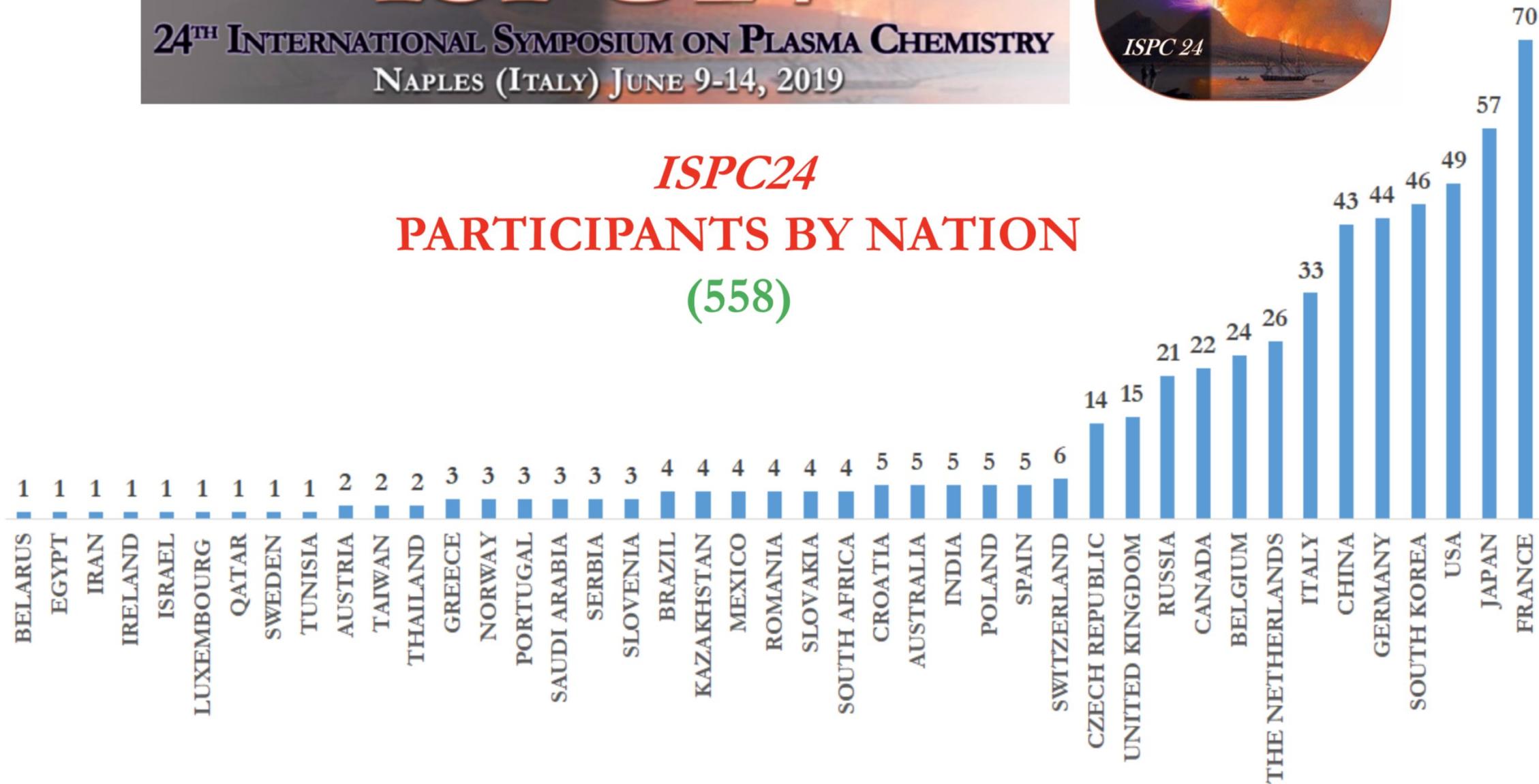
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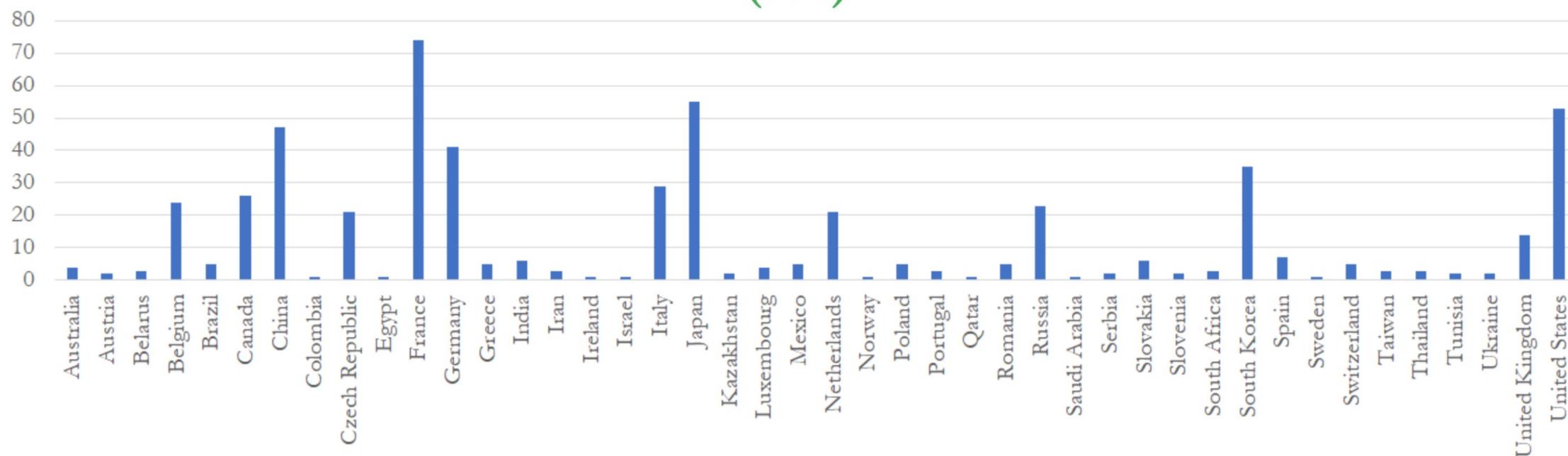


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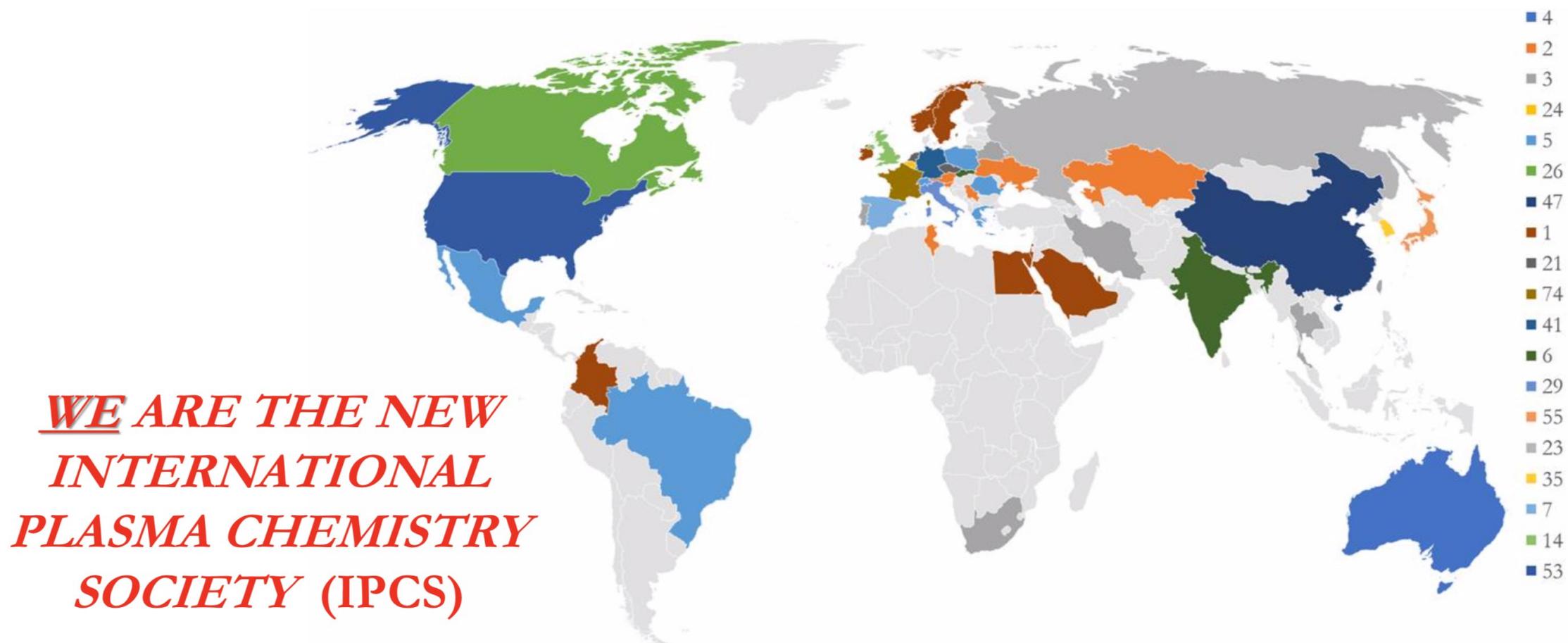


ISPC24 ABSTRACTS BY NATION (558)



ISPC 24

24TH INTERNATIONAL SYMPOSIUM ON PLASMA CHEMISTRY
NAPLES (ITALY) JUNE 9-14, 2019





27 IOC PEER- REVIEWERS

- (1) Fundamentals, diagnostics and modelling in plasma chemistry
- (2) Plasma sources design and characterization
- (3) Plasma processing of nanomaterials and nanostructures: synthesis, modification and nanofabrication
- (4) Plasma deposition of functional coatings and treatment of inorganic and organic materials
- (5) Thermal plasma fundamentals and applications
- (6) Plasma-assisted conversion, combustion, propulsion and aerodynamics
- (7) Plasma medicine and plasma agriculture
- (8) Plasma treatment of biomaterials
- (9) Plasma in and in contact with liquids
- (10) Plasmas for environmental applications and resource recovery

Abstract Assignment Show Details			Referee Review Show Details			
Abstracts	Assigned	Unassigned	Assignations	Completed	In progress	To do
558	382	176	1145	1145	0	0

- Committee Dashboard -

	1	2	3	4	5	6	7	8	9	10
	1	1	0	0	2	0	0	0	2	0
	16	8	14	8	6	9	8	3	7	11
	20	7	28	10	23	11	32	4	3	11
	69	35	26	44	7	31	45	9	20	17
	0	0	1	2	1	2	0	0	0	0
	0	0	0	1	1	1	0	1	0	0
TOTALS	106	51	69	65	40	54	85	17	32	39

TOTALS	558
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Metal vapour transport in tungsten-inert-gas welding

A.B. Murphy

Importance de la diffusion des vapeurs métalliques - TIG

Dans les applications TIG : les vapeurs métalliques viennent du weld pool - Electrodes en tungsten

Modèle: TIG dans Helium + vapeurs Fe / Cr

- Equations du modèle, utilisation des coefficients de diffusion combinés étendus à des mélanges ternaires
- But du modèle : montrer que la diffusion joue un rôle important

Résultats : Bon accord entre calculs et mesures radialement (basé sur l'émission des raies Cr à 520.8nm)

Sans vapeurs $T_{\max}=21000\text{K}$, avec vapeurs $T_{\max}=13000\text{K}$, **la diffusion sous effet du champ électrique** est un processus dominant (for upward transport of metal vapor). On observe des vapeurs Cr proche de la cathode, déposées dans des régions où $T > T_{\text{boil}}$

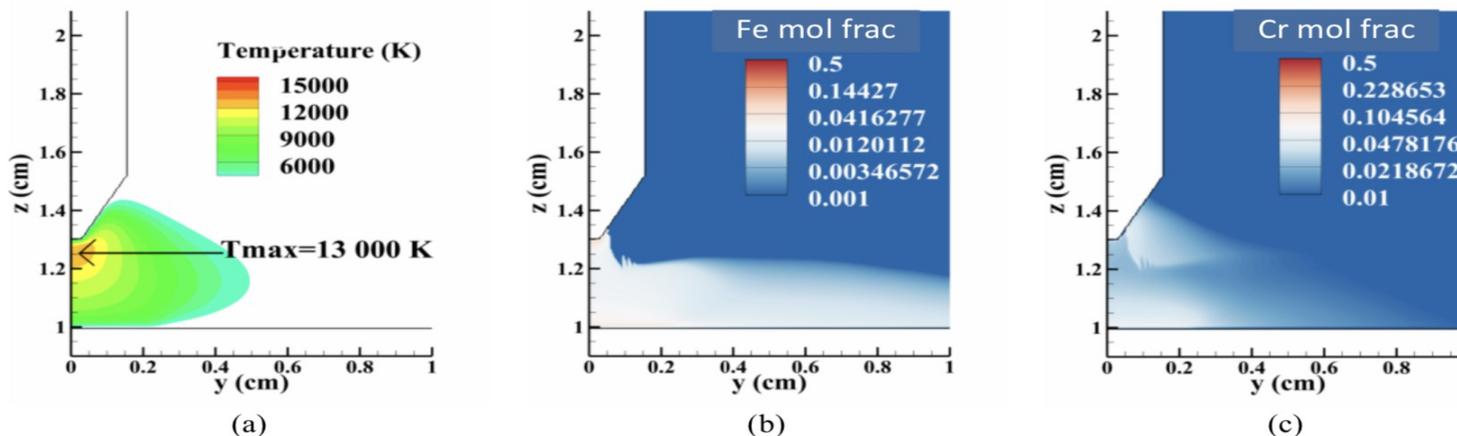


Fig. 4. Distributions of (a) temperature, (b) iron vapour mole fraction and (c) chromium vapour mole fraction in helium TIG welding of stainless steel.

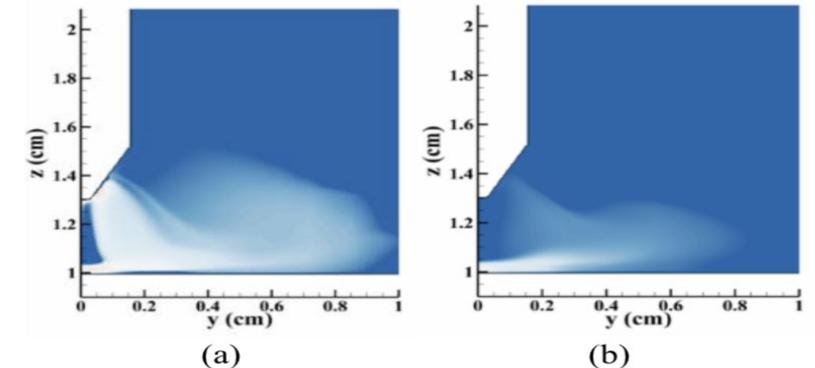


Fig. 2. Distributions of chromium vapour mole fraction neglecting (a) diffusion driven by electric fields and (b) diffusion driven by temperature gradients. The mole fraction scale is the same as in Fig. 1(c).

Metal vapour transport in tungsten-inert-gas welding

A.B. Murphy

Modèle: TIG dans Argon + vapeurs Fe / Cr

- Comparaison faite avec et sans diffusion sous Champ Electric, avec et sans diffusion sous gradient T

Résultats:

- **La diffusion à cause des gradients de températures** est dominant (pas par E), plus forte à basses T pour Ar-Fe-Cr que He-Fe-Cr, les coefficients de diffusion combinés sont plus faibles pour Ar-Fe-Cr que He-Fe-Cr
- Les vapeurs métalliques sont produites à l'anode, puis diffusion **upwards** to recirculating flow, et trapped near cathode tip by upward diffusion -> importance de la convection

Validation par mesures expérimentales : OES montre la présence de Cr proche cathode

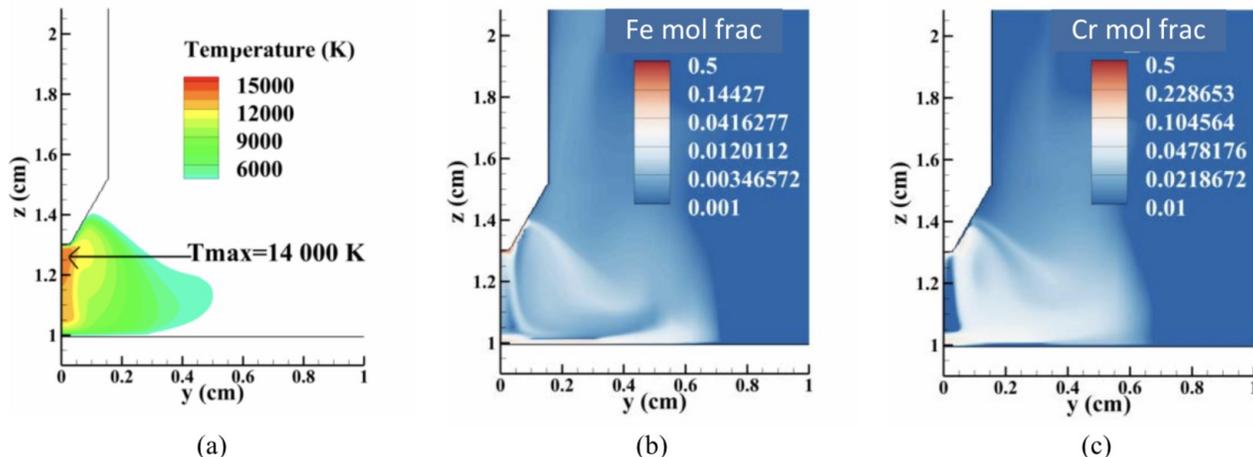


Fig. 1. Distributions of (a) temperature, (b) iron vapour mole fraction, (c) chromium vapour mole fraction in argon TIG welding of stainless steel.

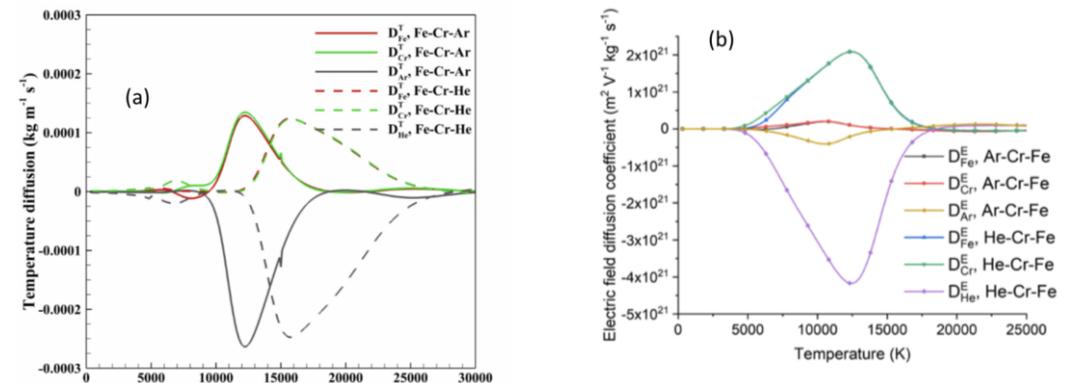


Fig. 3. Combined (a) temperature and (b) electric field diffusion coefficients for mixtures of 10% wt% iron and 10 wt% chromium with argon or helium.

Validated modeling of atmospheric pressure – anodic arc

I. Kaganovich

Développement d'un modèle pour la synthèse de CNT par arc dans C-He plasmas

-> déterminer les profils de champ électrique, densité d'électron, température électronique proche anode

-> avec mode « faible » ablation

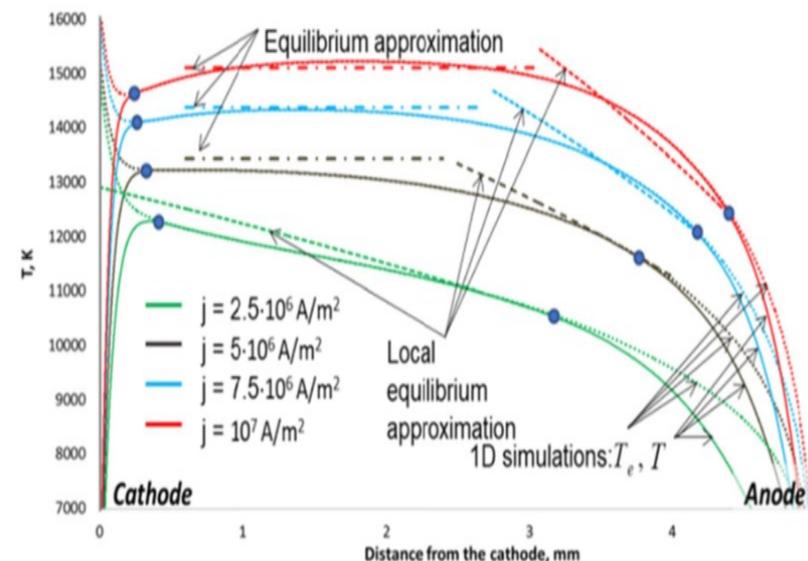
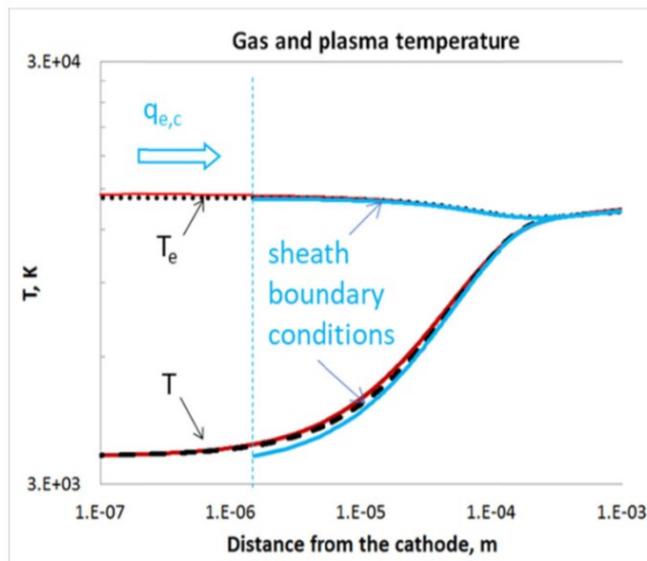
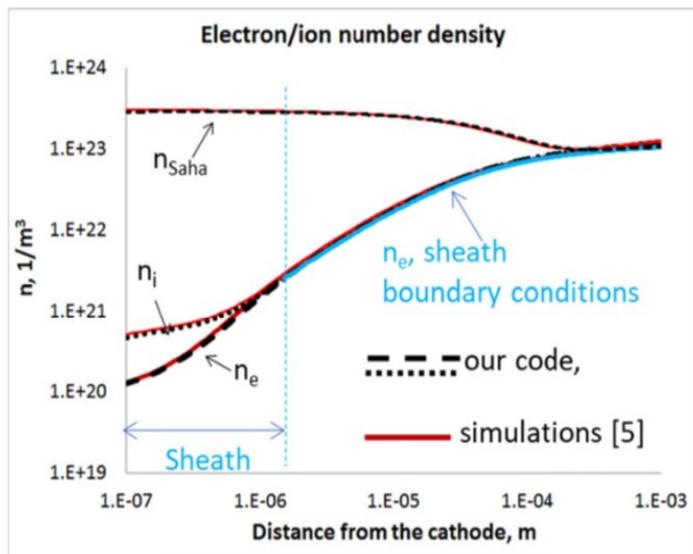
Modèle :

2D-3D modèle - Ansys CFX - Non equilibrium plasmas, P_{atm} , Self consistent model, $P=500$ torr

Plasma current, emission current, ion current, sheath voltage drop, heat fluxes at plasma-electrode interfaces

Momentum + continuity + neutral transport + ions transport + electron transport equations

Validation for 1D short nonuniform arc (arc core, near-cathode-anode regions, voltage drop, ion current)



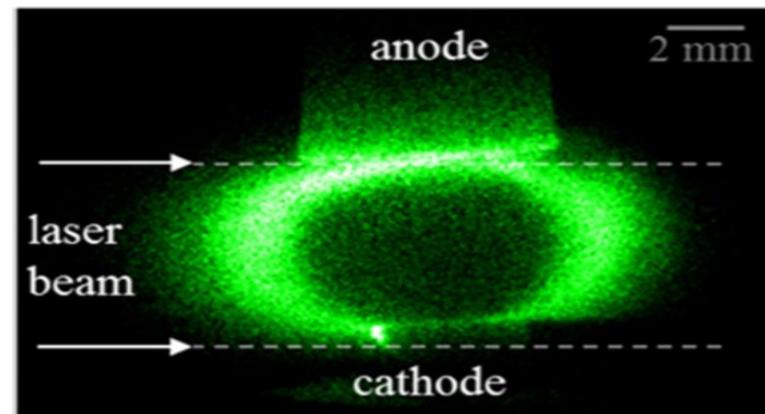
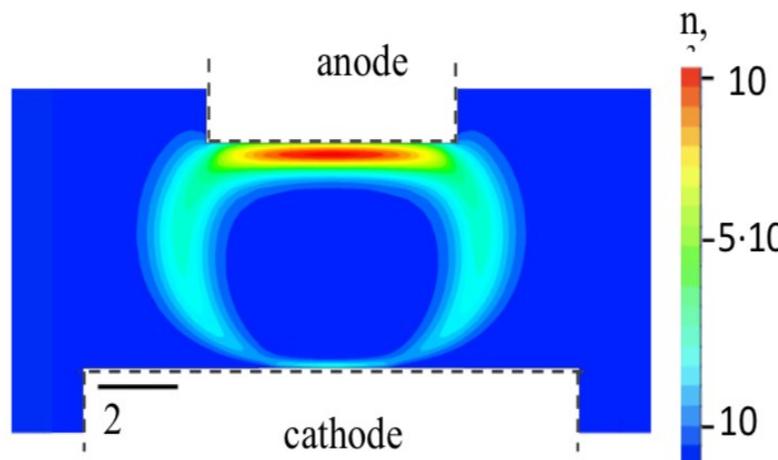
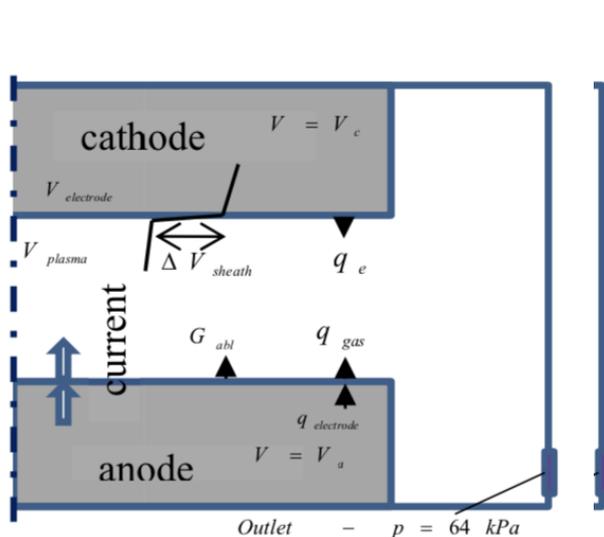
Validated modeling of atmospheric pressure – anodic arc

I. Kaganovich

2D simulations

2D- axisymmetric and steady-state

Navier-Stokes equations + heat transfer + current flow in solid electrodes (ablation anode et déposition cathode) + near-electrode space-charge sheathes + wall function (plasma-electrode interfaces) + radiation from electrodes surfaces, Joule heating of electrodes, and the thermal resistance of the deposit at the cathode.



Carbon dimer distribution has a bubble-like shape around the arc core. Comparison of (top) simulated and (bottom) measured C_2 density distribution (planar LIF: spectral image of carbon dimer, emission is at 470 nm and laser radiation is at 437 nm) in the arc at current 50 A

En mode « faible » ablation, courant d'arc à l'anode est drivé par diffusion électronique (V_{anode} faible \rightarrow flux chaleur faible)

Les profils de densité de courant sont affecté par la gaine pour de faibles gap : 1.5mm

Les profils de densité de courant sont plus uniformes pour de larges gap : 3mm

Les molécules de carbone se forment dans les région froides, périphériques du plasma

Fluctuation phenomena in diode-rectified multiphase AC arc for improvement of electrode erosion

M. Tanaka

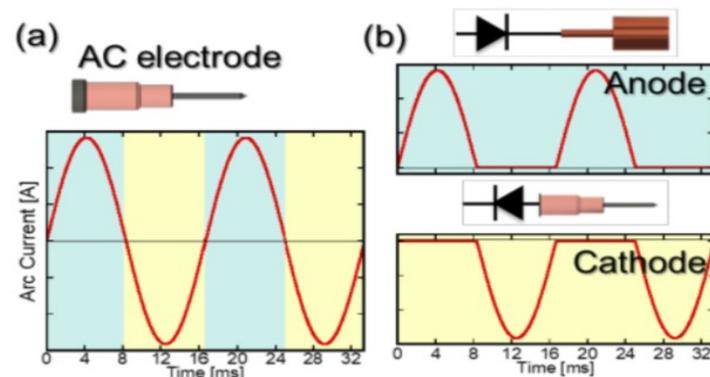
Inconvénients : arc instable et non uniforme dans l'espace et le temps, forte érosion des électrodes

Constat : à la cathode on veut Low work function et high melting point, à l'anode high thermal conductivity. Aucun matériau ne satisfait à la fois les propriétés requises pour cathode et anode : le plus gros problème=> forte érosion en AC des électrodes.

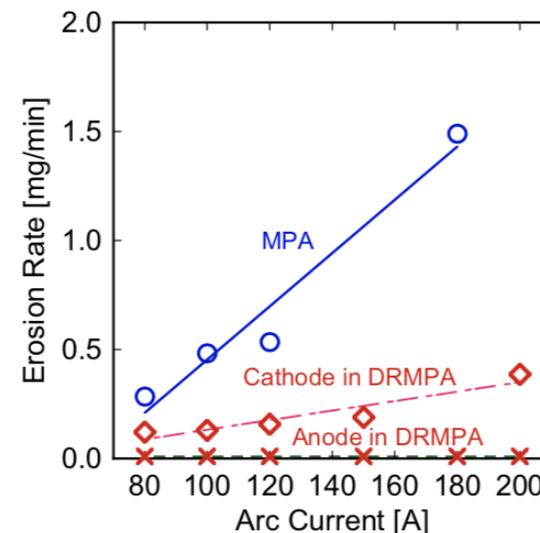
Intérêt de la Diode Rectification (DR) : séparer l'électrode en une paire de cathode et anode, et permettre ainsi de mieux visualiser efficacement les fluctuations

Objectif : comprendre et caractériser l'impact de la DR spatialement et temporellement par caméra rapide, observation du profil de température pour un MultiPhase-Arc (MPA)

Conclusion : l'érosion est mieux caractérisée avec DRMPA



3. Conceptual waveforms of arc current for MPA (a) and DRMPA electrode (b).



Fluctuation phenomena in diode-rectified multiphase AC arc for improvement of electrode erosion

M. Tanaka

Dispositif expérimental:

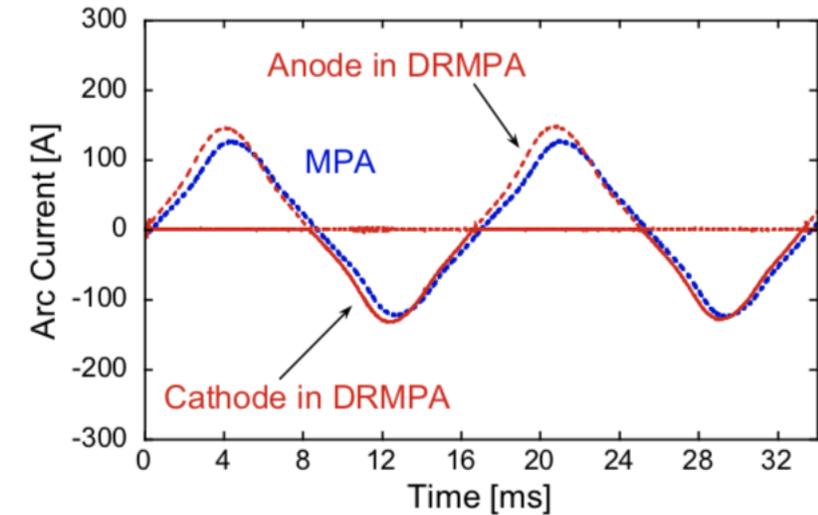
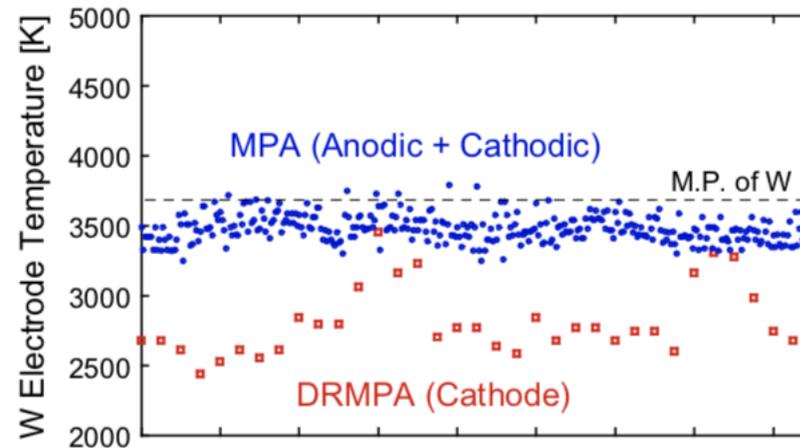
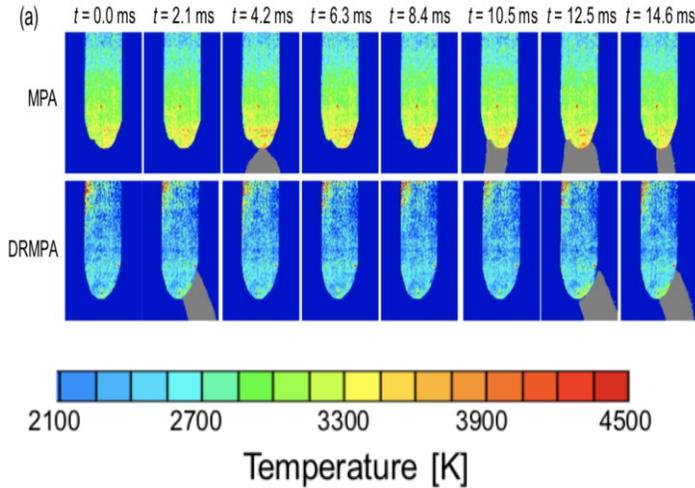
Patm, 6 phases, Argon, 100-150A, gap électrode 50mm, cathode WThO₂ (3.2mm diam), anode Cu (25mm diam)

Mesures par Camera rapide FASTCAM SA5.

Etude des raies atomiques (O, Ar, W) par OES -> distribution de la température, radiale et temporelle

Comparaison des observations faites MPA et DRMPA à 120A sur les raies à 794nm et 675nm

Arc temperature fluctuation

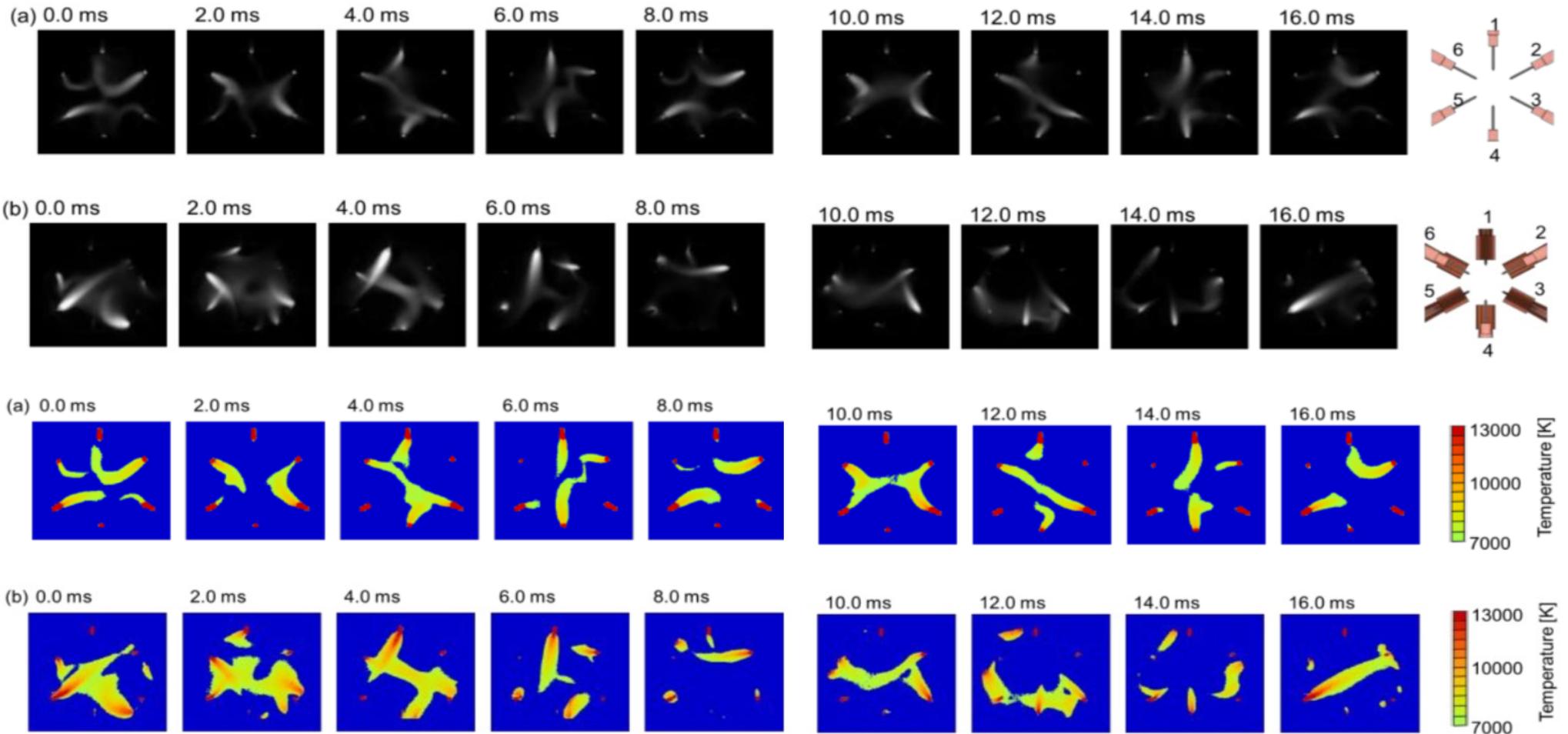


Fluctuation phenomena in diode-rectified multiphase AC arc for improvement of electrode erosion

M. Tanaka

Résultats :

Analyse à la cathode : T=13000K (MPA et DRMPA) - Diamètre : 5mm cathode ($9.106A/m^2$ pour les 2 méthodes),
Analyse à l'anode : T=9000K (DRMPA)-11000K(MPA) - Diamètre : 7mm+7mm (DRMPA 2 arcs présents, $2.106A/m^2$)
contre 7mm (1 arc en MPA $4.106A/m^2$)



Fluctuation phenomena in diode-rectified multiphase AC arc for improvement of electrode erosion

M. Tanaka

Conclusions :

Cathode jet >> anode jet pour DRMPA

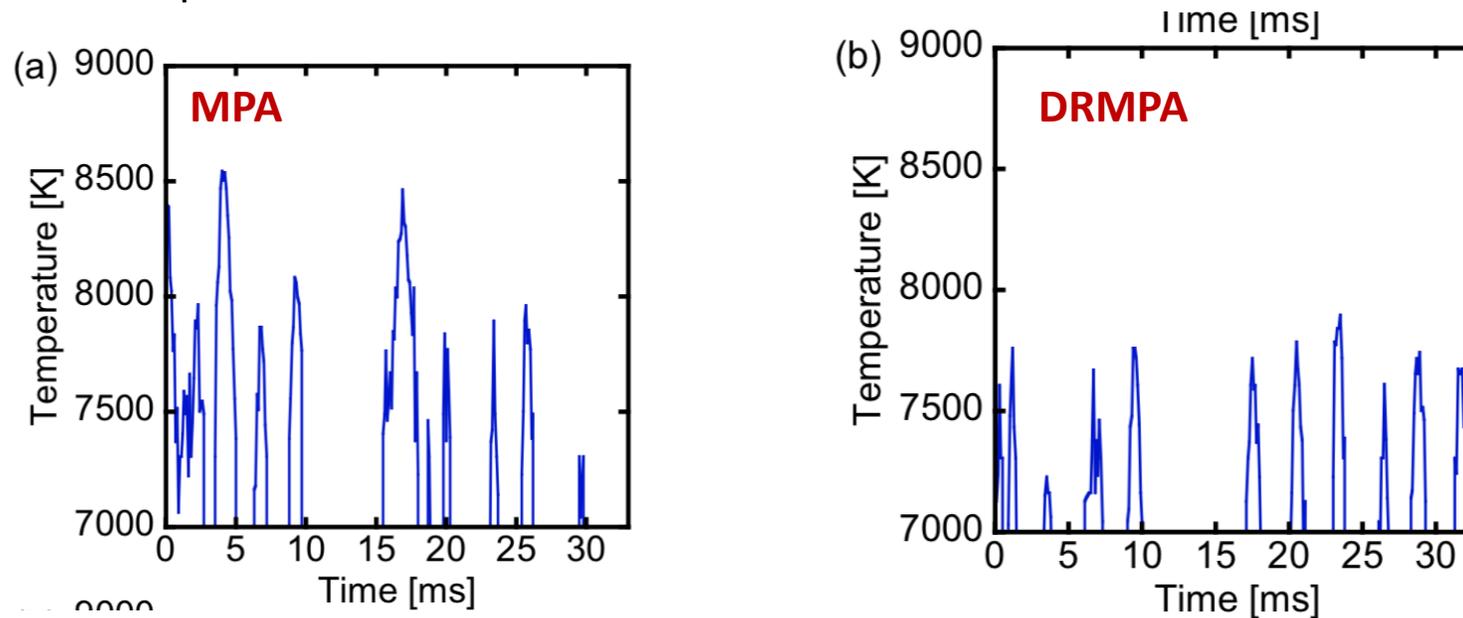
Cathode jet = Anode jet pour MPA

Le profil de température à la cathode est plus important qu'à l'anode

Différences aux électrodes est due à la présence de vapeurs métalliques, anode shape effet

Différences aux électrodes du jet de plasma en configuration DRMPA et MPA ont été analysées et clarifiées

Un courant plus fort conduit à plus d'uniformité de l'arc



Temperature fluctuation at the centre of the discharge region for the MPA (a) and the DRMPA (b)

Complementary studies of DC arc by experiments and combined modelling of the plasma bulk and the cathode boundary layer

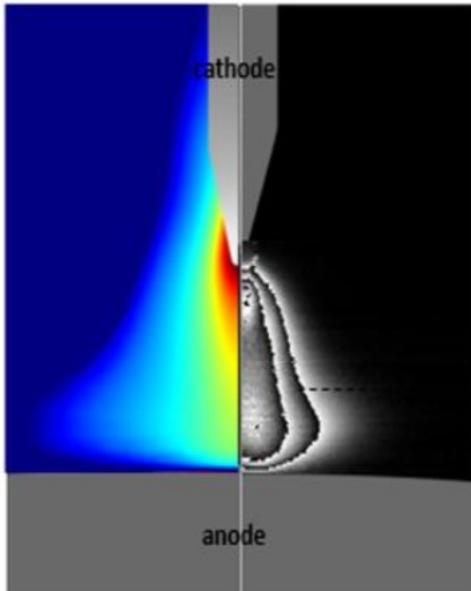
C. Mohsni

Motivation

- Meilleure description des phénomènes aux électrodes
- Comparaison modèle – mesures Air, CO2 gaz.

Dispositif expérimental

- Anode sphérique en graphite, cathode W, gap 5mm
- Mesures électriques (V et I) + Mesures OES (profil de température) at midplane of the arc



Modèle

Colonne d'arc LTE + nonequilibrium cathode boundary -> couplage

Cathode boundary layer : basé sur travaux de Benilov

Heat transfer+current transfer+boundary conditions+iterations till: on obtient J et T à la surface, couplé au reste du model

Resultats:

Densité de courant et chute de potentiel en fonction de la température de surface

Différents flux et température électronique en fonction de

Température en fonction de la distance à la surface de la cathode (0-12mm) : basé sur travaux de Baeva.

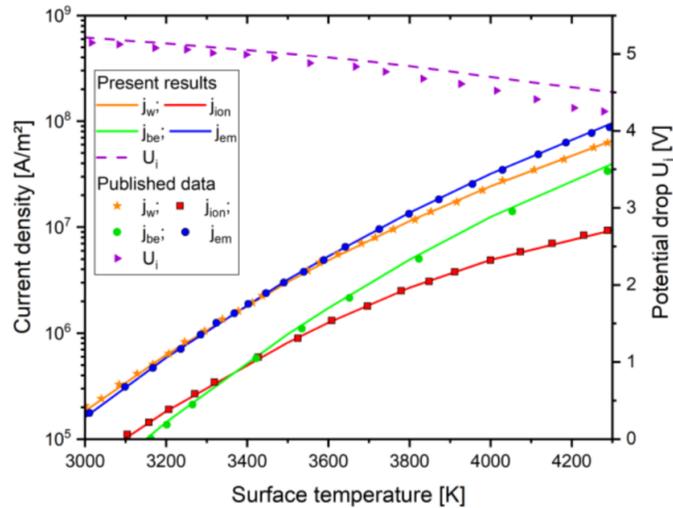


Fig. 2. Total current density and its components in the cathode space-charge sheath for $U_{tot} = 10$ V.

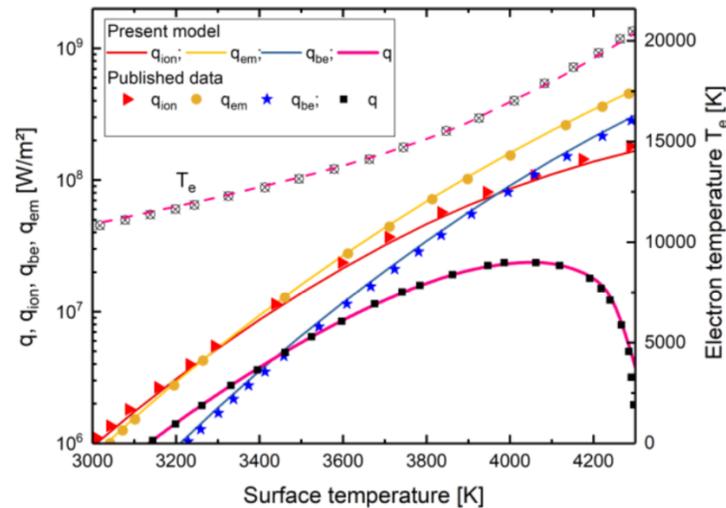


Fig. 3. Total heat flux from the plasma to the cathode surface and its components for $U_{tot} = 10$ V.

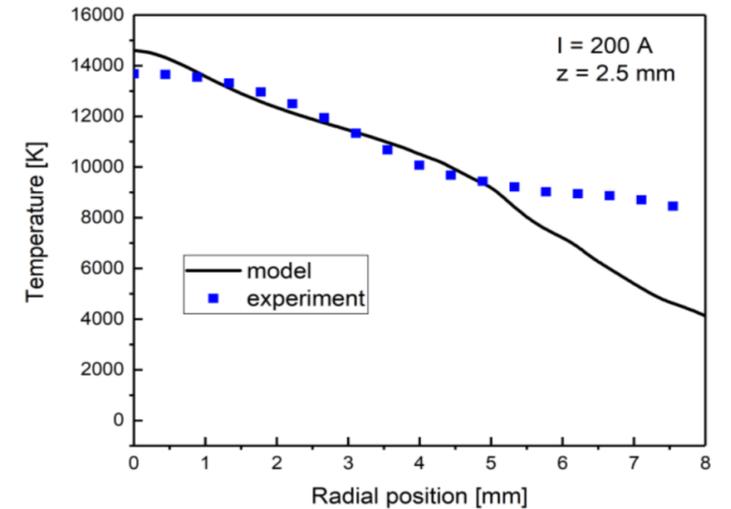


Fig. 4. Radial distribution of the plasma temperature in the midplane of the arc obtained in the combined modelling approach and OES for an arc current 200 A.

Combined arc model results

$I=200\text{A}$, profil de température, $U_{\text{arc}}=16.56\text{V}$ (mesuré 17.54V)

à $z=2.5\text{mm}$, « fair » accord jusqu'à 5mm en position radiale

Comparaison entre model à LTE et combined model : températures quasi pareilles, mais champ électrique différent

Accord acceptable sur la tension d'arc

Projet : appliquer le model combiné au CO_2

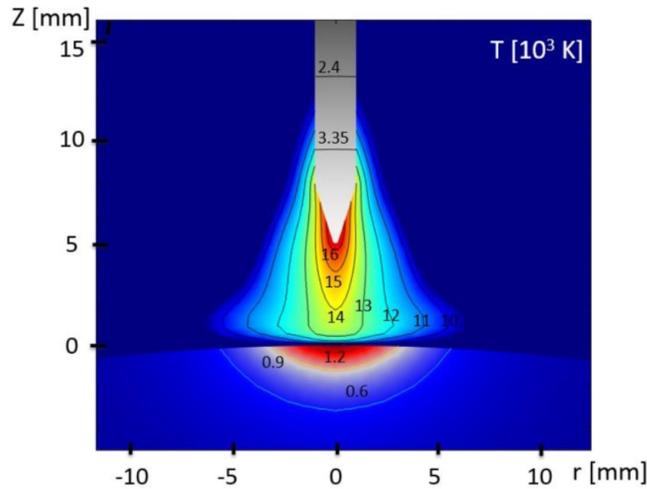


Fig. 5. Two-dimensional distribution of the plasma temperature and the temperature in the electrodes obtained in the combined modelling approach for arc current 200 A .

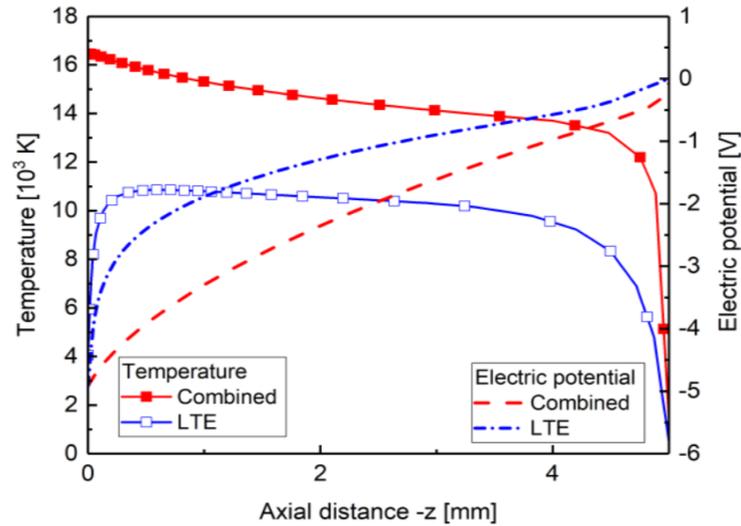


Fig. 6. Plasma temperature and electric potential in the plasma along the arc axis for an arc current of 200 A .

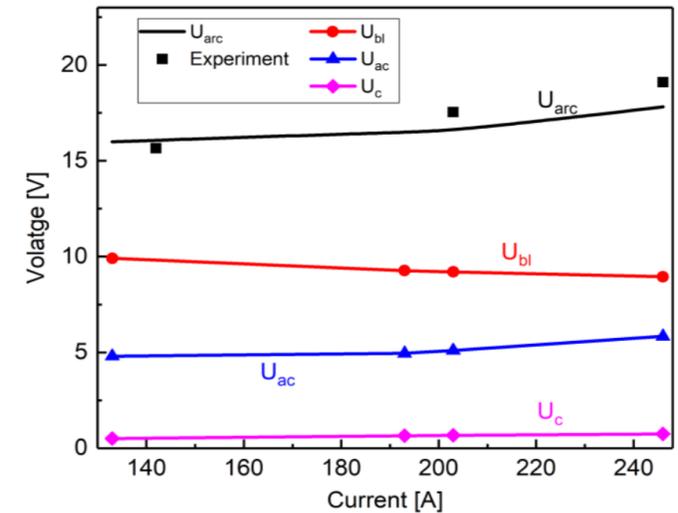


Fig. 7. The current-voltage characteristics of the arc obtained by the combined modelling approach and electric measurements. Additionally, the individual contributions of the boundary layer (U_{bl}), the voltage drop in the cathode (U_{c}) and the arc column (U_{ac}) are shown.

CO2 plasmas : from solar fuels to oxygen production on Mars

V. Guerra

Constats : augmentation des émissions de CO₂, réchauffement climatique

Solutions : produire du CO₂ « neutre », utiliser le CO₂ pour produire des gaz de synthèse CO+H₂, electrolysis vs plasmalysis

Motivation:

- L'activation du CO₂ par plasma - CO₂ dissociation peut être améliorée par l'excitation vibrationnelle
- Comprendre la relaxation du CO₂ -> Self consistent model kinetic model+experiment support (LPP/TU/e)
- Application ISRU (In Situ Resource Utilisation) Mars (96%CO₂+2%Ar+2%N₂, basses T et basses P=5Torr, V-T coefficients plus faibles, V-V plus importants)

CO₂ molécules : 3 modes de vibration : symmetric, bending, asymmetric

- Electron impact, vibration-to-vibration, vibration-to-vibration energy exchanges

Kinetic model :

- Niveaux hauts vibrationnels négligeables, rôle négligeable de la dissociation et produits issus de la dissociation
- 70 niveaux de vibration, équation Boltzmann pour les électrons couplée système équations taux réaction, E/N constant
- 250 direct réactions (e-V), 450 pour V-T, et 800 pour V-V

Manipulation

DC pulsée et continue, 1-5torr, 10-50mA, T_{gaz}=230K, Δt=5ms, diagnostique par FTIR

CO₂ pur : influence de T_g. Temperature room : influence de Ar/N₂

CO2 plasmas : from solar fuels to oxygen production on Mars

V. Guerra

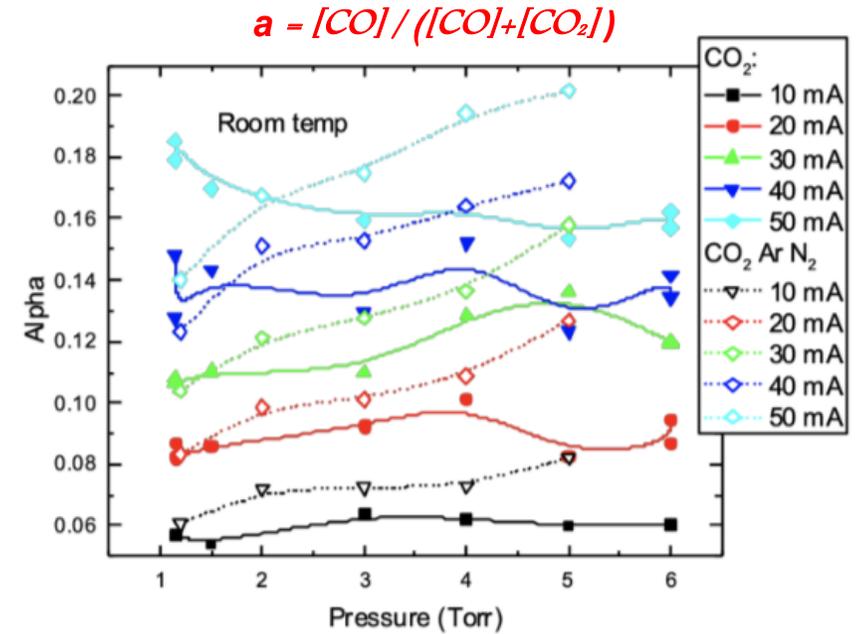
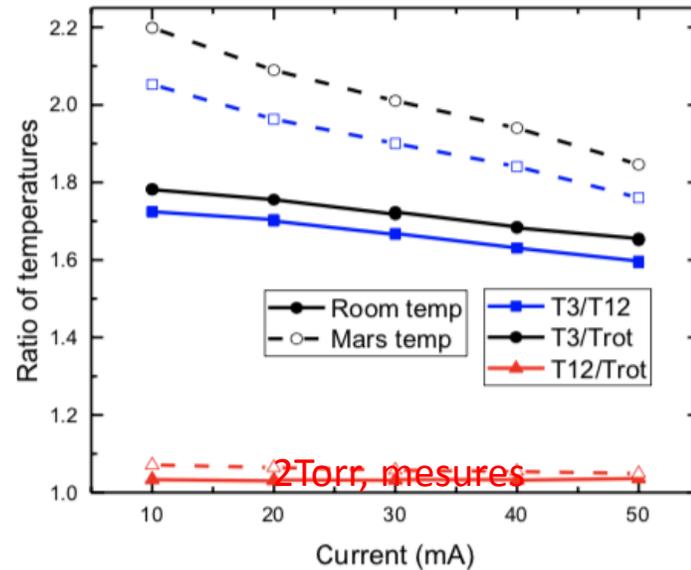
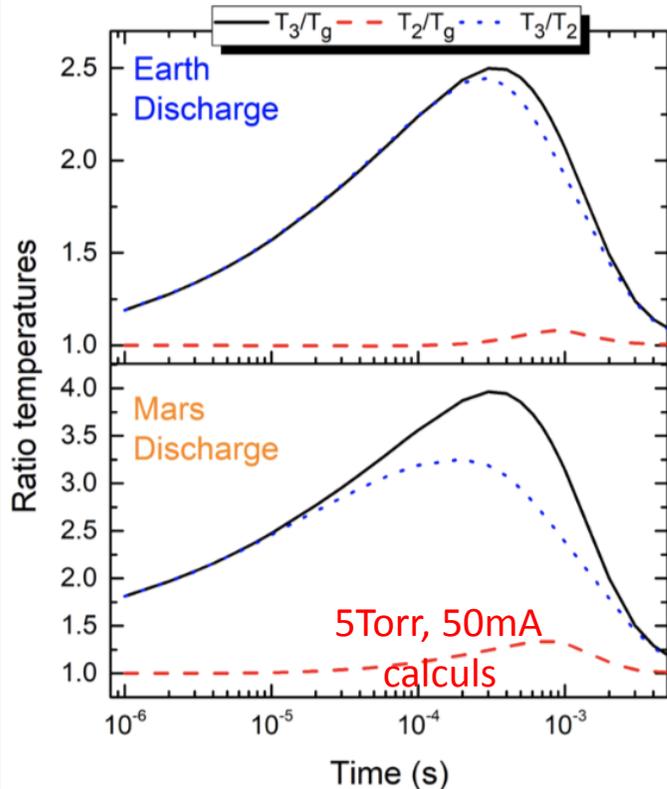
Résultats :

- Validation plutôt bonne du calcul des densités des niveaux vibrationnels (e-V, V-T et V-V) mais quelques différences pour la température

-> ajout d'une équation : $n_m C_p dT_g/dt = Q_{in} - 8\lambda(T_g - T_w)/R^2$

-> ajout des niveaux jusqu'à $v_3=21$

-> la section efficace de dissociation par impact électronique est mal connue



Plus fort déséquilibre sur Mars -> favorise dissociation vibrationnelle
 Facteur 1.2 (mesures), et 1.6 (calculs) du déséquilibre (Terre vers Mars)
 Effet positif de la composition de Mars sur la dissociation (facteur conversion $\alpha(\text{CO}_2 + \text{Ar} + \text{N}_2)$)

Plasma treatment of biomedical waste

A. Ustimenko

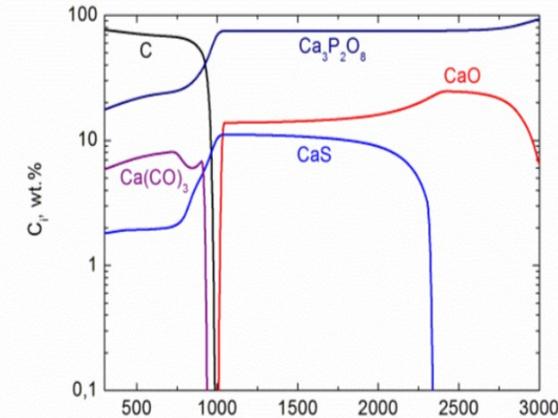
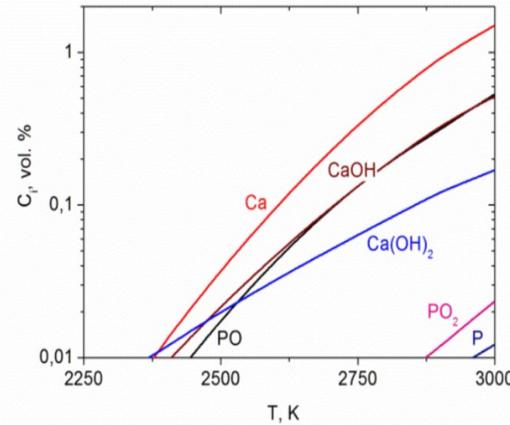
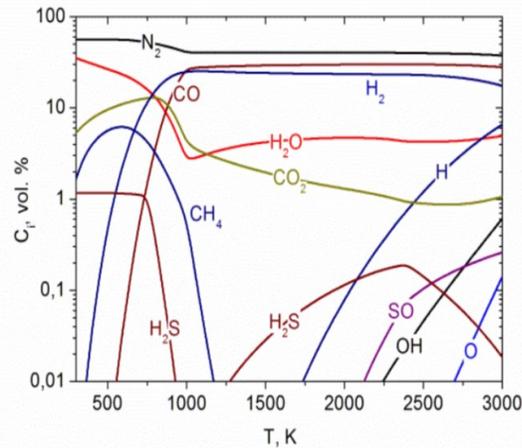
Thermodynamic analysis and experiments on gasification of biomedical waste (BMW)

Constituants le plus souvent constatés : C, H, O, N, S, P, CaCO_3

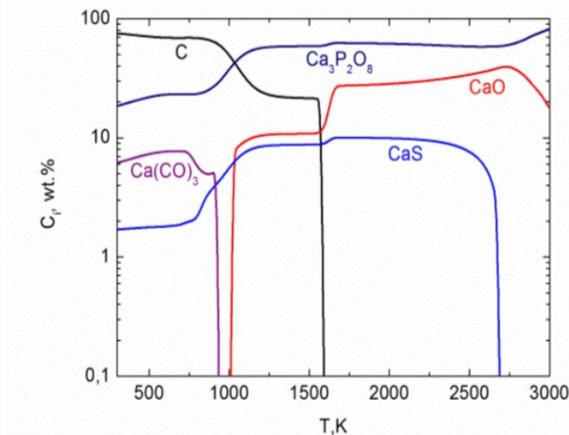
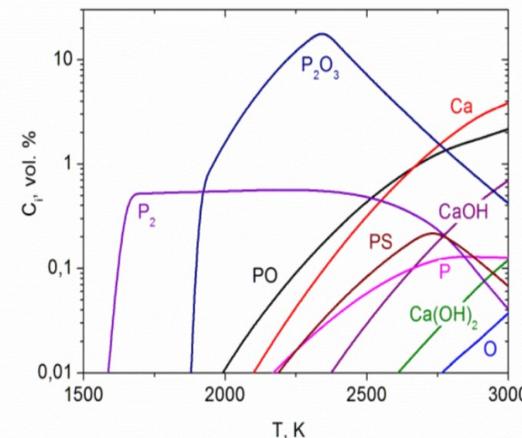
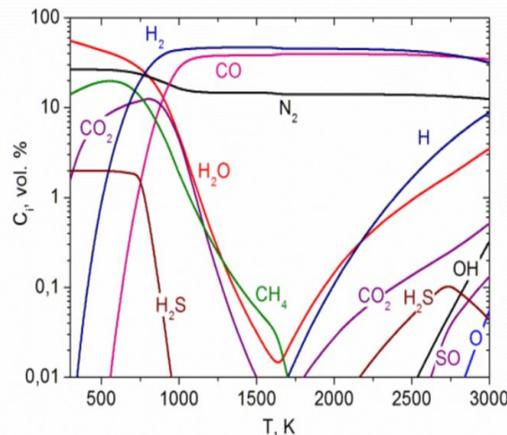
Espèces carbonées solides : TERRA thermodynamic code

300-3000K, 0.1MPa, cas 1 (dry 10kgBMW+5kg air) ou cas 2 (wet 10kgBMW+1kg air + 0.5 steam)

Cas 1



Cas 2



Observation:

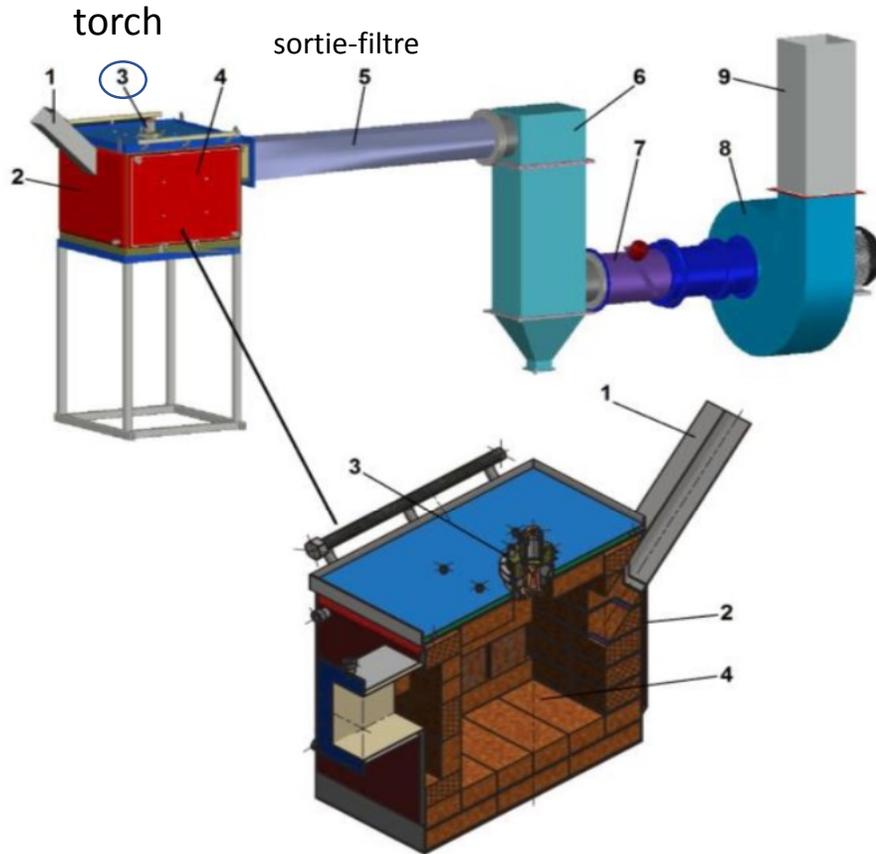
- des espèces formées
- espèces carbonées
- espèces condensées

Détermination des températures limites des phases condensées

Plasma treatment of biomedical waste

A. Ustimenko

Dispositif expérimental pour la gazéification



DC plasma torch – 35-70kW
 Air, 3.6kg/h (max 30kg/h)
 Dimension 0.33m x 0.22m x 0.22m
 Epaisseur (réfractaire) : 0.04m
 Volume = 0.016m³
 Mass process BMW : 5.4-10.8kg/h
 3.5-4.6 kWh/kg

Table 2. Comparison of modelling and experimental results on BT plasma processing.

Method	CO, vol. %	H ₂ , vol. %	N ₂ , vol. %	S, vol. %	Ca, wt. %	P, wt. %	O, wt. %	X _C , %	Q _{SP} , kWh/kg
Experiment	63.4	6.2	29.6	0.15	54.6	12.9	32	79.3	4.0
Calculation (variant 1)	28.7	24.7	40.4	0.2	40.9	18.7	40.4	100	1.7

Conclusion : synthèse max < 1600K, permet de dimensionner l'installation.

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*Papers on
nanopowders / nanoparticles
fabrication*

To simulate turbulent thermal plasma flows for nanopowder fabrication

M. Shigeta

* Review : Shigeta & Murphy : JPhysD 2011

3 catégories : processus de vaporisation, processus de refroidissement, processus de croissance

Challenges : transport properties, plasma flow dynamics inside a torch (heat source important), plasmas flows outside (nanopowders)

Processus de croissance par nucléation, condensation, et coagulation, transport par convection, diffusion et thermophoresis dans/autour du plasma, compliqué : transfert de masse de la microseconde à la milliseconde.

Historique 1990-2018 sur la modélisation de l'écoulement/turbulence en sortie de la torche, 1D, 2D, 3D : 27 ans pour simuler le phénomène (difficile à simuler car 300K-12000K, large banque de propriétés de transport, large variation de la densité (x45), mach number de 0.003 à 0.046, fluide incompressible avec variation de la densité compliqué à simuler.

Patankar est la solution pour la modélisation mais faible précision mais stable

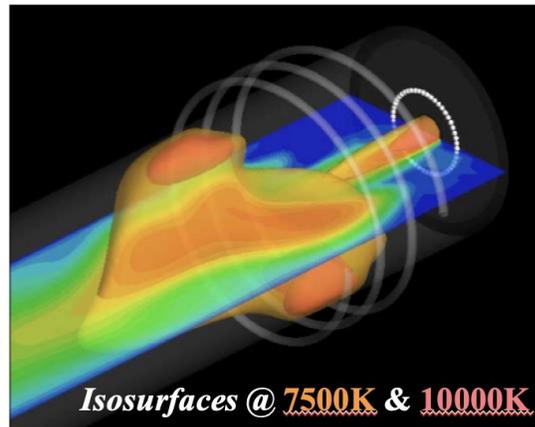
Solutions :

- 1/ faible précision avec très fin maillage et beaucoup de GPs, CVs (impossible en pratique, temps calcul très long)
- 2/ Haute précision mais maillage (more coarse), discrétisation et efforts mathématiques nécessaires (1st order Upwind, 2nd order Central, Hybrid upwind K-K*)
- EDDIES : tourbillons

Plasma flow **dynamics** inside a torch [Key: Interaction with EM field]

Example

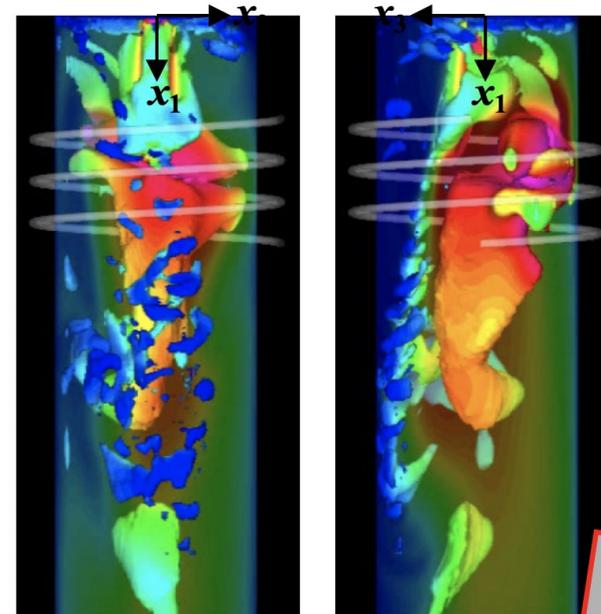
Inside an **RF plasma torch** with jet assisted



1000 Temperature (K) 12000

M. Shigeta:

- Plasma Sources Sci. Tech. (2012)
- J. Phys. D: Appl. Phys. (2013)



Eddies by Q-criterion

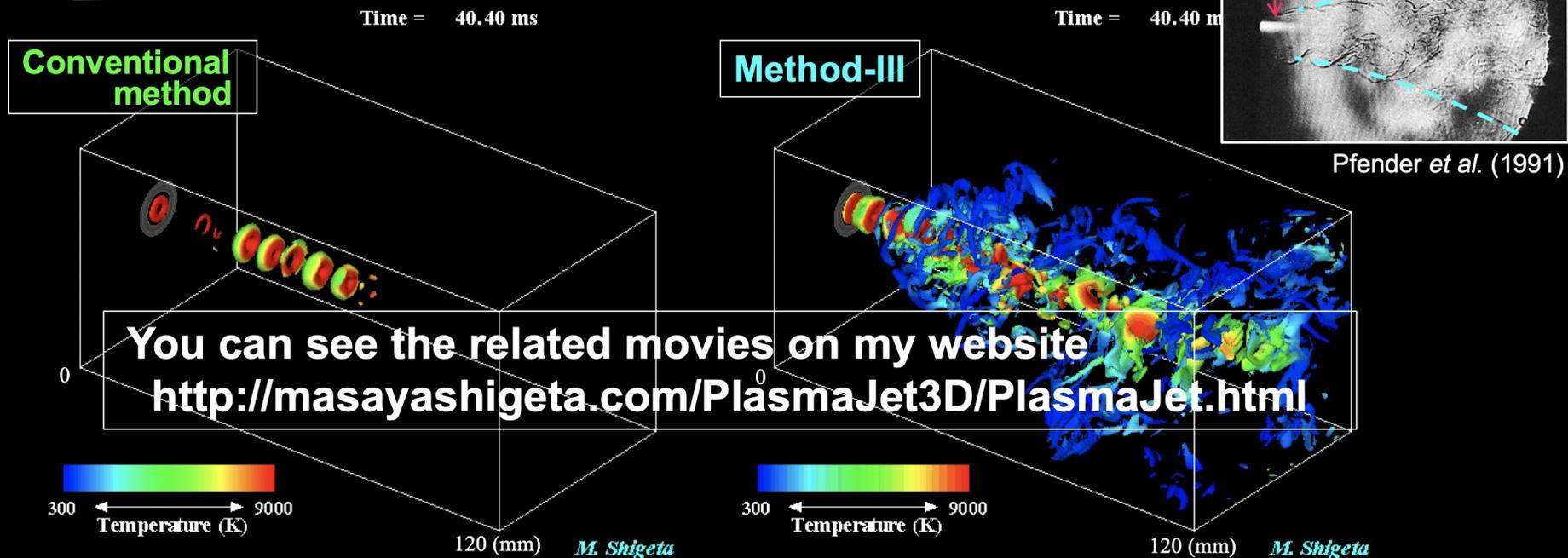
Standing on
the shoulders
of giants!!

M.I. Boulos, P. Proulx (U. Sherbrooke, Canada), J. Mostaghimi (U. Tronto, Canada),
S.L. Girshick (U. Minnesota, USA), T. Yoshida (U. Tokyo, Japan), T. Watanabe (Kyushu U., Japan),
V. Colombo, E. Ghedini (U. Bologna, Italy), Y. Tanaka (Kanazawa U., Japan) ... and more

To simulate turbulent thermal plasma flows for nanopowder fabrication

M. Shigeta

Dynamics of Eddies (Isosurface of $Q = 0.25 (-)$)



Method-III simulates multi-scale eddies of turbulence.

High temp. = Large eddies
Low temp. = Small eddies

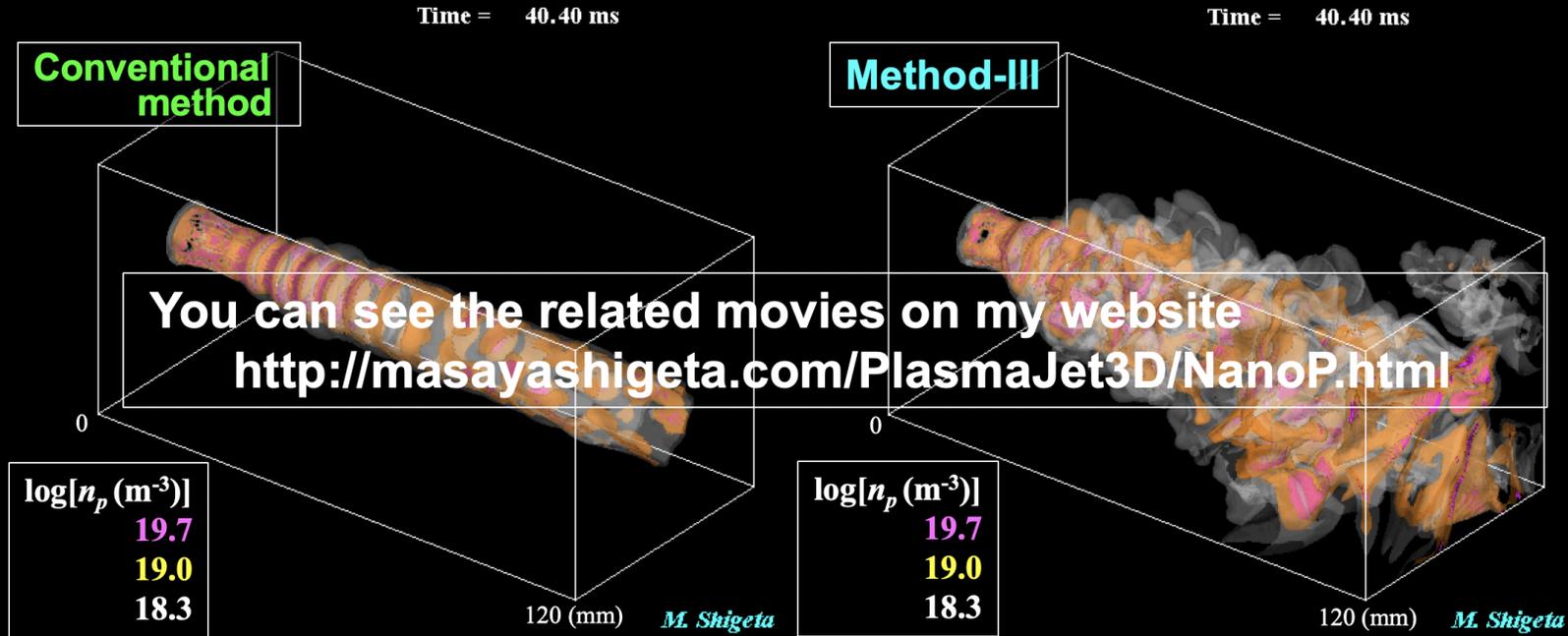
matches up with Kolmogorov theory.

Shigeta: *J. Flow Control, Measurement & Visualization* 6 (2018) 107.
(OPEN ACCESS)

To simulate turbulent thermal plasma flows for nanopowder fabrication

M. Shigeta

Distribution of Nanopowder



Method-III predicts wider distribution of **nanopowder**
because of **turbulent transport** .

Shigeta: *J. Flow Control, Measurement & Visualization* 6 (2018) 107.
(OPEN ACCESS)

To simulate turbulent thermal plasma flows for nanopowder fabrication

M. Shigeta

Modélisation Nanopoudres Si par plasma Argon

- Convection (Hybrid upwind K-K*) + Transient (3rd order Adams Bashforth-Moulton)
- Termes de diffusion et source (2nd order Central)
- Laminar et turbulent states dans le même run
- Modèle k-eps pas applicable, LES (Large Eddy Simulation) OUI

Résultats

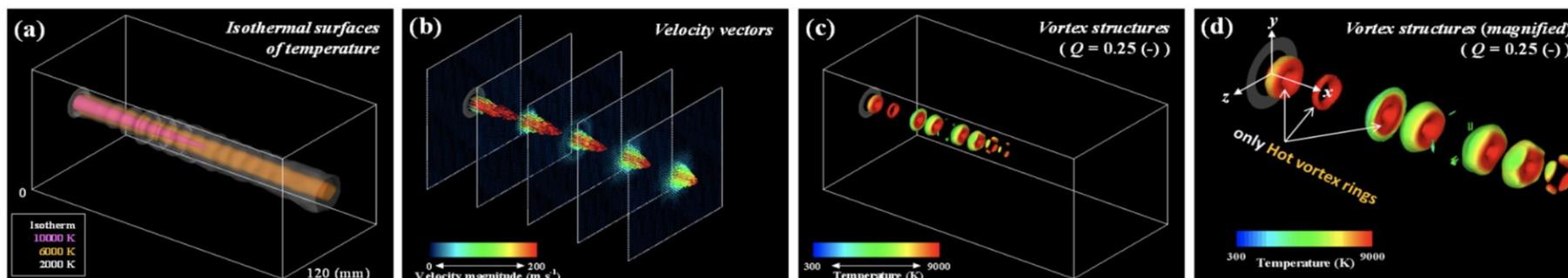


Fig. 2. Instantaneous thermal flow fields in and around a thermal plasma jet obtained by the conventional method.

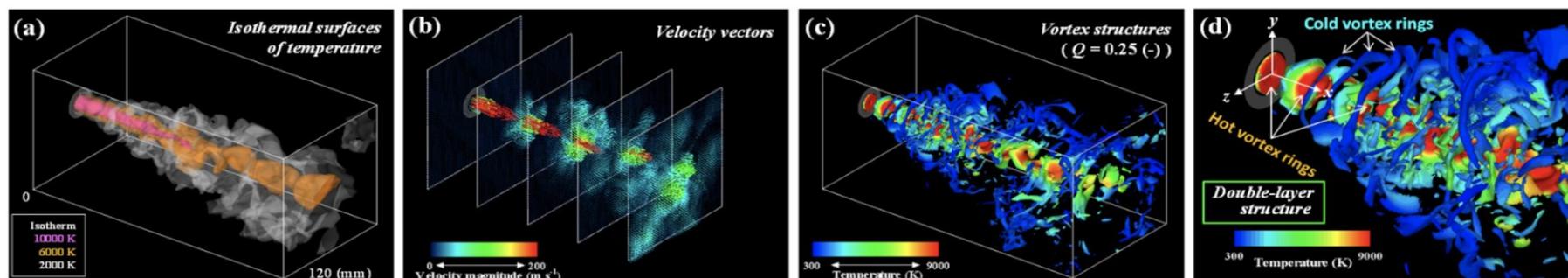


Fig. 3. Instantaneous thermal flow fields in and around a thermal plasma jet obtained by the advanced method.

To simulate turbulent thermal plasma flows for nanopowder fabrication

M. Shigeta

Modélisation de la croissance des nanopoudres

Moment model : nucléation+condensation+coagulation (Nemshinsky+Shigeta WWW)

Method III prédit bien la distribution des poudres à cause du transport sous effet de la turbulence

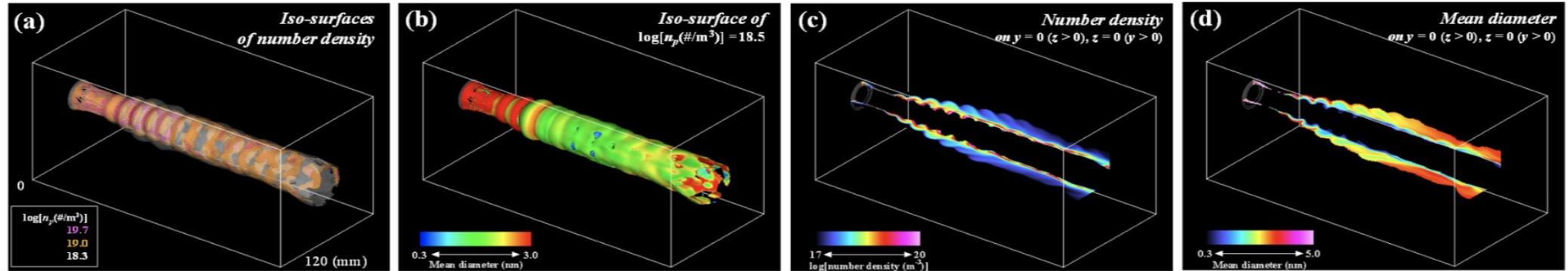


Fig. 4. Instantaneous distributions of nanopowder obtained by the conventional method.

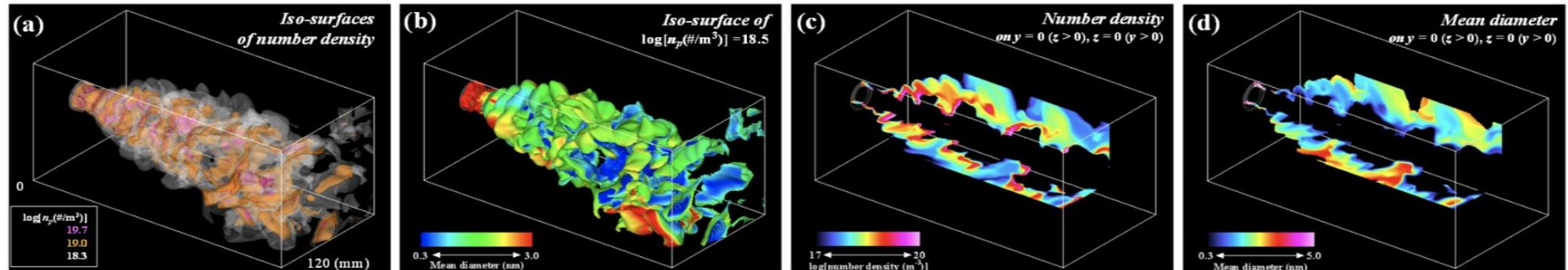


Fig. 5. Instantaneous distributions of nanopowder obtained by the advanced method.

*Design-oriented modelling for the synthesis of Cu nanoparticles by a RF thermal plasma :
impact of quenching solutions, radiative losses and thermophoresis*

V. Colombo

But : Développer des modèles axés sur le design pour réduire les essais couteux et souvent en échec
Avec prise en compte des effets/pertes du rayonnement + thermophoresis sur la synthèse de nanoCu + différence entre les modes active-passive quenching

Active quenching :

Passive quenching :

Papiers: PCPP 2017 (modelling solution quenching) + J.Phys.D.App.Phys 50 2017 (modelling thermophoresis + radiation losses) + PSST 22 2013 (modelling evaporation RF torch) + PSST 21 2012 (modelling nucleation and growth)

H2020 : TRL 6-7, « INSPIRED » pour impression électronique

- Utilisation du quenching gas pour « figer » la croissance des NPs Cu
- Produire 20kg/j avec une taille d'environ 60-70nm

Modèles :

TEKNA PL-50 plasmas torch

Equations fluides + MHD + Méthode des moments pour la synthèse des particules

Etude de Evaporation efficiency

Etude de production efficiency

Etude du Yield

Evaporation Efficiency	=	$\frac{\text{Evaporation rate inside the chamber}}{\text{Precursor feed rate}}$
Production Efficiency	=	$\frac{\text{Vapour to nanoparticle conversion rate}}{\text{Precursor feed rate}}$
YIELD	=	$\frac{\text{Nanoparticle rate to collection chamber}}{\text{Precursor feed rate}}$

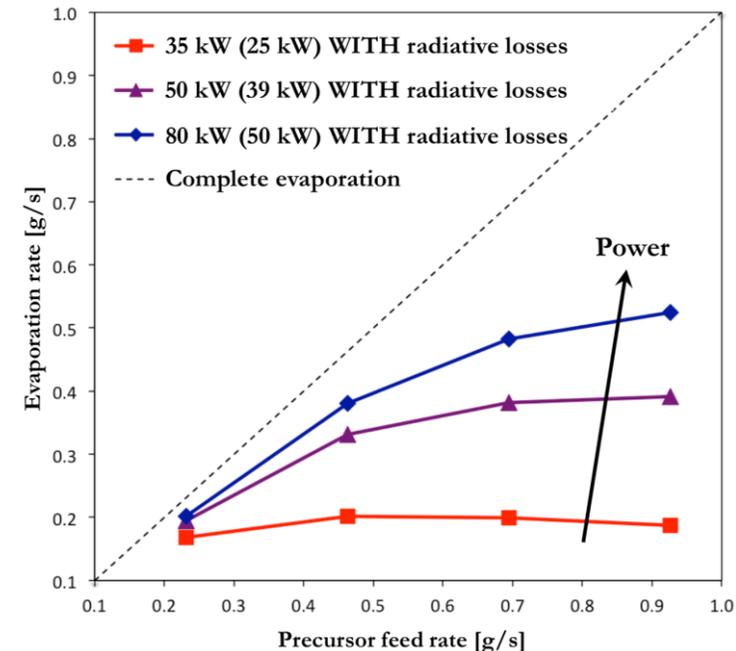
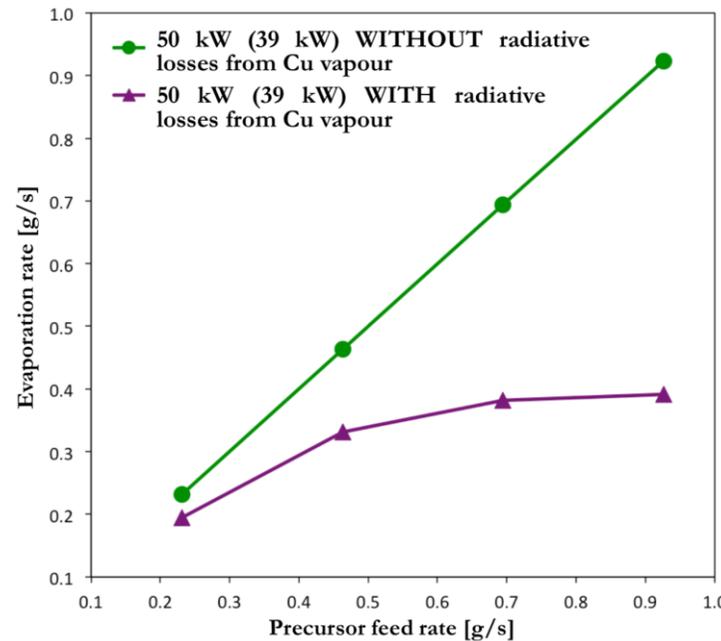
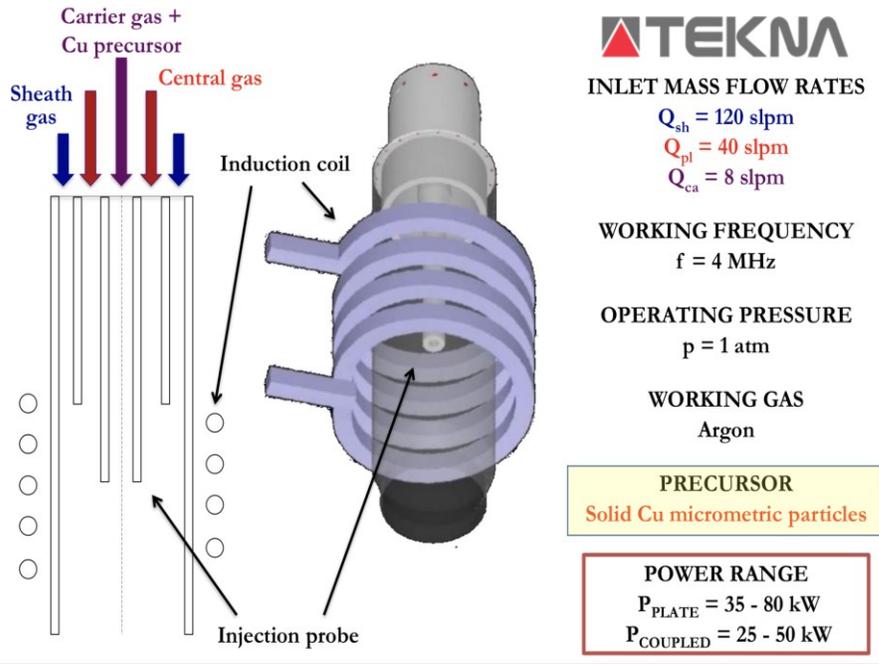
*Design-oriented modelling for the synthesis of Cu nanoparticles by a RF thermal plasma :
impact of quenching solutions, radiative losses and thermophoresis*

V. Colombo

Effet des pertes radiatives (vapeurs de Cu)

Fort refroidissement du au présence de vapeurs de cuivre
Evaporation plus élevée sans prise en compte des pertes radiatives
L'augmentation de la puissance a un faible impact sur l'évaporation

TEKNA PL-50 PLASMA TORCH



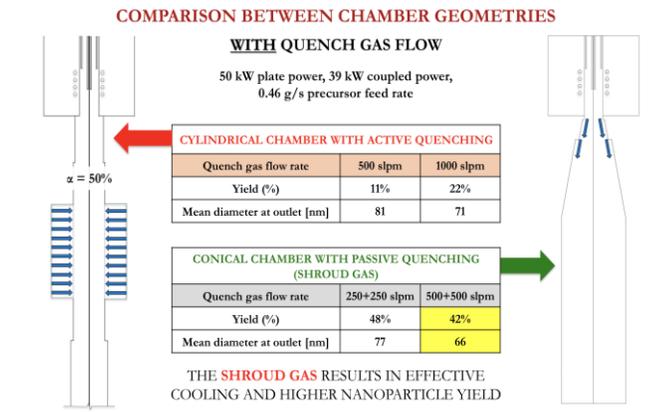
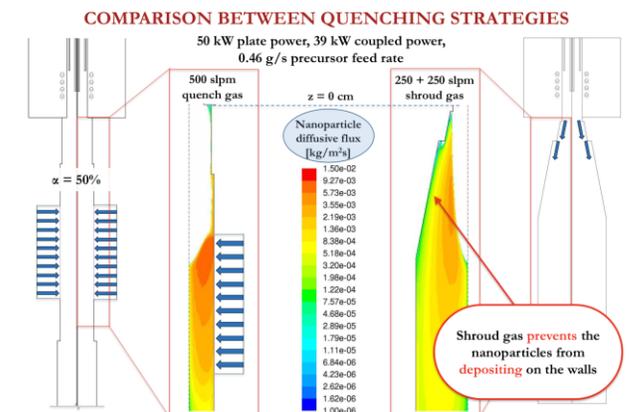
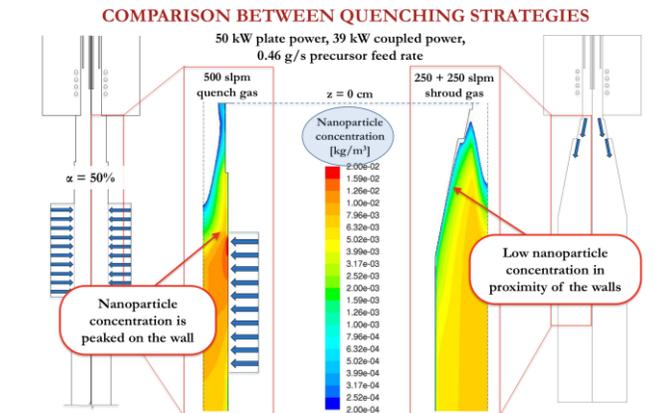
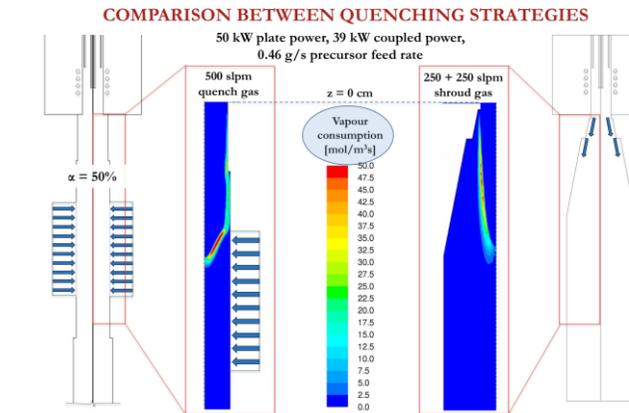
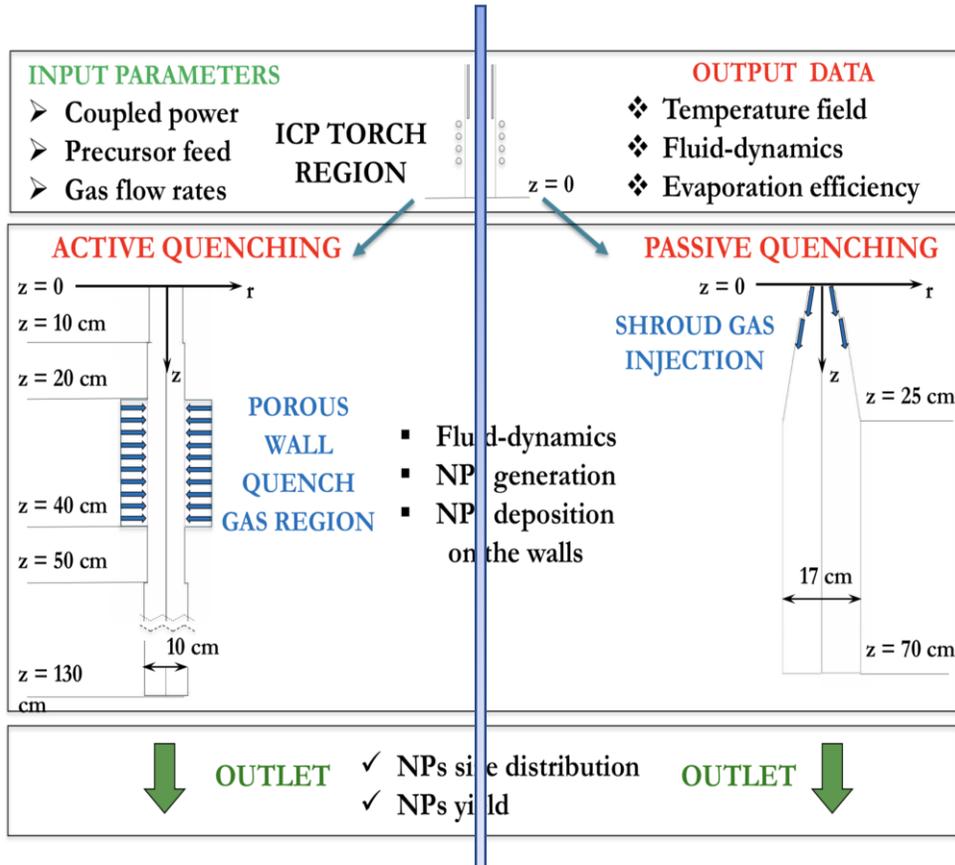
Design-oriented modelling for the synthesis of Cu nanoparticles by a RF thermal plasma : impact of quenching solutions, radiative losses and thermophoresis

V. Colombo

Effet des solutions quenching (passive/active)

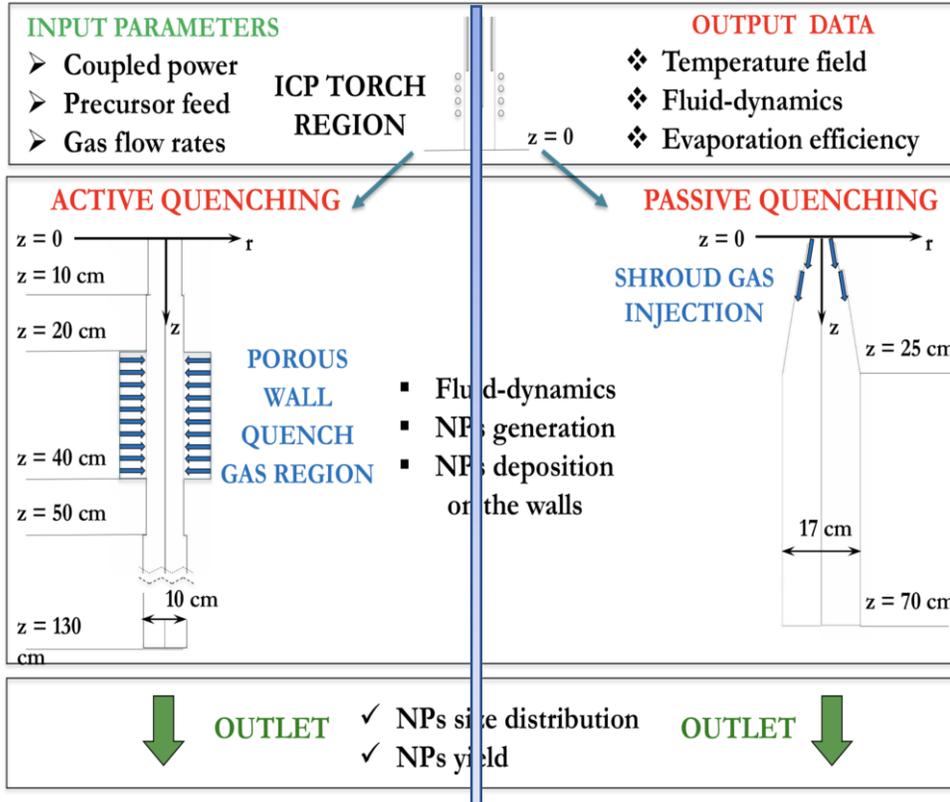
Avec active : %nano sur les bords

Avec passive : meilleur taux, %nano faible sur les bords + plus débit augmente, formation de vortex qui diminuent le taux de production



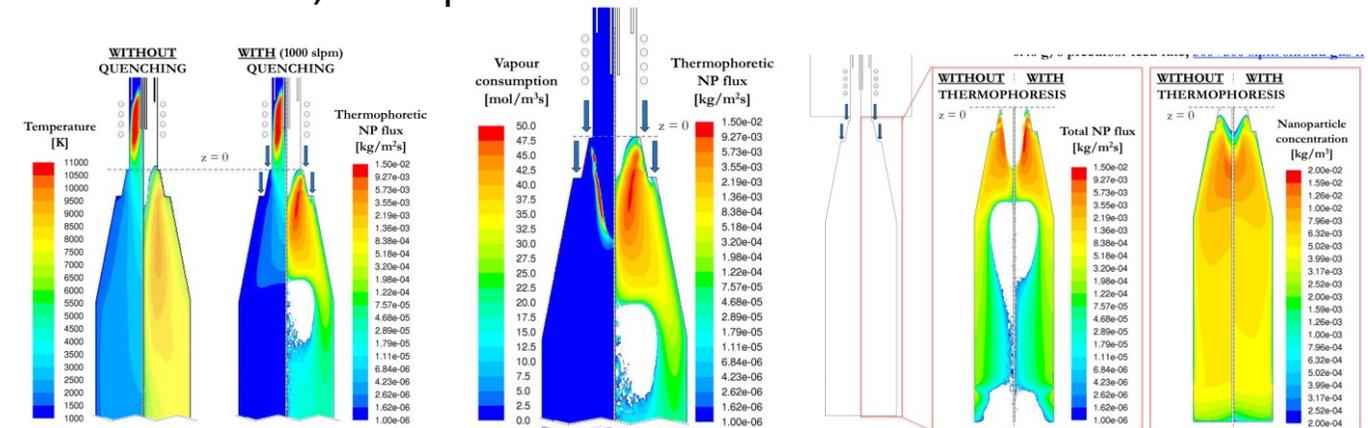
Design-oriented modelling for the synthesis of Cu nanoparticles by a RF thermal plasma : impact of quenching solutions, radiative losses and thermophoresis

V. Colombo



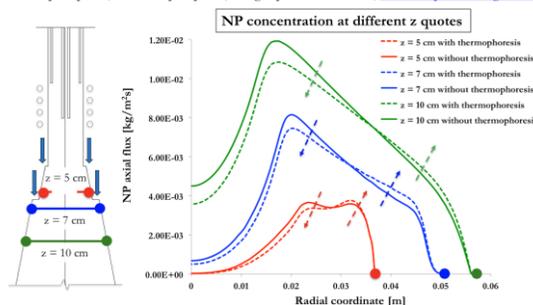
Effet de la thermophorese

Quenching induit de fort gradients de temperature (sortie de torche)
Flux thermophorese plus intense (at the top of the chamber)
Légère réduction du taux, dépôt plus important sur les bords, plus faible sur l'axe, taille plus petite



IMPACT OF THERMOPHORESIS ON PARTICLE SIZE DISTRIBUTION

50 kW plate power, 39 kW coupled power, 0.46 g/s precursor feed rate, 500+500 slpm shroud gas flow

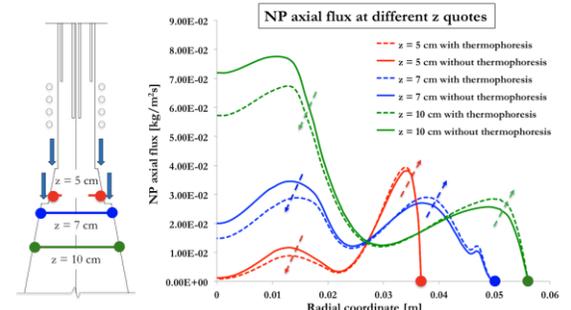


THERMOPHORESIS ALWAYS RESULTS IN A LOWER PARTICLE DIAMETER

Chamber and quenching strategy	Quench	Thermophoresis	Yield (%)	d_p at outlet [nm]
CYLINDRICAL WITH ACTIVE QUENCHING	No	No	11%	116
		Yes	7%	106
	1000 slpm	No	22%	71
		Yes	17%	65
CONICAL WITH PASSIVE QUENCHING	No	No	16%	93
		Yes	10%	81
	1000 slpm	No	42%	66
		Yes	38%	64

IMPACT OF THERMOPHORESIS ON PARTICLE SIZE DISTRIBUTION

50 kW plate power, 39 kW coupled power, 0.46 g/s precursor feed rate, 500+500 slpm shroud gas flow



Effect of alternating gas injection on temperature fields in reaction chamber using inductively coupled thermal plasma for nanoparticle synthesis

Y. Tanaka

The work done

Further control of ICTP-NP synthesis

-New ideas: To be presented in Poster P3-77

(1) To adopt **tandem-modulated ICTP**
→ Stable operation & more evaporation of feedstock

(2) To adopt **alternating (intermittent) quenching gas (QG) injection**

-Expected effect of alternating QG

1. Deeper penetration of QG
2. More cooling effect for vapor

Effective synthesis of nanoparticles

The present work

1. Numerical approach
→ 3D numerical thermo-fluid simulation on temperature distribution in the reaction chamber with
(1) No QG, (2) continuous QG and (3) alternating QG injection.
2. Experimental approach
→ Fe³⁺-doped TiO₂ nanoparticle synthesis using Ar-O₂ ICTP with
(1) No QG, (2) continuous QG and (3) alternating QG injection

Effect of alternating QG injection was studied on nanoparticle synthesis

Background Metal nanoparticles market: JPY 380 billion@2020

Nanoparticles(NPs): defined as ultrafine particles with $d < 100$ nm

→ Anticipated for use as promising elements in the next generation electronics, medicals, energy & environmental fields

A mass production method for industrial applications is strongly desired.

PMITP +TCFF method: Our original & unique method

-PMITP: Pulse-Modulated Induction Thermal Plasmas
→ The coil current is modulated to change T & u fields in thermal plasmas.

-TCFF: Time-Controlled Feeding of Feedstock
→ Feedstock is supplied intermittently and synchronously with coil current modulation.

#Advantage: High efficient evaporation of feedstock during on-time + High efficient nucleation of evaporated materials during off-time

→ High production rates of nanoparticle synthesis in the actual experiments:
e.g.: 500-800 g/h@20 kW for Al³⁺-doped TiO₂ NPs, Fe³⁺-doped TiO₂ NPs
300 g/h@20 kW for Si NPs, 1.0 g/h@20 kW for Si nanowires

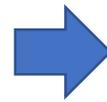
The PMITP+TCFF method is found to be one unique and promising method for synthesizing nanomaterials with high production rates

→ Development of further controlled *Modulated Induction Thermal Plasma System.*

Objectif : synthèse de nanoparticules

- Utiliser PMITP + TCFF method
- Adopter « alternating quenching gas injection AQGI »

Voir l'effet AQGI sur synthèse nano.



Modèle 3D pour obtenir T(r) dans réacteur

- (1) No quenching gas,
- (2) continuous QG
- (3) alternating QG injection
- (4) ICTP torch, COMSOL 5.3

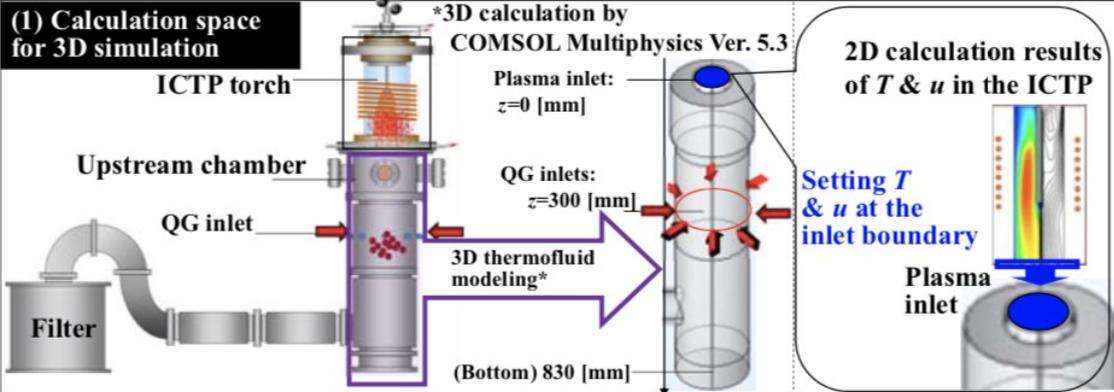
Etudes expérimentales

- (1)+(2)+(3)

Effect of alternating gas injection on temperature fields in reaction chamber using inductively coupled thermal plasma for nanoparticle synthesis

Y. Tanaka

Calc. space & procedure for 3D thermofluid simulation



- (2) Calculation procedure of 3D thermofluid modeling**
- 1) 3D calculation space was defined for the chamber downstream of the ICTP torch.
 - 2) For the thermal plasma flow at plasma inlet, 2D calculation was made to obtain the temperature and gas flow velocity.
 - 3) These were given as the boundary condition.
 - 4) QG was set to be supplied from 8 ports located at the wall of the chamber.
 - 5) QG flow rate was set to be modulated in case of alternating injection.

(3) Gas flow velocity of alternating QG

-QG was assumed to be supplied with a sinusoidal waveform at a given cycle T_{cyc} with a given time-averaged flow rate:

$$Q_{avg} = \frac{1}{T_{cyc}} \int_0^{T_{cyc}} f_{QG}(t) dt$$

Governing equations & calculation condition

Governing equation	Common condition
-Mass conservation $\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$	-Laminar flow -Gas species: 100%Ar -Wall temp.: 300 K -Time-averaged QG flow rate: 50 L/min -QG gas temp.: 300 K
-Navier Stokes equation $\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla \mathbf{u}) = \nabla \cdot [-p\mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}]$	
-Energy transport equation $\rho c_p \frac{\partial T}{\partial t} + \rho c_p \mathbf{u} \cdot \nabla T = \nabla \cdot (\kappa \nabla T) - p \nabla \cdot \mathbf{u} + Q_{vd}$	-Equation of state: $p = \rho R(T)T$

ICTP condition

- Mod. of power: **Non-mod.**
- Input power: 20 kW
- Pressure: 300 torr
- Sheath gas: 90 L/min Ar gas
- Feedstock: Not supplied

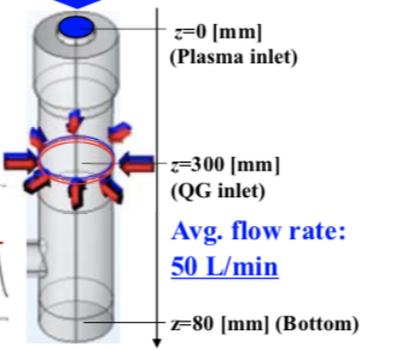
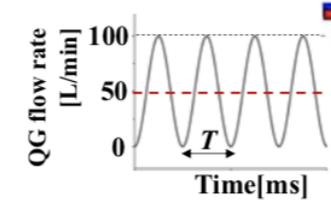
The T & u calculated in advance by 2D simulation of ICTP were used for boundary condition at the plasma inlet.

Conditions for comparison

	Modulation of QG	Cycle-time T
Condition-1	Continuous	—
Condition-2	Alternating	30 ms
Condition-3	Alternating	100 ms

Modulation of QG

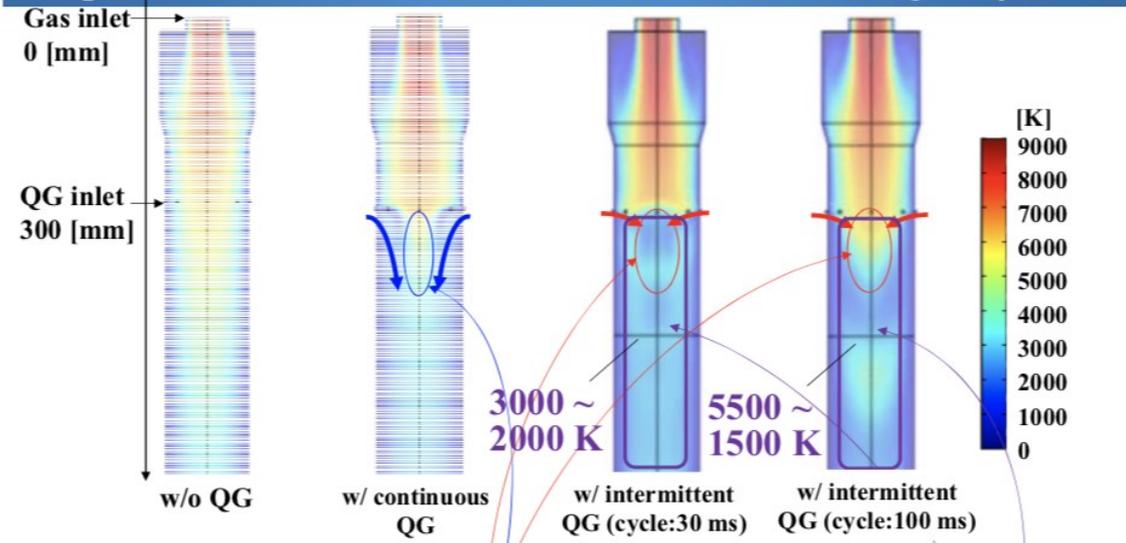
-QG was set to change as sinusoidal waveform with an avg. rate of 50 L/min & a maximum peak rate of 100 L/min.



Effect of alternating gas injection on temperature profiles in reaction chamber using inductively coupled thermal plasma for nanoparticle synthesis

Y. Tanaka

Temperature distribution in the chamber w/o or w/ QG gas injection

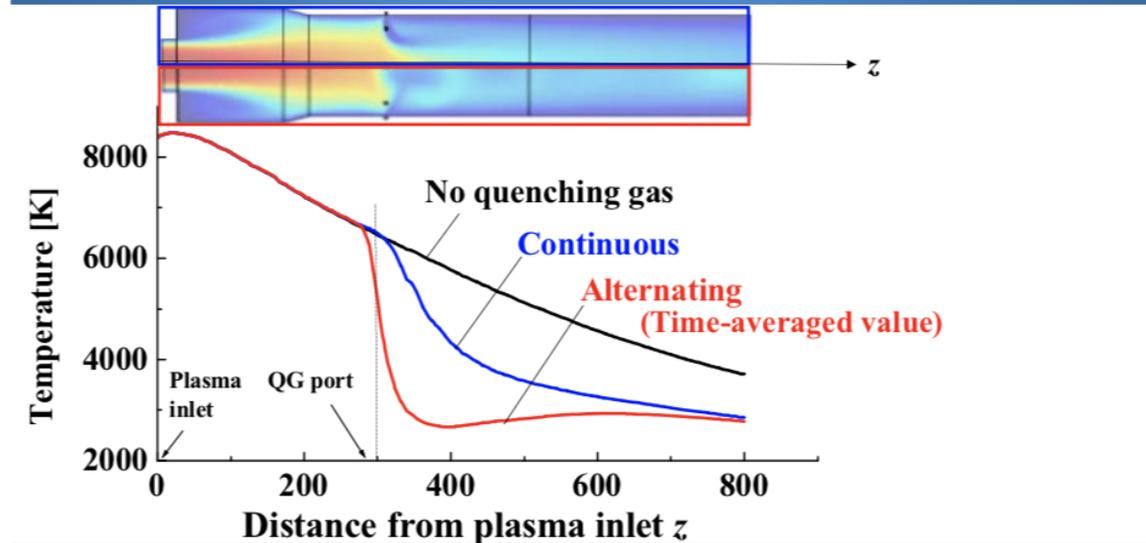


Results for different QG conditions

- Continuous inject. → QG hardly reaches to the axis → Axis T is weakly decreased.
- Alternating inject. → QG is transported more deeply → T effectively decreases.
- (Cycle:30 ms) Alternating QG offers relatively uniform T distribution.
- (Cycle:100 ms) Alternating QG produces periodical T distribution.

→Next, axial temperature distribution.

Axial temperature distributions in the chamber at three QG injections



Results for different QG conditions

- Alternating QG injection results in the lower time-averaged temperature and minimum temperature than continuous QG injection.
- ←Deep penetration of alternating QG injection.

Next, we conducted experiments for nanoparticle synthesis using this intermittent alternating quenching gas injection technique.

→Results indicated that alternating QG can penetrate the ICTP, resulting in effective cooling of the thermal plasma in the chamber.

Effect of alternating gas injection on temperature profiles in reaction chamber using inductively coupled thermal plasma for nanoparticle synthesis

Y. Tanaka

Etude expérimentale

Synthèse nanoparticules (Fe^{3+} dopées TiO_2)

Ar- O_2 torch

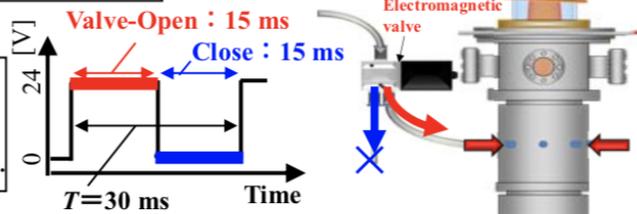
Experimental condition for Fe^{3+} -doped TiO_2 nanoparticle synthesis using continuous or intermittent (alternating) QG injection

Common condition		Condition for comparison	
Thermal plasma condition		QG	Cycle: T
-Input power (Non-mod.)	20 kW	Cond.-No	No-injection
-Pressure	300 torr	Cond.-Cnt	Continuous
-Sheath gas flow	Ar: 90 L/min + O_2 : 10 L/min	Cond.-Int	Intermittent
			30 ms

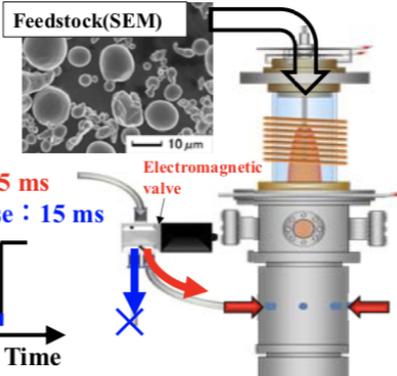
Feedstock	
-Species	5wt% Fe +95wt% Ti
-Feeding rate	~3.0 g/min
-Feeding method	Continuous
Quenching Gas (QG)	
-Species	100%Ar
-Time-averaged flow rate	50 L/min
-Position of QG supply	Port: B

QG supply method

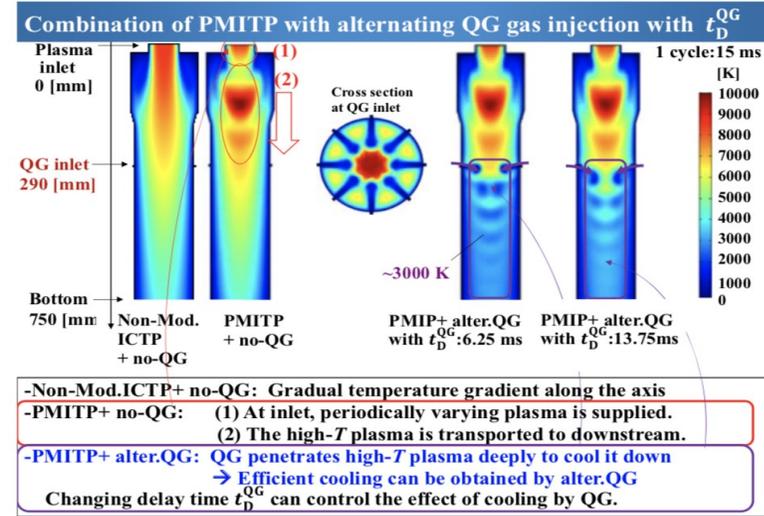
-QG was controlled to be supplied at 100 L/min during valve-open, otherwise it was not supplied.



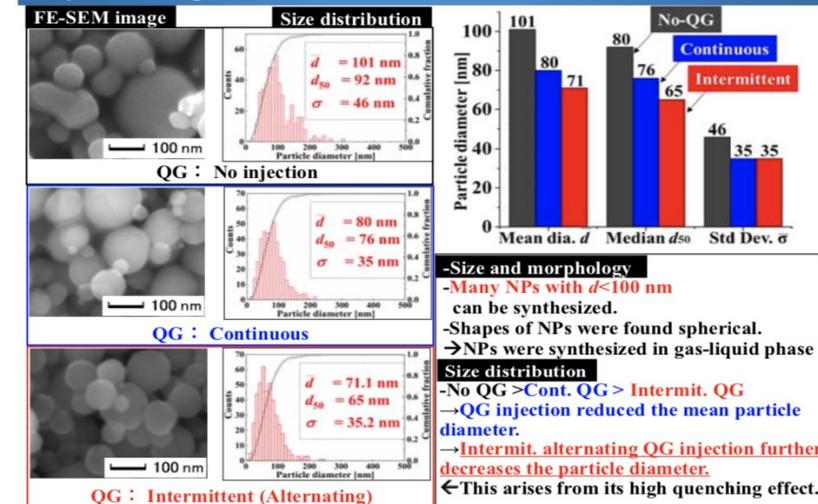
Aim
Intermittent supply of Ar QG reaches to the axis.
→ Effective cooling of vapor → NPs



alternating QG provides smaller nanoparticles.
This is due to its high cooling effect on thermal plasma and vapor of feedstock, avoiding particle growth in the chamber.



FE-SEM images and particle size distribution of synthesized particles -Influence of continuous or intermittent QG-



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Papers on Non-equilibrium phenomena

Non equilibrium phenomena in thermal plasmas

J.P. Trelles

Non equilibrium

Microscopique

-> Kinetic non-equilibrium

- Imbalance between particles and fields (T_e, T_h)
- Quasi-neutrality
- With low gradients
- Anode sheath, near sheath
- When molecules exist (synthesis processes, with vapeurs...)
- Mass action law is invalide
- Linear relaxation system
- **Thermodynamic nonequilibrium** (deviation from LTE)
- **Chemical nonequilibrium** (deviation from mass action law)
- **Multi-phase interaction** (plasma-solid interactions, plasma-anode, liquid, vapors)
- **Radiation transport** (if molecules or high θ) -> motivation solar fuel, Solar+electricity+CO2-> fuels, Solar enhanced Microwave plasma (SEMP) : greater solar absorption by plasma, increase conversion and efficiency à la Patm

Thermal Nonequilibrium

- Condition for $T_e \neq T_h$: $\frac{T_e - T_h}{T_e} = \frac{\pi m_e}{24 m_e} \frac{(e E \lambda_{De})^2}{k_B T_e} \sim \left(\frac{E}{p}\right)^2$ (from: $\dot{Q}_{th} = \dot{Q}_j$)
- ... yet often $T_e/T_h \gg 1$ even though $E/p \ll 1$
- More general, transport-based condition: $\tau_{equil} > \tau_{transport}$
- $\frac{\rho h_h}{Q_{ch}} > \frac{\rho h_h}{Q_j} \frac{l}{\rho u} \frac{\rho h_e l^2}{\kappa_e T_e}$

Chemical Nonequilibrium

- Chemical composition deviates from mass-action law
- Condition: $\tau_{equil} > \tau_{transport}$ (e.g. large velocities, large species/pressure/temperature gradients)
- $\frac{\rho_s}{\rho} > \frac{l}{\rho u} \frac{\rho l}{J_s}$

Plasma – Solid Material Interaction

- Essential in plasma sources & processes: heat transfer to workpiece, cooling load, process contamination, electrode erosion ...
- Plasma spray torch: Plasma temperature (300-28000 K), Electrode temperature (1000-3800 K)
- Arc welding: temperature (K) and mass fraction iron (-)
- Microplasma: cathode (1500 K), 313 m/s, 5% mol, 59 cm/s, steel, 7 cm/s, melt (2500 K)

Alters balances: species/energy transport, electrical characteristics (sheaths) -> significant kinetic nonequilibrium

Plasma – Radiation Interaction

- Motivation: solar fuels
- Greater efficiency + resiliency -> viability
- Solar + electricity + CO2 -> chemicals (e.g. fuels)
- Solar-Enhanced Microwave Plasma (SEMP): parabolic concentrator, solar power, electric power (microwave), input gas, waveguide, processed gas, radiation influx, solar simulator

Non equilibrium phenomena in thermal plasmas

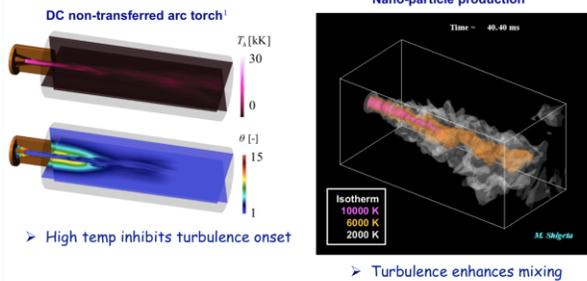
J.P. Trelles

Non equilibrium

Macroscopique
-> Dissipative non-equilibrium

Turbulence

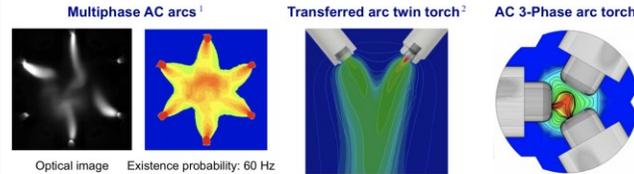
- **The ultimate computational challenge:** largest range of scales
- **Relevance:** high-throughput applications (flow rates, dimensions)
- **Highly-effective energy dissipation**



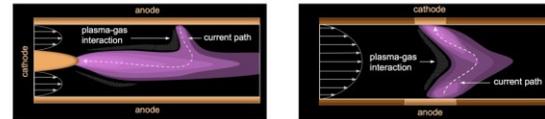
¹ S. M. Modir Khazemi, J. P. Trelles, Journal of Thermal Spray Technology (2018), 27(8), 1447-1464; ² M. Shigeta, Journal of Flow Control, Measurement & Visualization, 2018, 6, 107-123

Plasma – Gas Interaction

- **At the core of applications:** effective processing of feedstocks (gas/liquids/solids)

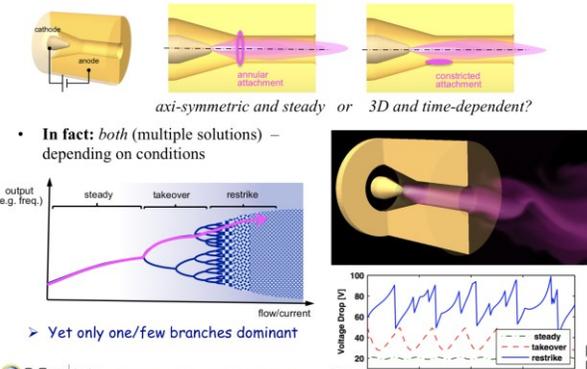


- **Fundamental:** parallel-flow and cross-flow



Parallel-flow Plasma – Gas Interaction: Arc Torch

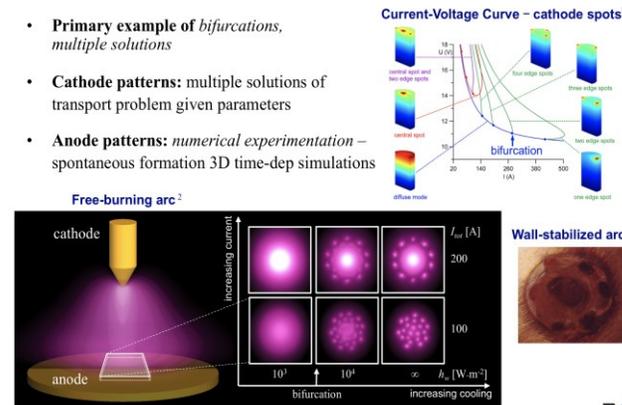
- **Axi-symmetric domain + constant operating conditions:** solutions ...



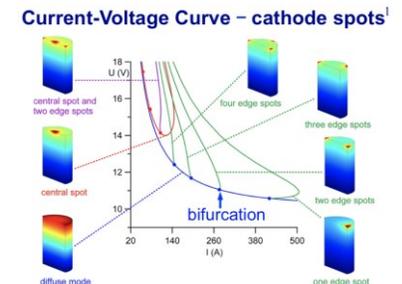
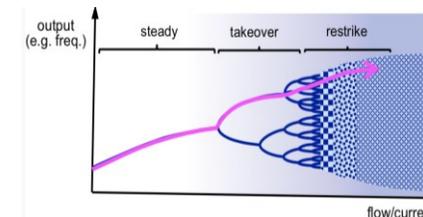
¹ Trelles J.P. 2013 J. Phys. D: Appl. Phys. 46(25) 255201

Pattern Formation

- **Primary example of bifurcations,** multiple solutions
- **Cathode patterns:** multiple solutions of transport problem given parameters
- **Anode patterns:** numerical experimentation – spontaneous formation 3D time-dep simulations



- Instability due to external forces(mass flow, heat flux, voltage)
- High variations, deviations
- Anode attachment, liquid-cooled metal anode, multiple anode attachment configurations
- Non linear system
- Multiple solutions, bifurcation when $P=P_{critic}$ (dissipative equilibrium if $P<P_{crit}$, non equilibrium if $P>P_{crit}$), ultim=chaos and turbulence
- θ increase, nbre solutions increases
- **Flow stability** (plasma-gas flow interaction, fluid dynamic, thermal, electromagnetic)
- **Pattern formation** (erosion of electrodes cathode-anode)
- **Turbulence**
- **Multi-electrodes**



A 3D two-temperature model of loop type of arc inductively coupled thermal plasmas for large-area materials processing

Y. Tanaka

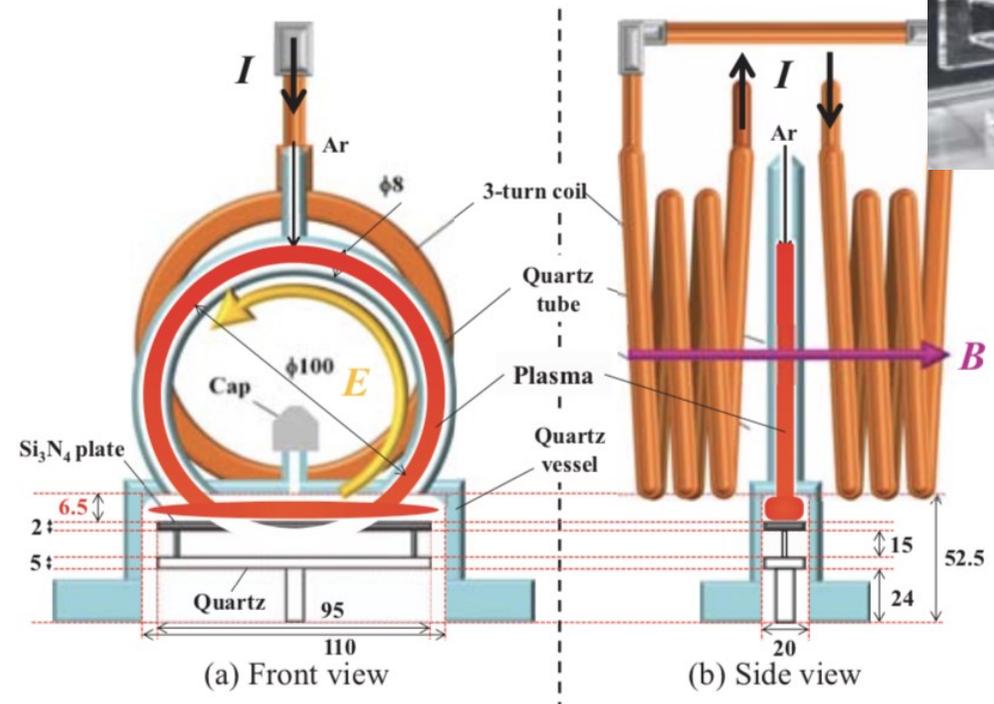
Constats : ICTP est avantageux : haute température du gaz, haute enthalpie, haute densité des radicaux, pas d'érosion
Mais avec ICTP, difficile de contrôler la forte enthalpie (impact Temp sur substrat), et les applications sont limitées
-> développement d'une loop ICTP torch : plus rapide et surface de traitement plus large

Expérience : Linear ICTP torch Ar/O₂ sur substrats Si, SiC (pour semi-conducteurs)
Développement méthode ultra-rapide de la modification de la surface
Taux d'oxydation : 100nm/min (contre 10nm/min habituellement)

Ar/O₂ loop-ICTP, 140A, 2.5kW, 360kHz, 10 torr, Q=0.1L/min
Traitement de surface en 2D

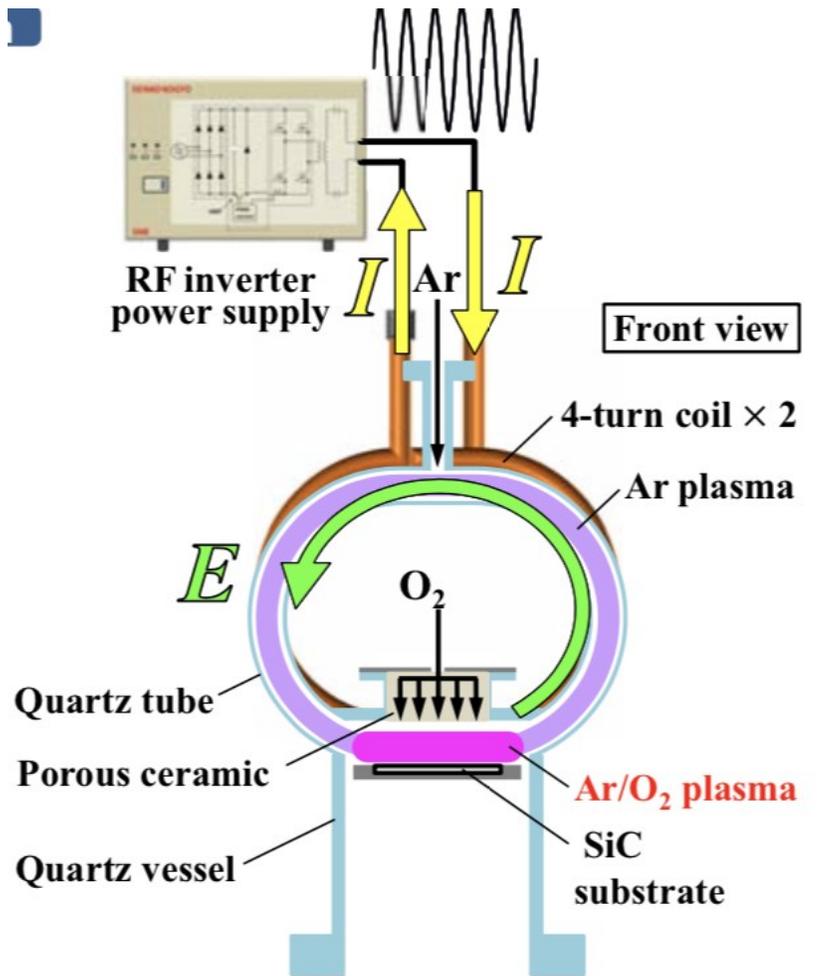
Résultat :

Substrat SiC oxydé uniformément sur 25mm de diamètre en seulement 3min
2D rapid oxidation 4H-SiC substrates à 20nm/min.
Profondeur de l'oxydation : 70mm



A 3D two-temperature model of loop type of arc inductively coupled thermal plasmas for large-area materials processing

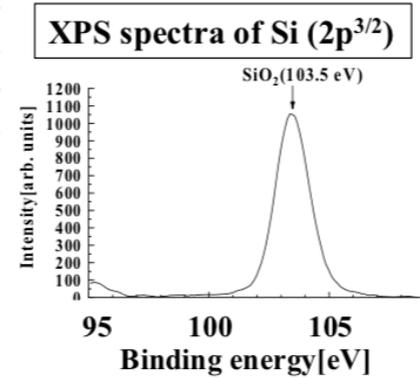
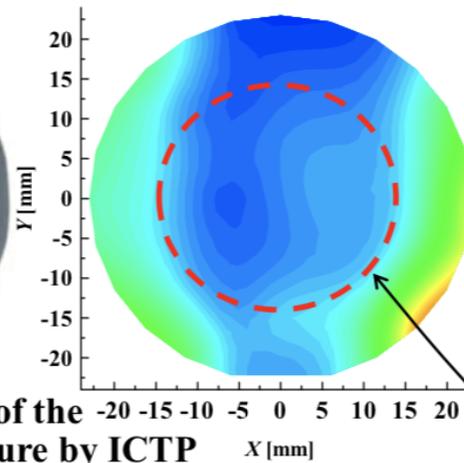
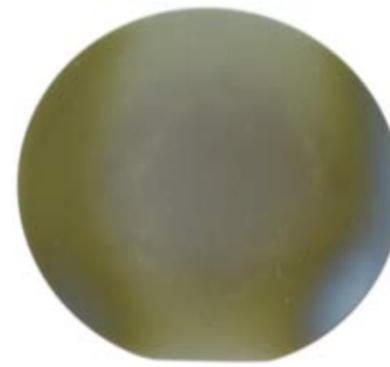
Y. Tanaka



Surface oxidation result for 2-inch 4H-SiC substrate

A photo of a 4H-SiC(0001) substrate after scanning exposure by Ar/O₂ loop-ICTP

2D distribution of oxide layer thickness



Backside temperature of the substrate during exposure by ICTP was **1213 K** at exposure point.

-The SiC substrate surface was oxidized almost uniformly in a region of 25 mm ϕ only by 3 min scanning exposure of Ar/O₂ loop-ICTP.

→ -The resultant oxide layer thickness is about 70 nm in that region.

-Effective oxidation rate was estimated as **20 nm/min**, which is **20 times faster** than those by the conventional thermal oxidation method.

This extremely rapid oxidation rate may be attributed to high-*T*_h & high density atomic oxygen.

A 3D two-temperature model of loop type of arc inductively coupled thermal plasmas for large-area materials processing

Y. Tanaka

Modélisation : COMSOL 5.3, modélisation 3D (1D fluide, 2T température plasma pour transfert le énergie des électrons vers les lourds par collision élastique)

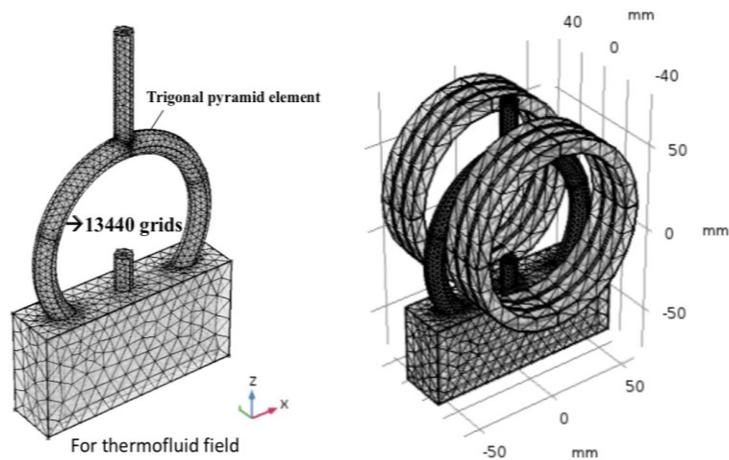
Sphère de calcul de 250mm

Equations classiques + 2 eqns k-eps pour effets turbulence (pour simplifier)

T_e et T_h traitées séparément, équilibre ionisation et excitation

Plasma optiquement mince, $T_{vib}=10000K$, $T_{rot}: 3000K$, 10torr, 140A_{rms}, 360Hz, 2.51kW

Calculation domain, mesh for calculation



-COMSOL Multiphysics ver.5.3 was used for this 3D calculation.

For electromagnetic fields, we took a sphere calculation space with a diameter of 250 mm.

Governing equations for a 1-fluid and 2-temperature plasma

-Mass

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$

-Momentum

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla : \boldsymbol{\tau}$$

-Energy for heavy particles

$$\rho C_p \frac{\partial T_h}{\partial t} + \rho C_p (\mathbf{u} \cdot \nabla T_h) = \nabla \cdot (\kappa_{eff} \nabla T_h) + E_{ch}$$

-Energy for electrons

$$\nabla \cdot (\kappa_e \nabla T_e) = en_e \mu_e \mathbf{E} \cdot \mathbf{E} - E_{ch} - P_{rad}(T_e)$$

-Energy transfer from electrons to heavy particles

$$E_{ch} = \frac{2m_e m_{Ar}}{(m_e + m_{Ar})^2} \frac{3}{2} k(T_e - T_h) n_e (n_{Ar} \pi \bar{\Omega}_{eAr} + n_{Ar+} \pi \bar{\Omega}_{eAr+}) \bar{v}_{eAr}$$

-Saha's equation for ionization

$$\frac{n_e n_{Ar+}}{n_{Ar}} = 2 \left(\frac{2\pi m_e k T_e}{h^2} \right)^{\frac{3}{2}} \frac{Z_{Ar+}(T_e)}{Z_{Ar}(T_e)} \exp\left(-\frac{E_{Ar}}{k T_e}\right)$$

-Vector potential

$$\nabla \times (\nabla \times \mathbf{A}) = \mu_0 (\omega^2 \boldsymbol{\epsilon} - j n_e \mu_e \omega) \mathbf{A}$$

$$\mathbf{B} = \nabla \times \mathbf{A}$$

$$\mathbf{E} = -j \omega \mathbf{A}$$

-To solve electron energy and Saha's equations, general partial differential equation (PDE) solver was used.
 -2 eqns k-ε model was used to consider turbulent effects for simplicity.

cf. Exp. → 2T-state
 $T_{vib} \sim 10000K$,
 $T_{rot} \sim 3000K$ in Ar/N₂ loop-ICTP @10,20 torr, 10 kW

Boundary conditions

3D calculation

Ar
 Quartz: Outer: $T=300K$, Inner: Non-slip
 $u=0$
 $\mathbf{n} \cdot \nabla T_e = 0$

All the quartz wall is water-cooled.

Condition
 -Gas: Ar
 -Gas flow rate: 0.1 L/min
 -Pressure: 10 torr
 -Coil current: 140 Arms
 -Current freq.: 360 kHz
 → 2.51 kW

Substrate holder: Non-slip $u=0$,
 $q = h(T_h - T) - \epsilon_r \sigma_s (T^4 - T_a^4)$

Outlet: free outflow
 $\mathbf{n} \cdot \nabla \phi = 0$

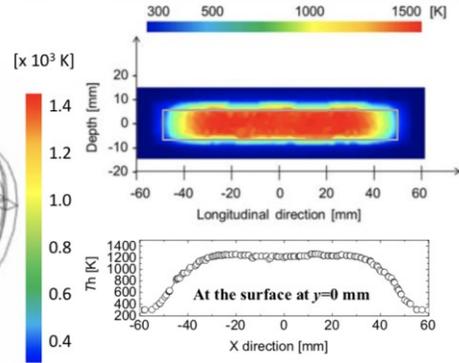
Operated in COMSOL

A 3D two-temperature model of loop type of arc inductively coupled thermal plasmas for large-area materials processing

Y. Tanaka

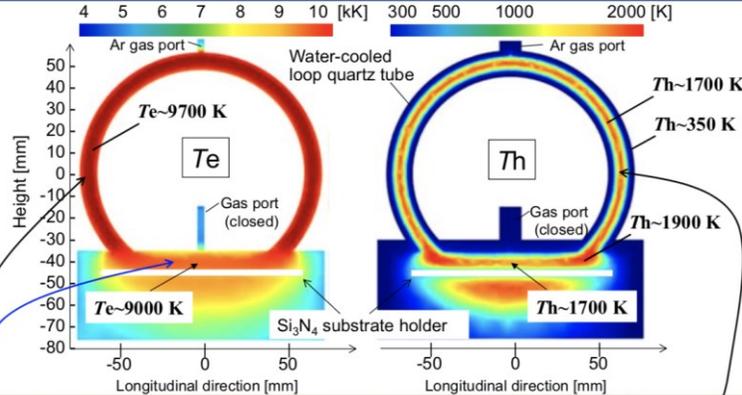
Temperature at surface plane

Surface temperature at $z=-43$ mm



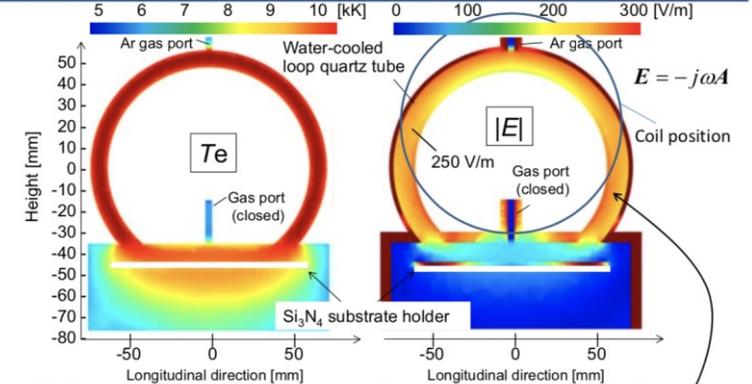
-Surface temperature of the substrate holder is almost uniform at 1350 K from $x=-25$ mm to $x=25$ mm (with a length of 50 mm).
→ Almost uniform exposure of ICTP can be obtained.

Electron and heavy particle temperatures



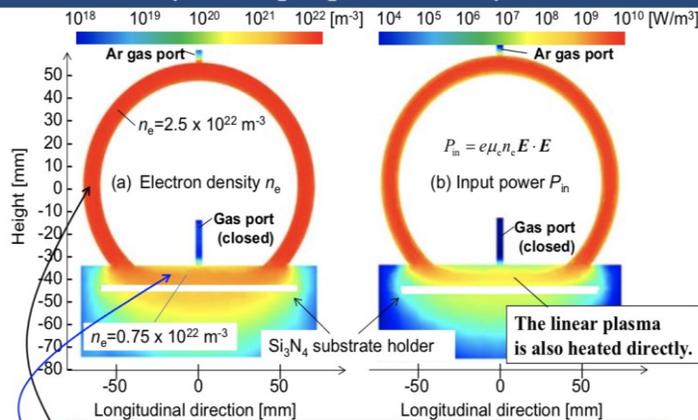
-Electron temperature T_e inside the tube reaches to 9700 K almost uniformly.
-Heavy particle temperature T_h in the tube is around 1700 K on the loop tube core, while $T_h \sim 350$ K near the water-cooled wall. → Two-temperature (2T) state.
-On the substrate holder, there formed a linear plasma lying with $T_e \sim 9000$ K, and $T_h \sim 1700$ K → T_h is almost uniform in this linear plasma.
-At gas outlet from the loop tube, $T_h \sim 1900$ K. ← Stagnation points w/ low conv. loss.

Electron temperature and electric field strength



-Rf electric field strength $|E|$ is high especially in outer shell of the quartz tube.
← The quartz and Si_3N_4 have high relative dielectric constant ($\epsilon_r \sim 3.8-8$).
-In the tube, $|E|$ has a value about 250 V/m almost uniformly.
→ This electric field accelerates and heats electrons in the tube, resulting in high T_e .
- $|E|$ is 80 V/m on the substrate holder → Lower E is applied to the linear plasma.

Electron density and input power density



-We assumed Saha's equilibrium for ionization with respect to T_e .
-In the tube, n_e reaches to $2.5 \times 10^{22} \text{ m}^{-3}$ almost uniformly.
-On the substrate holder, n_e is about $0.75 \times 10^{22} \text{ m}^{-3}$.
-Through this conductive channel, the input power density to electrons reaches to $1.0 \times 10^9 \text{ W/m}^3$ in the tube. $\sim 1000 \text{ W/cm}^3$

Résultats du modèle:

- T_e proche de 9700K dans le tube, uniformément
- T_h proche de 1700K dans le tube, 350K bord du tube (2T state)
- Sur le substrat : plasma linéaire formé : $T_e=9000$ K
- E dans le tube proche de 250V/m uniforme, 80V/m sur le substrat
- N_e proche de $2.5 \cdot 10^{22} \text{ m}^{-3}$, uniforme, $7.5 \cdot 10^{21} \text{ m}^{-3}$ sur le substrat
- Température uniforme en surface

POSTERS

Three dimensional nonequilibrium numerical simulation of anode region of high intensity transferred arc

Three dimensional nonequilibrium numerical simulation of anode region of high intensity transferred arc

Tao Zhu, Su-Rong Sun, Hai-Xing Wang, Jin-Yue Geng, Yan Shen
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Abstract

A three-dimensional chemical non-equilibrium plasma model is developed and applied to the simulation of a high intensity argon transferred arc with cross flow. The modelling result shows the arc attachment position is determined by the balance of different forces acting on the plasma. Compared to the symmetric distribution of case without the cross flow, an asymmetric distribution of Lorentz force with larger value upstream is formed to act on the plasma flow against the cross flow.

Keywords: High intensity argon arc, cross flow, chemical non-equilibrium model.

Calculation Domain

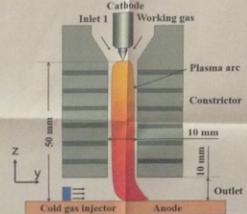


Fig. 1 Geometry of transferred arc plasma torch

Results and Discussions

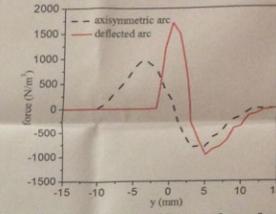


Fig. 2 Distribution of Lorentz forces for the deflected arc (a) and stable diffuse arc (b) above the anode surface.

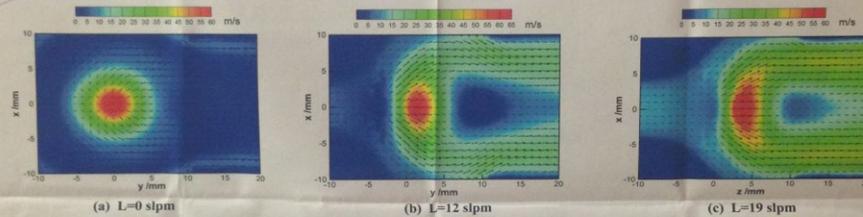


Fig. 3 Velocity distribution of x-y plane at axial position of 5 mm from anode for different cross flow rate (L: slpm)

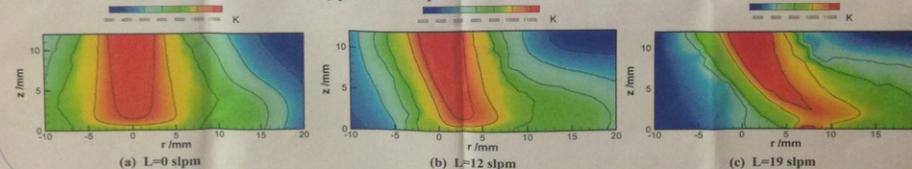


Fig. 4 Electron temperature distribution of symmetry plane(x=0 mm) for different cross flow rate (L: slpm)

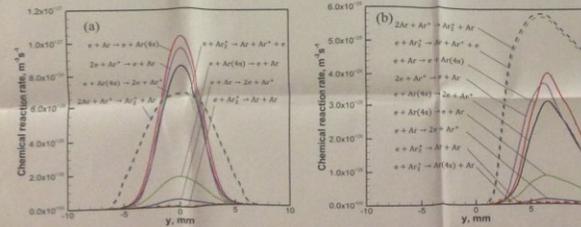


Fig. 5 Reaction rates distribution at 3 mm above the anode for different cross flow rate ((a): 0 slpm, (b): 19 slpm)

Under the influence of cold cross flow, peak values of chemical reaction rates move to the positive half-axis. It is interesting that reaction rates not involving molecular ion almost halved with cross flow. That is because these reaction rates are more sensitive to electron temperature than that of heavy species.

Conclusions

Three-dimensional chemical non-equilibrium modelling is performed to investigate the effect of cross gas flow on the plasma characteristics in a high intensity transferred arc. The results show that with the cross gas flow, the plasma column acts like a solid obstacle to the cross flow. Drag of the cross flow affects predominantly the low-viscosity layer of the plasma flow, leading to a horseshoe temperature distribution. The arc attachment position is determined by the balance of different forces acting on the plasma.

High-speed visualization of temperature fluctuation in multiphase AC arc

High-speed Visualization of Temperature Fluctuation in Multiphase AC Arc
 H. Maruyama¹, M. Tanaka¹, T. Watanabe¹, H. Nagai², T. Koiwasaki² and T. Okuma^{1,2}
¹ Department of Chemical Engineering, Kyushu University, ² Panasonic Corporation

Introduction

Material Processing by Multiphase AC Arc (MPA)

Advantages

- i. High energy efficiency
- ii. Low gas velocity
- iii. Large plasma volume
- iv. Easy to scale-up

Disadvantages

- Only few researches
- Arc stability
- Temporal, spatial characteristics
- Electrode erosion

Objective

• To clarify the arc fluctuation phenomena and temperature fluctuation characteristics of multiphase AC arc by high-speed visualization.

Experimental Setup & Visualization

High-speed Visualization of temperature fluctuation

Arc Conditions

AC applied-condition	12-phase double 6-phase
Frequency	AC 60 Hz
Arc Current	150, 300A
Pressure	100 kPa

Observation conditions

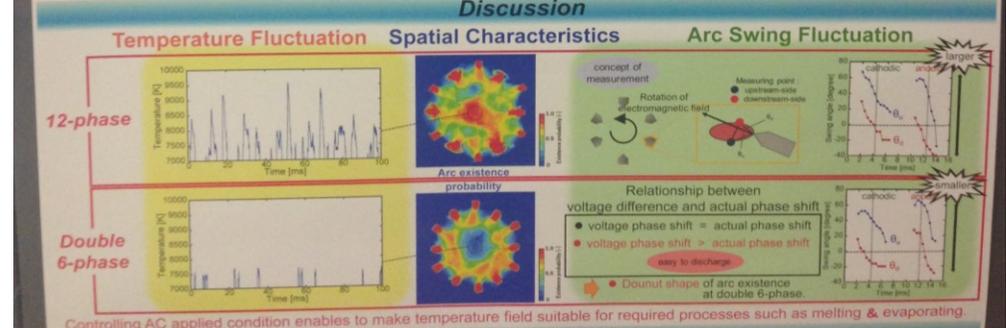
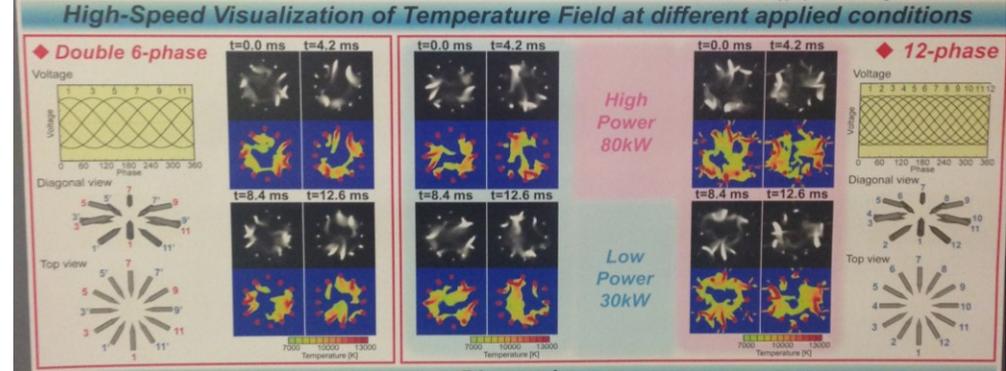
Camera	FASTCAM SA-5 (Photron)
Frame rate	1000frames/s
Shutter Speed	10 ⁻⁵ s

Temperature estimation by Boltzmann plot

$$I_{pq} = \frac{A_{pq} g_{pq} S}{\lambda} \cdot \frac{h_c n(T)}{4\pi U(T)} \exp\left(-\frac{E_{pq}}{k_B T}\right)$$

$$\ln\left(\frac{I_{pq}}{A_{pq} g_{pq}}\right) = -\frac{1}{T} \left(\frac{E_{pq}}{k_B}\right) + \ln\left(\frac{A_{pq} g_{pq} S}{4\pi U(T)}\right)$$

Appropriate wavelengths were selected.



Conclusion

Temperature fields of multiphase AC arc was successfully visualized by high-speed camera system.

1. Temperature in multiphase AC arc is sufficient high to melt or evaporate refractory metal or ceramics.
 2. Arc existence probability of 12-phase at center of discharge region is higher than that of double 6-phase.

Practical use of multiphase AC arc can be achieved on the basis of understanding of spatiotemporal characteristics

Visualisation of electrode phenomena in nitrogen DC arc

Visualization of Electrode Phenomena in Nitrogen DC Arc

P3-88

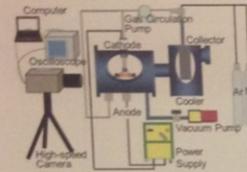
Takayuki Watanabe, Masaki Yoshida, Naoki Sakura, Manabu Tanaka

Dept. Chemical Engineering, Kyushu University, Fukuoka, Japan



Introduction

Free Burning DC Arc



Pressure 101.3 kPa
Arc current 100, 200 A
Arc voltage 20-40 V
Plasma gas Ar-N₂
N₂ concentration 50vol%

Cathode: W with Emitter

ThO₂ (2.0wt%) Er₂O₃ (1.43wt%)
ZrO₂ (0.37wt%) HfO₂ (1.34wt%)
CaO (0.97wt%) Dy₂O₃ (1.30wt%)
Lu₂O₃ (1.32wt%) Sm₂O₃ (1.17wt%)
Y₂O₃ (1.31wt%) Ce₂O₃ (1.94wt%)
Gd₂O₃ (1.07wt%) Nd₂O₃ (1.94wt%)



Cathode Erosion
Nitrogen addition → Severe erosion

Recombination Temp.	Electrode Erosion
H ₂ 3500 K	Negligible
N ₂ 7500 K	Severe

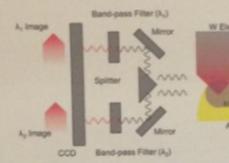
Purpose of this study

Understand cathode phenomena in N₂ Arc to investigate appropriate cathode material

Challenges

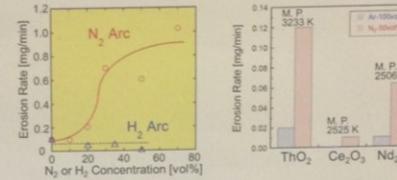
High-speed camera observation
✓ Visualization of tungsten vapor
✓ Temperature Measurement

Band-Pass Filter System



Metal Vapor Observation
BPF: 430 nm (W), 738 nm (Ar I)
Temperature Measurement
BPF: 785 nm, 860 nm

Cathode Erosion

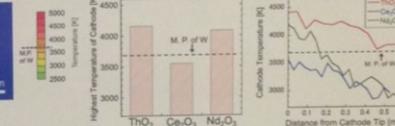
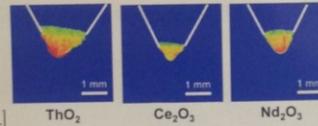


Cathode Temperature Distribution

Two-Color Pyrometry

$$I_{\lambda_1} = \frac{2hc^2}{\lambda_1^5} \frac{1}{\exp\left(\frac{hc}{\lambda_1 T}\right) - 1}$$

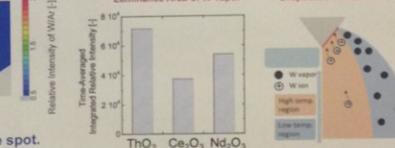
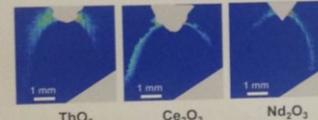
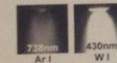
$$T = \frac{hc(\lambda_1 - \lambda_2)}{k\lambda_1\lambda_2 \left[\ln(I_1/I_2) + 5 \ln(\lambda_1/\lambda_2) \right]}$$



Tungsten Evaporation Visualization

Emission Coefficient Line Spectrum

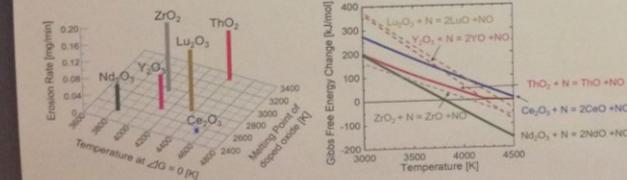
$$I_{pa} = \frac{A_{pa} \theta_{pa} S}{\lambda} \cdot \frac{h \nu c N(T)}{4\pi U(T)} \exp\left(-\frac{E_p}{k_B T}\right)$$



Evaluation of Relative Intensity $\frac{I_{pa}}{I_{Ar}} \approx \frac{N_W}{N_{Ar}}$

W evaporates only from periphery of cathode spot.

Discussion on Erosion Mechanism

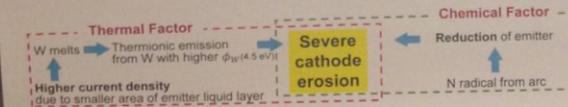


High-speed camera with band-pass filter was successfully applied to visualization of cathode surface and metal vapor.

Lower Melting Point, Higher ΔG
↓
Negligible cathode erosion

Nitrogen DC Arc

- Ce₂O₃-W is suitable material due to its low melting point and high chemical stability.
- Cathode erosion is determined by thermal factor and chemical factor.



Development of a novel swirl flow induced rotating arc discharge reactor for CO₂ conversion

1. Introduction

Due to anthropogenic activities in the recent years, there is a rise in CO₂ concentration in the atmosphere, which is a major greenhouse gas responsible for global temperature rise [1]. Majority of CO₂ emissions is from power sector by the combustion of fossil fuels.

To limit this, some approaches are employed
 Renewable feedstocks instead of coal
 Use of non-carbon energy sources
 Carbon Capture and Utilization (CCU)
 CCU seems to attract many researchers due to its possible economic market and cost-effective way of CO₂ mitigation [2]. Use of plasma process to convert CO₂ to valuable products appears to be a viable technique.

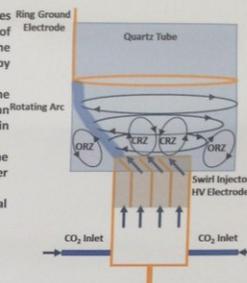
Objective

The main objective of this work is to develop a rotating arc discharge (RAD) by creating a swirl induced turbulent flow between two electrodes for CO₂ dissociation and investigate the effects of CO₂ flowrate on CO₂ dissociation.

2. Development Strategy

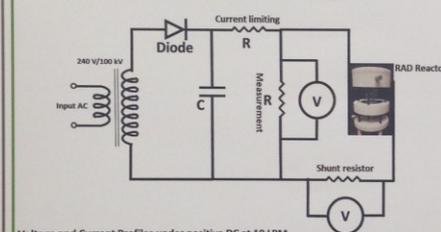
- Swirl injector acting as a high voltage electrode and ring ground electrode of 1.6 mm diameter was placed at 25 mm above the exit.
- Applying high voltage across these electrodes creates an arc discharge, due to the swirl motion of incoming CO₂ the arc tends to rotate along the edges of injector wall. The swirl flow is created by 8 guided vanes at a constant angle of 60°.
- The spiralling motion of CO₂ stream exiting the swirl injector high voltage electrode creates an axial and radial pressure gradient, resulting in central recirculation zone (CRZ).
- Due to sudden expansion outer recirculation zone (ORZ) is formed between quartz wall and swirlier exit.
- The degree of swirl is characterised by geometrical swirl number S as follows

$$S = \frac{2}{3} \left[\frac{1 - (d_{h1}/d)^3}{1 - (d_{h1}/d)^2} \right] \tan \phi = 1.57$$

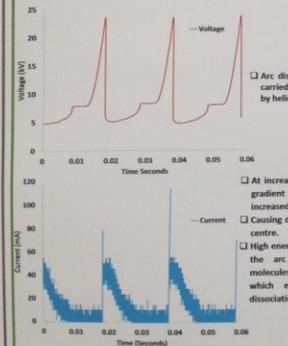


3. Results and Discussion

Electrical Characterization under High Voltage DC



Voltage and Current Profiles under positive DC at 10 LPM



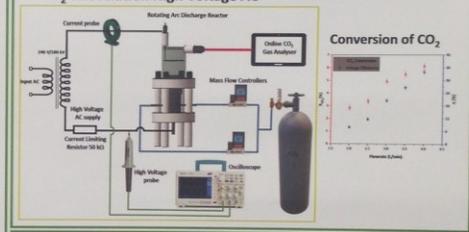
□ Arc discharge being generated is carried along the tip of electrodes by helical motion of gas stream

□ At increased flowrates the pressure gradient along radial direction is increased.

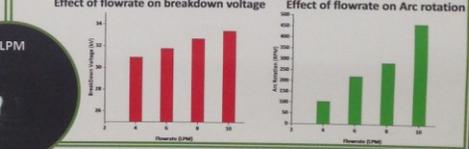
□ Causing discharges to move towards centre.

□ High energetic electrons produced in the arc is transferred to gas molecules in the recirculation zones which enhances the bulk CO₂ dissociation.

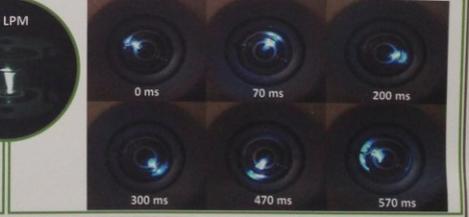
CO₂ dissociation High Voltage AC



Effect of flowrate on breakdown voltage Effect of flowrate on Arc rotation



Arc rotation under positive DC at 4 LPM



4. Conclusion

In this study, we developed a novel swirl-induced turbulent rotating arc discharge reactor for the conversion of CO₂ to CO and O₂. Highest conversion of 6.12% and energy efficiency of 34% were achieved at CO₂ flow rate of 4 L/min due to strong swirl-induced turbulence. The investigation of the effects of flow field characteristics using quantitative visualization techniques are currently underway. The effects of other parameters such as the influence of DC and pulsating voltages on the conversion of CO₂ and the selectivity of the products are worthy of investigation.

5. References

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Atmospheric pressure radio frequency hydrogen induction TP diagnostics by OES

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INTERNATIONAL SYMPOSIUM ON PLASMA CHEMISTRY
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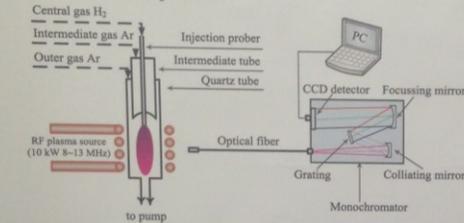
Atmospheric pressure radio frequency hydrogen induction thermal plasma diagnostics by optical emission spectroscopy

H. Zhang^{1,2}, L. Bai², P. Hu², L. Yang¹, Q. Chen¹, F. Yuan²

¹ Laboratory of Plasma Physics and Materials, Beijing Institute of Graphic Communication, Beijing, PR China
² State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, PR China

Introduction, RF thermal plasma OES diagnostics system and experimental parameters

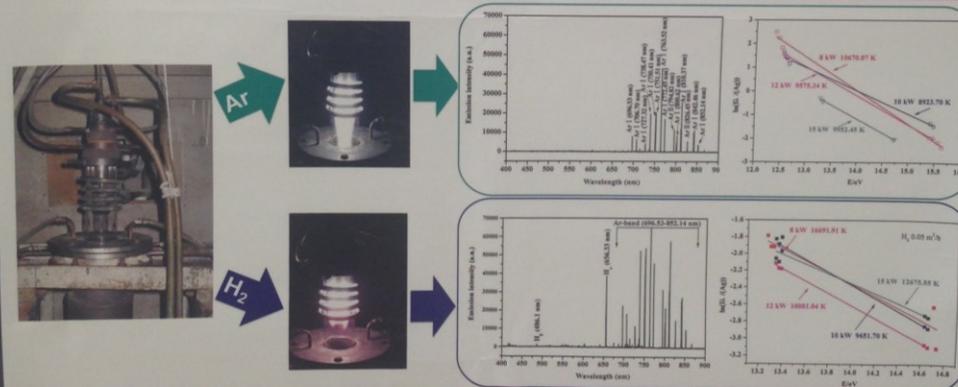
Thermal plasma at atmospheric pressure with the characteristics of ultra-high temperature and ultra-strong reactivity have been extensively used for high temperature pyrolysis process intensification. It is still a challenging work to exactly detect the plasma temperature in thermal plasma due to its ultrahigh temperature. In present work, in situ OES diagnostics was adopted to collect the spectra in the atmospheric pressure Ar-H₂ induction thermal plasma. The plasma temperature was calculated based on Boltzmann plot method. Furthermore, the thermal efficiency of Ar induction thermal plasma with or without H₂ was also calculated based on the obtained plasma temperature.



Parameters of the thermal plasma process

Parameters	Values
Plasma power, kW	8~15
Central gas, hydrogen, L min ⁻¹	0~1.67
Intermediate gas, argon, L min ⁻¹	8.33
Outer gas, argon, L min ⁻¹	83.33
Working pressure, atm	1

Characterization results



Conclusions

- Established stably discharged RF induction thermal plasma system and in situ OES diagnose system;
- Both Ar atom spectra lines located in the area of 696.53~852.14 nm and hydrogen atom spectra lines of H_α (656.33 nm) and H_β (486.10 nm) were detected in the Ar-H₂ RF induction thermal plasma;
- Based on Boltzmann plot method the calculated electron excitation temperature were varied from 9651.70 K to 16691.91 K in Ar-H₂ RF thermal plasma when the applied powers were raised from 8 kW to 15 kW. The electron excitation temperature in Ar-H₂ RF induction thermal plasma was higher than that in Ar RF induction thermal plasma;
- The thermal efficiency of 8 kW Ar ICTP was estimated at 17.19 %, whereas it was 30.69 % for Ar-H₂ RF induction thermal plasma. It means that adding H₂ into Ar RF induction thermal plasma enhanced its thermal efficiency.

Acknowledgment: Financial support from National Natural Science Foundation (No. 11505013, 11875090), Natural Science Foundation of Beijing Municipality (No. 1192008) and Beijing Municipal Excellent Talents Foundation (No. 2016000026832K12).

The on-going development of a CFD model to better understand the plasma arc discharge in a waste-water treatment application



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THE ON-GOING DEVELOPMENT OF A CFD MODEL TO BETTER UNDERSTAND THE PLASMA ARC DISCHARGE IN A WASTE-WATER TREATMENT APPLICATION

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1. Introduction

- The degradation of hazardous organic pollutants in water is one of the urgent topics in environmental research.
- Non-thermal plasma is an emerging technique in environmental pollution control technology. The plasma is produced by a high voltage discharge.
- In the direct method, the electrodes are immersed in liquid water in what is referred to as a pin-to-plane reactor arrangement.
- Computational Fluid Dynamics (CFD) can be used to study the relevant chemistry and fluid dynamics effects at the plasma-liquid interface.
- STAR-CCM+ version 13.04.010 (win64/intel16.3-r8 Double Precision) is currently being used to model a plasma arc.

2. Model assumptions

- As the electric arc passes through a gas, the gas particles are heated strongly and become ionised. Since the particles are ionised strongly, local thermodynamic equilibrium is assumed (LTE).
- The plasma is considered as a single continuous fluid.
- The thermodynamic properties, transport coefficients and absorption coefficient for the plasma gas (air) depend only on the temperature and the given pressure.
- The effect of gravity has not been taken into account.

3. Mathematical model

- Electromagnetism studies the behaviour of continua in response to electromagnetic fields. The fundamental laws that describe the electromagnetic behaviour of a continuum are Maxwell's equations and the conservation of electric charge. Maxwell's equations can be written as:

$$\frac{\partial \mathbf{B}}{\partial t} + \nabla \times \mathbf{E} = 0$$

$$\frac{\partial \mathbf{D}}{\partial t} - \nabla \times \mathbf{H} = -\mathbf{J}$$

$$\nabla \cdot \mathbf{D} = \rho$$

$$\nabla \cdot \mathbf{B} = 0$$

Where \mathbf{B} is the magnetic flux density, \mathbf{E} is the electric field, \mathbf{D} is the electric flux density, \mathbf{H} is the magnetic field, \mathbf{J} is the electric current density and ρ is the electric charge density.

- The conservation of charge within a control volume is given by the continuity equation, $\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0$
- STAR-CCM+ allows for the modelling of the interaction between electrically conducting fluids (such as a plasma) and electromagnetic fields.
- A conducting fluid in relative motion to a magnetic field induces an electric current density, $\mathbf{J}_e = \sigma \mathbf{v} \times \mathbf{B}$ where σ is the electrical conductivity, \mathbf{v} is the flow velocity and \mathbf{B} is the magnetic flux density.
- \mathbf{J}_e in turn induces a magnetic flux density which contributes to the total magnetic flux density.
- When using a two-way coupled approach, STAR-CCM+ calculates the total magnetic flux density (\mathbf{B}), which also accounts for the magnetic flux density induced by \mathbf{J}_e .
- With the two-way coupled MHD approach, $\mathbf{J} = -\sigma \nabla \phi - \sigma \frac{\partial \mathbf{A}}{\partial t} + \sigma \mathbf{v} \times \mathbf{B}$, with $\mathbf{B} = \nabla \times \mathbf{A}$, where ϕ is the electric scalar potential and \mathbf{A} is the magnetic vector potential.
- The conducting fluid experiences a body force per unit volume known as the Lorentz force, $\mathbf{f}_L = \mathbf{J} \times \mathbf{B}$. STAR-CCM+ includes the Lorentz force in the momentum equation.

4. Boundary conditions

	Cathode	Anode	Walls
$v_x (m/s)$	0	0	0
$v_y (m/s)$	0	0	0
$v_z (m/s)$	0	0	0
$T (K)$	$\frac{\partial T}{\partial n} = 0$	$\frac{\partial T}{\partial n} = 0$	$\frac{\partial T}{\partial n} = 0$
$I (A)$	0.4	0	$\frac{\partial I}{\partial n} = 0$
$p (Pa)$	$\frac{\partial p}{\partial n} = 0$	$\frac{\partial p}{\partial n} = 0$	$\frac{\partial p}{\partial n} = 0$
$A_x (Wb/m)$	$\frac{\partial A_x}{\partial n} = 0$	$\frac{\partial A_x}{\partial n} = 0$	0
$A_y (Wb/m)$	$\frac{\partial A_y}{\partial n} = 0$	$\frac{\partial A_y}{\partial n} = 0$	0
$A_z (Wb/m)$	$\frac{\partial A_z}{\partial n} = 0$	$\frac{\partial A_z}{\partial n} = 0$	0

5. The computational domain

- The volume mesh is applied to the computational domain which includes an initial hot channel as shown in Figure 1.
- In plasma arc simulations, the Ohmic Heating energy model heats the plasma. However, forcing an electrical current through an isolated gas at room temperature causes numerical instability due to the large scale of the ohmic heating. To avoid destabilisation, the plasma arc is initialised using a temperature which is large enough to result in a sufficiently large electrical conductivity (1 Sim = 100 Sim).

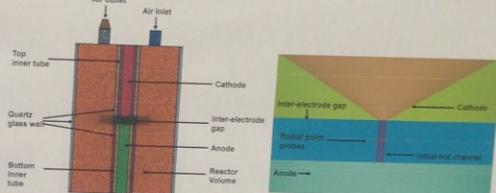


Figure 1. The computational domain.

6. Results

Iteration	Description
0.16	It was observed that at approximately 18000 iterations the Magnetic X-potential residual begins to diverge and is soon followed by the Magnetic Z-potential residuals.
0.20	The radiation models were disabled and the impact on the residuals monitored. The same phenomena of the diverging residuals were observed.
0.23	Radiation models disabled with a time step of 1E-5 s till 8000 iterations and thereafter a time step of 1E-7 s till 18000 iterations.

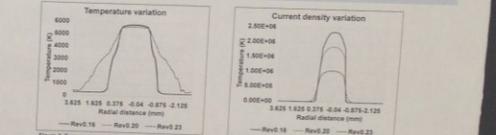


Figure 3. Temperature variation in the radial direction at the centre of the inter-electrode gap.

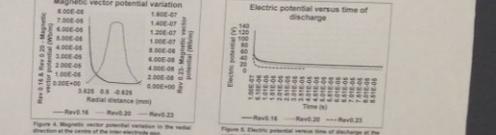


Figure 4. Magnetic vector potential variation in the radial direction at the centre of the inter-electrode gap.

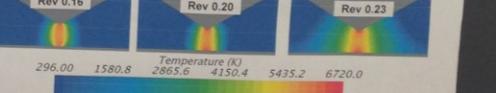


Figure 6. Temperature contours showing the arc for the different cases.

7. Discussion and Conclusion

- The computational results will aid in 1) understanding the experimental data and magnetohydrodynamics, 2) the design of a more effective reactor.
- The progress to date has included a comparison of simulation results with the radiation models activated and deactivated, which has shown minimal impact on the plasma arc shape.
- Stopping the simulation before the magnetic vector potential residuals diverge has a significant impact on the arc shape, indicating further investigation towards this topic.

8. Acknowledgement

Support of the Water Research Commission, South Africa, for funding

Non-equilibrium transport processes in a free-burning argon arc plasma under different operating pressures

Non-equilibrium transport processes in a free-burning argon arc plasma under different operating pressures

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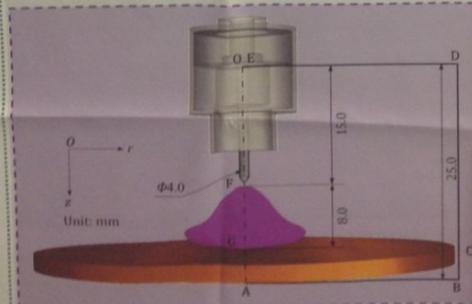
Background

Under different operating pressures, the non-equilibrium mass-momentum-energy exchange (MMEE) processes will be quite different, which will definitely result in different non-equilibrium characteristics of the collision-dominated plasmas (CDPs). This would determine the applicability, treatment result and efficiency of a specific CDP source in a certain application field.

Numerical Model

- Mass conservation equation $\nabla \cdot (n v_i) = R_i$
- Momentum conservation equation $\nabla \cdot (\rho v_i v_j) = -\nabla p + \nabla \cdot \tau + j \times B$
- Poisson equation $\nabla \cdot (\sigma \nabla \psi) = 0$
- Energy conservation equation for heavy particles $\nabla \cdot \left(\frac{5}{2} k_B T_e (V_e + V_i) \right) = \nabla \cdot (\lambda_e \nabla T_e) + \left[(\lambda_e^0 + \lambda_e^i) T_e \nabla \ln \theta \right] + e j \cdot E + Q_{e,0}^m + Q_{e,0}^{em}$
- Energy conservation equation for electrons $\nabla \cdot \left(\frac{5}{2} k_B T_e V_e \right) = \nabla \cdot (\lambda_e \nabla T_e) + \left[(\lambda_e^0 T_e \nabla \ln \theta) - e j \cdot E - Q_{e,0}^m + Q_{e,0}^{em} - S_e \right]$

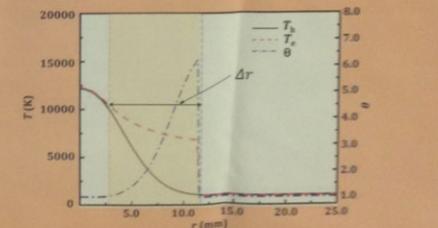
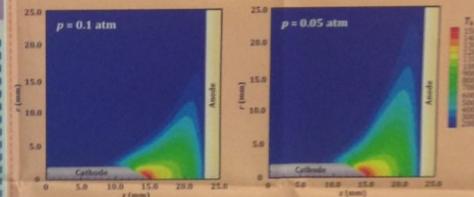
The calculation domain includes the electrode regions, the arc column region and the electrode sheaths. For the arc column region, a completely self-consistent non-equilibrium fluid model^[1] is employed; while the energy and current conservations are satisfied in the solid electrode regions.



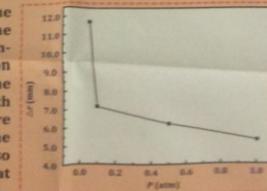
The sheath region at the interface between the plasma and the electrode is calculated using a one-dimensional collision-free sheath model^[2] to provide boundary conditions for the electrode region and the plasma region. The entire calculation process is solved iteratively using the SIMPLE algorithm.

Results and Discussions

At a constant arc current of $I = 100$ A, the spatial distributions of the heavy particle temperatures at the pressures of $p = 0.1$ and 0.05 atm are predicted. The radial profiles of the electron and heavy-particle temperatures and their ratio are also presented at $p = 0.1$ atm. It is seen that the electron temperature decreases much more slowly than that of heavy particles in the radial range of 4.1-11.2 mm; and then, it approaches to the temperature of heavy particles quickly in the cold gas region.



With the increase of the operating pressure, the radial width of the non-equilibrium transition region decreases as the electrons collide with heavy particles more frequently, and thus, the energy exchanges also become more intense at a higher pressure level.



Acknowledgement & References

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RF plasma for environmental and agriculture applications

RF PLASMA FOR ENVIRONMENTAL AND AGRICULTURE APPLICATIONS

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Dual-Chambers Plasma Furnace for solid waste treatment

Power: 100 kW
 Production: up to 75 kg/hour

Recycling: 100 kW RF Plasma prototype (Singapore)

Schematic diagram of plasma gasification system for carbonaceous wastes treatment.

1 - gasification zone of carbonaceous wastes, 2 - ash for charging (transport) carbonaceous wastes into the facility, 3 - reactor, 4 - catalytic gas plasma generator, 5 - plasma torch, 6 - off-gas cooling unit, 7 - gasification unit with a bag filter, 8 - gas treatment for gas analysis, 9 - exhaust combustion system, 10 - slag formation zone.

RF Plasma System-Drum Configuration

Carbon Black - Chemical Composition

Chemical composition of carbonaceous waste, % wt.

Element	Wt. %
C	85.0
H	10.0
O	3.0
N	1.0
S	0.5
Cl	0.2
Ca	0.1
Fe	0.1
Al	0.1
Mg	0.1
K	0.1
Na	0.1
P	0.1
Si	0.1
Other	0.1

Variation of the concentration of gaseous composition versus process temperature in air gas and steam gasification of carbonaceous wastes.

Saw Palmetto

Standard Plate Count

Carbon Black - Particle Size Distribution

AC plasma torch

Seeds Treatment

Parameter	Value
Germination rate (%)	95
Seedling height (cm)	15
Root length (cm)	10
Stem diameter (mm)	2
Leaf area (cm²)	10
Chlorophyll content	High
Stress tolerance	High

Energy balance - greenhouse with related based on experimental data

Parameter	Value
Energy input (kWh)	100
Energy output (kWh)	80
Energy loss (kWh)	20
Efficiency (%)	80

AC Plasma Torches model PPT

Power range of 80 to 160 kW

Parameter	Value
Power range	80 to 160 kW
Gas flow	100 to 200 L/h
Pressure	1.0 to 2.0 bar
Temperature	1000 to 2000 °C

CWRU Results - Tomatoes

Treatment	Yield (kg/m²)
Control	1.5
Plasma 1	2.0
Plasma 2	2.5
Plasma 3	3.0

100 applications for plasma

3D modelling of a DC transferred arc twin torch plasma system for the synthesis of copper nanoparticles



3D MODELLING OF A DC TRANSFERRED ARC TWIN TORCH PLASMA SYSTEM FOR THE SYNTHESIS OF COPPER NANOPARTICLES

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 Department of Industrial Engineering, Alma Mater Studiorum University of Bologna, Italy



INDUSTRIAL ENGINEERING

SUMMARY OF THE WORK

DC transferred arc twin torch plasma systems are devices consisting of two electrodes generating a plasma arc between the tips of the electrodes, with the plasma flowing through the bulk of the discharge, that are typically characterized by a very high plasma temperature [1]. They exhibit an extremely non-stationary behavior, with stochastic and chaotic characteristics being first observed in the discharge generated by the particular plasma system configuration characterized by a conical shape and fluid dynamic behavior and a 3D description is needed in order to realistically predict a 3D model. There have been previous work to study temperature and velocity distribution of such devices [2] by using a static 3D LTE twin torch model that considers the synthesis of copper nanoparticles in order to investigate the effect of geometric parameters on precursor evaporation. The authors propose herein a numerical simulation of a twin torch plasma system for the synthesis of copper nanoparticles with an assumed precursor fed vertically with a conical gas along the axis of the chamber. The precursor are evaporated by interaction with the plasma arc and nanoparticles are synthesized in the reaction chamber by reacting with a quenching gas flow rate. The radiative power loss contribution due to the copper production in the plasma by the twin torch system has been numerically predicted as an use of the model, including knowing the evaporation efficiency of the thermal precursor that is effectively evaporated in the plasma in a thermal plasma system for the synthesis of nanoparticles [3]. Especially in the twin torch system, where the electric arc intensity directly with the response, this finding offers an insight into the behavior of the system or what can be regarded as control parameter distribution and increase the acceptance rate when type of quenching gas can be adapted with different values [4].

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MODEL EQUATIONS

Continuity: $\nabla \cdot (\rho \mathbf{u}) = 0$

Momentum: $\rho (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \mathbf{F}_v$

Energy: $\rho (\mathbf{u} \cdot \nabla) T = \nabla \cdot (\kappa \nabla T) + \sum_i h_i \nabla \cdot (\rho_i \mathbf{u}_i) + \dot{q} - \dot{q}_r$

Species: $\rho (\mathbf{u} \cdot \nabla) Y_i = \nabla \cdot (\rho D_i \nabla Y_i) + S_i - R_i$

Electron: $\nabla \cdot \mathbf{j} = -\rho_e \nabla \cdot \mathbf{E}$

Ohm's law: $\mathbf{j} = \sigma (\mathbf{E} + \mathbf{u} \times \mathbf{B})$

LAGRANGIAN PRECURSOR TRACKING MODEL

Equation: $\frac{d\mathbf{r}}{dt} = \mathbf{u} + \mathbf{v}_p$

where $\mathbf{r} = (x, y, z)$, $\mathbf{u} = (u, v, w)$, $\mathbf{v}_p = (v_p, w_p)$

MODEL ASSUMPTIONS

- LTE plasma is considered optically thin.
- The effect of the magnetic field on the ionization and dissociation processes of the gas mixture is neglected.
- A constant precursor evaporation rate is assumed.
- The precursor evaporation rate is assumed to be constant.

NANOPARTICLE NUCLEATION AND GROWTH

Monodisperse nucleation is considered to be described by the second order kinetic equation (GZM):

$$\frac{dN}{dt} = \beta - \gamma N^2$$

where $\beta = \sum_i \sum_j K_{ij} n_i n_j$ and $\gamma = \sum_i \sum_j K_{ij} n_i n_j$

METHOD OF MOMENTS (MoM)

GZM is mathematically approximated using moments of the Particle Size Distribution:

$$\frac{dM_k}{dt} = \int_0^\infty v^k \frac{dN}{dt} dv \quad k = 0, 1, 2, 3$$

Conservation equation for moments:

$$\frac{dM_k}{dt} = M_k^{(0)} \frac{dM_0}{dt} + M_k^{(1)} \frac{dM_1}{dt} + M_k^{(2)} \frac{dM_2}{dt} + M_k^{(3)} \frac{dM_3}{dt}$$

where $M_k^{(i)} = \int_0^\infty v^k v^i N dv$, $k = 0, 1, 2, 3$

When diffusion term also take account the production or destruction of nanoparticles due to nucleation, coagulation and condensation:

NODAL METHOD

A Lagrangian with linear distribution of the PSD function is applied:

$$N = \sum_{i=1}^N N_i \delta(v - v_i)$$

where v_i is the geometric spacing factor, based on 1, 0, 1, by the particle volume and N_i is the number of nodes, $i = 1, 2, 3$.

Therefore, the discretized GZM for each particle distribution N_i with a constant nucleation effect, can be given by:

$$\frac{dN_i}{dt} = \beta_i - \gamma_i N_i^2$$



Copper jet input
Copper jet output

Work supported by European Union's Horizon 2020 research and innovation program under grant agreement No 101017113

INSPIRED-Industrial Scale Production of Innovative Nanomaterials for green Chemistry

WT2 - Synthesis and Scale up of nanomaterials
 Task 2.1 - Synthesis of Nano-copper
 Innovation for precursor vaporization and scale-up

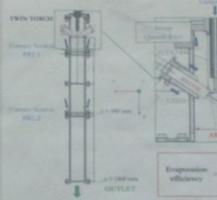
PRODUCTION TARGET

- throughput of 10 kg/day or more
- particle size distribution with average diameter of 40-70 nm

Several operating conditions that satisfy the project target have been found through modelling activities performed on RF thermal plasmas with a conical reaction chamber.

Investigations have also been performed on a 240 kW DC Twin Torch System

TWIN TORCH CHAMBER GEOMETRY



Explosion efficiency
Precursor feed rate

TEMPERATURE ISOCONTOURS AT DIFFERENT CURRENT LEVELS



100 A - 100 kW
200 A - 200 kW

Linear current scaling of the temperature, with a reduction in radius that increases the plasma arc length. It significantly decreases the temperature efficiency system.

OPERATING CONDITIONS

Pressure: 1 atm

Gas flow rates:
 Carbon: 40 slpm Ar
 Anode electrode: 50 slpm Ar
 Cathode electrode: 25 slpm Ar
 Spray Quench Gas: 150 slpm Ar
 Purge gas velocity: 700 slpm Ar

Electric current: 520-1200 A (70-240 kW)

Copper precursor: 6-72 kg/hr feed rate (7 μm mean diameter)

PRECURSOR EVAPORATION EFFICIENCY

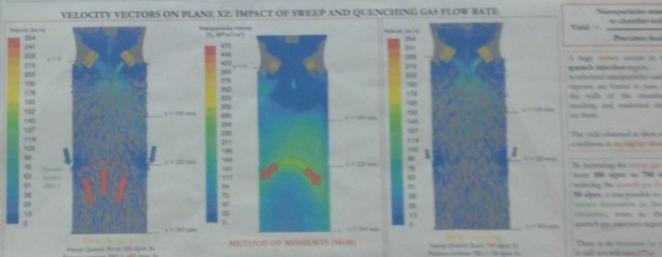
Predecessor evaporation efficiency have been investigated for different precursor feed rate.

At 520 A of operating current the evaporation efficiency is close to 80% range up to 20 kg/hr of precursor feed rate.

Experiments performed by an INSPIRED project partner in 520 A show an average precursor evaporation efficiency of ~70 kg/day of precursor feed rate, which is in good agreement with simulation output (80%).

An increase of operating current up to 600 A reduces evaporation efficiency of ~70 kg/day of precursor feed rate. Similarly, an increase to 800 A shows an average evaporation efficiency of 80% up to 72 kg/day.

VELOCITY VECTORS ON PLANE XZ: IMPACT OF SWEEP AND QUENCHING GAS FLOW RATE



Method of Moments (MoM)

Velocity vectors on plane XZ at different flow rates

NANOPARTICLES CONCENTRATION AND MEAN DIAMETER IN THE REACTION CHAMBER

Method of Moments (MoM)

Nanoparticles concentration and mean diameter in the reaction chamber

CONCLUSIONS

- A 3D model for the synthesis of copper nanoparticles with a twin torch plasma system has been developed.
- The system allows a good precursor vaporization efficiency. However, preliminary simulations on the actual reaction chamber and operating conditions show a very low nanoparticles yield (~10%) compared to RF systems with conical chamber (up to 50-60%).
- Comparison with experimental results is in progress, in joint collaboration with project partners to investigate best operating conditions and quenching strategies.



Project team photo

HORIZON 2020

Synthesis of aluminium nitride nano-powder using IP technology: effect of feedstock molar ratio and reactor pressure

Synthesis of Aluminium Nitride Nano-powder using Induction Plasma Technology Effect of Feedstock Molar Ratio and Reactor Pressure

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Department of Chemical and Biotechnological Engineering, Université de Sherbrooke, Québec, Canada J1K 2R1

1. Introduction

AlN has become the key component of semiconductor equipments, crucibles for handling corrosive chemicals and reaction vessels due to its:

1. Elevated thermal conductivity [1], chemical/physical stability at fairly high temperature regions, hardness [2] and resistance of molten metals, wear and corrosion [3, 4, 5].
2. Low thermal expansion coefficient [6].

Thermal plasma technology has become popular because of:

- The fast reaction rate [6], flexibility in the choice of various feedstock materials [7], high conversion rate and energy efficiency [6, 8], rapid quenching [9, 10].

2. Objectives of this research

- O1. Replacing ammonia plasma nitridation (dangerous precursor) by urea plasma nitridation (safe alternative).
- O2. The effect of feedstock molar ratio (MR) (Al:urea) on the formation of aluminium nitride (AlN) nano-powder.
- O3. The effect of reactor pressure on the formation of aluminium nitride (AlN).

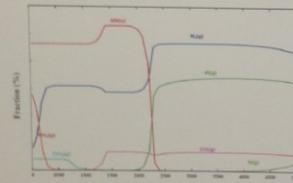


Figure 1: Thermodynamic plots showing calculated compositions during AlN production through plasma

According to Factsage thermodynamic computation software [11] results:

- Formation of AlN begins at about 2400°C and reaches to its maximum at 2200°C.
- The formation of CO, NH₃, CO₂ gases is considered as the plasma gas species

3. Experimental conditions

- Plasma pressures of 67, 30, 15, 9 kPa and Al:urea MR of 1:2, 1:4 and 1:6.
- Carrier gas (Ar) = 1 SLPM; Central gas (Ar) = 21 SLPM; Sheath gas (Ar/H₂/N₂) = 40/2/22 SLPM; Feed rate = 0.5 g.min⁻¹; Power = 45 kW.

Table 1: Experimental conditions of AlN synthesis using RF induction thermal plasma

Run #	Al:Urea MR	Preparation condition	Pressure (kPa)
1	6	Melting	30
2	4	Hexane	30
3	4	Melting	30
4	2	Melting	30
5	4	Melting	67
6	4	Melting	30
7	4	Melting	15
8	4	Melting	9



Figure 2: Al and urea precursor prepared a) by melting urea b) in hexane medium

4. Effect of Al:Urea molar ratio

1. No AlN formation was observed with Al:urea MR of 6.
2. Using a molar ratio of 4, the intensity of AlN peaks was the highest.
3. Decreasing the MR to 2, resulted in reduction of the AlN peaks intensity.
4. Rietveld semi-quantitative method shows formation of 20 % AlN in Run# 3.
5. Particle size of 40 to 100 nm.

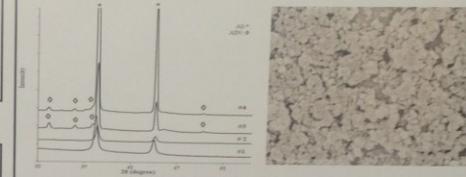


Figure 3: XRD patterns of synthesized powder with different molar ratio



Figure 4: SEM image of the plasma-synthesized powder with Al:Urea molar ratio of 1:4

5. Effect of chamber pressure

By decreasing the chamber pressure from 67 to 9 kPa:

1. Al₂O₃ peaks were eliminated.
2. The residence time becomes shorter, and the particles leave the high temperature zone more quickly which resulted in formation of AlN - residual Al.
3. Nitrogen derived from the decomposition of urea which reacted more easily.
4. Rietveld semi-quantitative method shows formation of 20 % AlN in Run# 8.

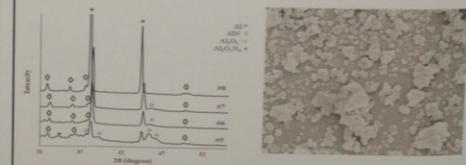


Figure 5: XRD patterns of plasma-synthesized powder at various pressures



Figure 6: SEM image of the plasma-synthesized powder at 9 kPa chamber pressure

6. Conclusion

1. The optimum molar ratio of the Al:urea reactants is 1:4 obtained under plasma chamber pressure of 9 kPa.
2. Rietveld XRD method shows formation of 20% AlN composition in run (#8).
3. Cubic and Hexagonal crystal structures of AlN are present.
4. Post treatments are needed to recrystallize the AlN.
5. Apart from post heat treatments, effect of other plasma parameters including the injection process should be investigated.

7. References

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The effect of H₂ on the transport of graphene to amorphous carbon by DC arc discharge

The effect of H₂ on the translation of graphene to amorphous carbon by DC arc discharge

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Advantages of DC arc discharge

- ✓ Reliability
- ✓ Safety
- ✓ High efficiency
- ✓ High-quality nanomaterials
- ✓ Doped nanomaterials
- ✓ Environmental friendliness

Effect of hydrogen

- Facilitating planar growth of carbon by reducing pentagons;
- Efficient quencher due to the highest thermal conductivity;
- Etching amorphous carbon.

Schematic diagram of DC arc discharge and experimental parameters

Experimental Conditions

Pressure	70 KPa
Gas	H ₂ /Ar, H ₂ /N ₂
Ratio of gases	1:0, 2:1, 1:1, 1:2, 1:4, 1:5, 1:6, 0:1
Current	100-200 A
Diameter of anode	10 mm
Diameter of cathode	10 mm
Raw material	Graphite rod

Results and discussion

Fig.1 TEM of carbon nanomaterials prepared in atmosphere of H₂ and Ar with different ratios of H₂/Ar (V/V): (a) 1:0 and insert shows graphene sheets, (b) 2:1, (c) 1:1, (d) 1:2, (e) 1:4 and insert shows carbon nanocages, (f) 1:5, (g) 1:6, (h) 0:1 and insert shows amorphous carbon.

Sample/H ₂ :Ar	1:0	2:1	1:1	1:2	1:4	1:5	1:6	0:1
I _{sp} /I _c	0.2	0.2	0.2	0.25	0.4	0.5	0.6	0.8

Fig.2 I_{sp}/I_c of carbon nanomaterials synthesized with different ratios of H₂/Ar.

Fig.3 TEM of the carbon nanomaterials prepared in atmosphere of H₂ and N₂ with different ratios of H₂/N₂ (V/V): (a) 1:0, (b) 2:1, (c) 1:1, (d) 1:2, (e) 1:4, (f) 1:5, (g) 1:6, (h) 0:1 and insert is HRTEM of carbon nanohorns.

Sample/H ₂ :N ₂	1:0	2:1	1:1	1:2	1:4	1:5	1:6	0:1
I _{sp} /I _c	0.2	0.2	0.2	0.25	0.4	0.5	0.6	1.0

Fig.4 I_{sp}/I_c of carbon nanomaterials synthesized with different ratios of H₂/N₂.

Growth mechanism

Effect of Hydrogen

Conclusions

- (1) In mixture of H₂/Ar, with reducing H₂ concentration, the tendency of transition from graphene to carbon nanocages, polyhedral graphite, and amorphous carbon balls.
- (2) In mixture of H₂/N₂, with reducing H₂ concentration, the tendency of transition from graphene to carbon nanocages, polyhedral graphite, amorphous carbon balls, and carbon nanohorn.
- (3) Due to the C-H bonds are bonding and rupturing at the edges of graphite sheet, hydrogen facilitates the forming of graphene sheets, C-N bonding leads to the formation of carbon nanohorn.

Formation mechanism of carbon-coated amorphous Si nanoparticules synthesized by induction thermal plasmas

P3-19

Formation Mechanism of Carbon-Coated Amorphous Si Nanoparticles Synthesized by Induction Thermal Plasmas

R.Hayashida, K.Yamano, H. Sone, M. Tanaka, T. Watanabe
Department of chemical engineering, Kyushu University

Introduction

Silicon as Negative electrode material of lithium ion battery

Advantage

- Large capacity
- Capacity of Si is 4200 mAh/g
- Capacity of carbon is 372 mAh/g

Disadvantage

- Pulverization of Si particles due to large volume change of 400%
- Formation of insulating material at solid electrolyte interface (SEI)

Carbon-coated amorphous Si nanoparticles

Purpose of this study

- To synthesize carbon coated silicon nanoparticles (NPs) by induction thermal plasma
- To investigate the formation mechanism of carbon coated silicon NPs

- Carbon-coating: Improve chemical and mechanical stability
- Amorphization: Suppress pulverization of Si
- Nanoparticulation: Improve reactivity

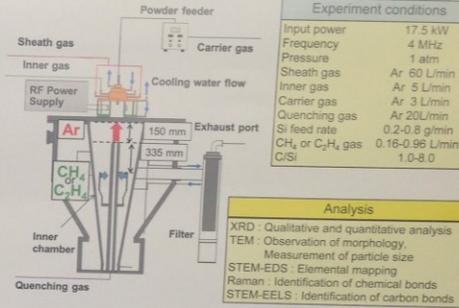
Synthesis process requires rapid quenching process.

- Electroless plasma
- Long residence time
- Rapid quenching rate

RF thermal plasma

Experimental Setup & Conditions

Experimental Setup



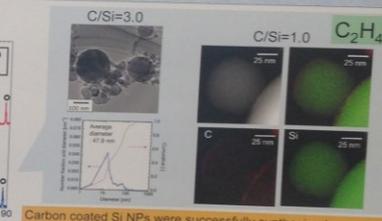
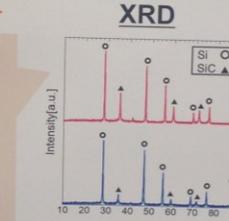
Experiment conditions	
Input power	17.5 kW
Frequency	4 MHz
Pressure	1 atm
Sheath gas	Ar 60 L/min
Inner gas	Ar 5 L/min
Carrier gas	Ar 3 L/min
Quenching gas	Ar 20 L/min
Si feed rate	0.2-0.8 g/min
CH ₄ or C ₂ H ₄ gas	0.16-0.96 L/min
C/Si	1.0-8.0

Analysis

- XRD: Qualitative and quantitative analysis
- TEM: Observation of morphology, Measurement of particle size
- STEM-EDS: Elemental mapping
- Raman: Identification of chemical bonds
- STEM-EELS: Identification of carbon bonds

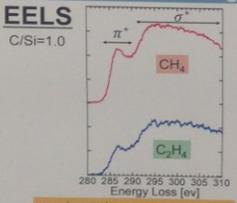
Analysis of Carbon coating

Analysis of Nanoparticles

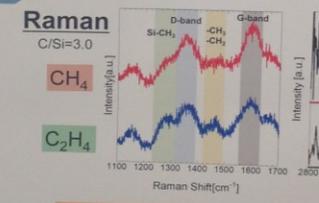


Carbon coated Si NPs were successfully synthesized. Si nanoparticles with 43-48 nm and nanowires were observed.

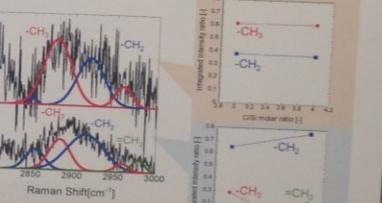
Analysis of Coating



pi* and sigma* peak were detected. These peak were similar with DLC.

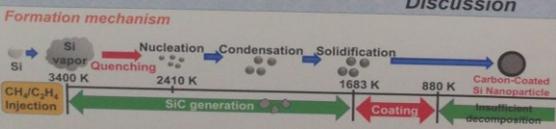


Carbon-coated Si NPs synthesized with C₂H₄ included =CH₂. The difference of carbon sources affects to the composition of carbon coating.



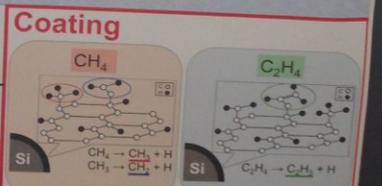
Integrated intensity ratio of D/G band vs C/Si molar ratio.

Discussion



Conclusion

- Carbon coated silicon nanoparticles were successfully synthesized
- The difference of carbon sources affects to the composition of carbon coating.
- Thermal Plasma enables to produce carbon coated silicon nanoparticle at high-productivity.



Synthesis of Lithium oxide composite with refractory metal by induction thermal plasmas

P3-23 Synthesis of Lithium Oxide Composite with Refractory Metal by Induction Thermal Plasmas

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EXPERIMENTAL CONDITIONS

Plasma condition	
Plasma power plate	20 kW
Pressure	1 atm
Frequency	4MHz
Sheath gas	60 L/min
(Ar/O ₂)	(57.5/2.5)
Inner gas	Ar 5 L/min
Carrier gas	Ar 3 L/min
Powder feed rate	300 mg/min

Raw materials	
Li-Nb-Ni system	Li ₂ CO ₃ (3.5 μm), Nb (20 μm), Ni (3-5 μm)
Li-Nb-Fe system	Li ₂ CO ₃ (3.5 μm), Nb (20 μm), Fe (5 μm)
Li-Nb-Mo system	Li ₂ CO ₃ (3.5 μm), Nb (20 μm), Mo (1.5 μm)

RESEARCH MOTIVATION

Lithium-ion Battery

Layered rock-salt [R-3m]

Required characteristics

- High power density
- High cycle performance
- High safety
- Long life
- Low cost

Li₂CO₃ commonly used

- High cost
- Safety issue

Alternative material is strongly required

Cubic rock-salt [Fm-3m]

The host structure of High-capacity & High-reversible capacity

To improve battery characteristics

- Nb site is substituted by other elements
- Doping Ni, Fe ⇒ Improved capacity
- Doping Mo ⇒ Improved cyclic stability

Advantages of Induction Thermal Plasma

- Electrodeless discharge
- Large plasma volume
- Low gas velocity

Synthesis of nanoparticles with high purity at high productivity

RESULTS

Li-Nb-Ni system

Li-Nb-Fe system

Li-Nb-Mo system

Relative integrated intensity

Li-Nb-Ni system & Li-Nb-Fe system
Cubic rock-salt type NPs were synthesized at $\leq \text{Nb}/(\text{Nb}+\text{Metal}) \leq 0.75$

Li-Mo composite NPs can be synthesized in large range
at $\leq \text{Nb}/(\text{Nb}+\text{Mo}) \leq 0.75$

STEM-EDS

Elements mapping co-existed in the same NPs

Li-Mo composite NPs were synthesized

But Li-Nb-Ni system & Li-Nb-Fe system have different composition ratio

Different deviation of composition ratio in each system

These differences were considered from formation mechanism

DISCUSSION

Nucleation rate

$$J = \frac{\beta_0 n_s^2 S}{12} \sqrt{\frac{\theta}{2\pi}} \exp\left[\theta - \frac{4\theta^3}{27(\ln S)^2}\right]$$

$\theta = \frac{\sigma s_1}{kT} \quad S = \frac{P}{P_s}$

J : Nucleation rate [$\text{m}^{-3} \text{s}^{-1}$]
 β_0 : Collision frequency [1]
 n_s : Saturation ratio [1]
 θ : Number density of saturation pressure [m^{-3}]
 S : Non-dimensional surface tension [1]
 σ : Surface tension [N m^{-1}]
 s_1 : Surface area of monomer [m^2]
 P : Partial pressure [Pa]
 P_s : Saturation pressure [Pa]

Melting point, Boiling point, Nucleation temperature

Formation mechanism

Li-Nb-Mo system
3074 K: Nb nucleation, 2903 K: Mo nucleation → Li-Nb-Mo composite oxide (Small deviation)

Li-Nb-Ni system & Li-Nb-Fe system
1738 K: Nb nucleation, 1809 K: Fe nucleation → Li-Nb-Ni or Li-Nb-Fe composite oxide (Large deviation)

High nucleation temperature of Nb
Sufficient reaction time for Ni vapor
Mo has insufficient reaction time with Nb than Ni & Fe
⇒ Li-Nb-Mo composite oxide NPs easily synthesized
Composition deviation depend on Nucleation temperature

CONCLUSION

- Li-Nb-Ni oxide were successfully synthesized
- Li-Nb-Fe oxide were successfully synthesized
- Li-Nb-Mo oxide were successfully synthesized



Synthesis of Transition Metal Boride Nanoparticles by Induction Thermal Plasma

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Introduction

Transition metal (Mo & W) boride (TMB)

Advantages

- High hardness,
- Thermal and electric conductivity,
- High wear and corrosion resistance,
- Radiation shielding performance.

Difficulties

- Hard to produce refractory metal boride
- Difficult manufacturing process
- Production efficiency
- Oxidation problem
- Synthesis of TMB nanoparticles

Purpose of this study

- I. Investigate the formation mechanism
- II. Apply to large-scale industrial production

Induction Thermal Plasma

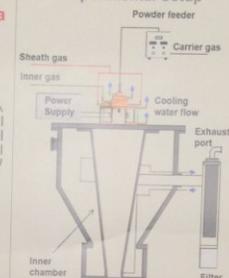


- Electrodeless plasma
- Long residence time
- large high temperature area

✓ High purity of TMB nanoparticles at high productivity

Experimental Setup and Conditions

Experimental Setup



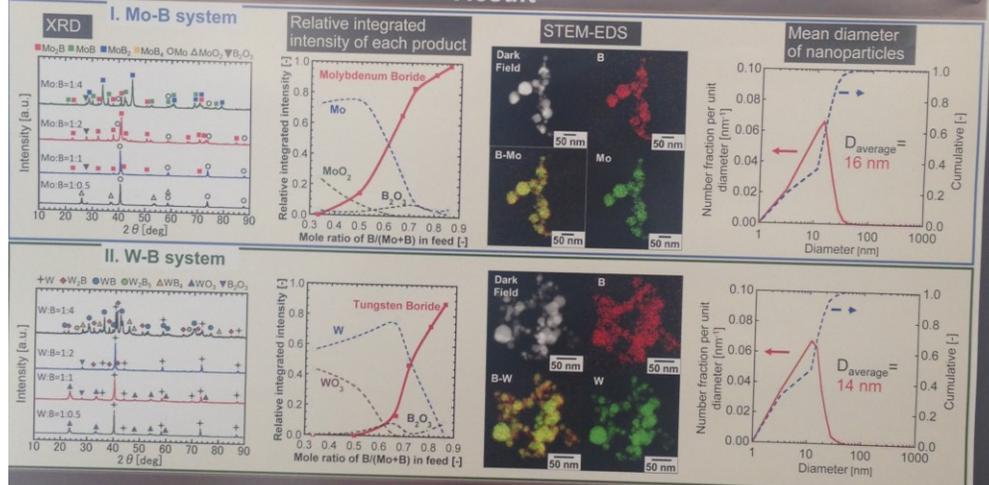
Experimental condition

Plasma power [kW]:	20
RF frequency [MHz]:	4
Operation pressure [atm]:	1
Sheath gas flow rate Ar [L/min]:	60
Inner gas flow rate Ar [L/min]:	5
Carrier gas flow rate Ar [L/min]:	3
Powder feed rate [mg/min]:	300
Composition: (Mo or W):B=	1:0.5, 1:1, 1:2, 1:2.5, 1:4, 1:6

Analysis methods

- XRD: Identification of products
- STEM-EDS: Elements mapping

Result



Discussion

Nucleation temperature

$$J = \frac{\beta_1 n_2^2 S}{12} \sqrt{\frac{\theta}{2\pi}} \exp\left[\theta - \frac{4\theta^3}{27(\ln S)^2}\right]$$

$\theta = \frac{\sigma s_1}{kT}$

J : homogeneous nucleation rate [$m^{-3}s^{-1}$]
 θ : dimensionless surface tension [-]
 S : saturation ratio [-]
 β_1 : collision frequency function between monomers [-]
 n_2 : equilibrium saturation monomer concentration [m^{-3}]

Melting Point, Boiling Point and Nucleation Temperature

Nucleation Temperature Difference (D_1 & D_2) between metal and B

Mo and B: Small difference → well-mixed Mo and B vapors → efficient reaction → better preparation of thermodynamically stable phases

W and B: Large difference → W has started to solidify before B vapors condense → difficult reaction → far deviation from the thermodynamically stable phases

Product phases and expected product phases according to the phase diagram

Molar ratio	Main product	Expected product
1:0.5	W	W, B, W
1:1	W	WB, W ₂ B ₃
1:2	W, W ₂ B	WB, W ₂ B ₃
1:4	W, B, WB	W ₂ B ₃ , WB ₂ , B
1:0.5	Mo	Mo, B, Mo
1:1	Mo, Mo ₂ B	Mo ₂ B, Mo ₃ B ₄
1:2	Mo ₂ B, Mo ₃ B ₄ , Mo	Mo ₂ B, Mo ₃ B ₄
1:4	Mo ₂ B, Mo ₃ B ₄ , Mo, B, Mo	Mo ₂ B ₃ , Mo ₃ B ₄ , B

Formation mechanism

Mo-B: 2495-2524 K → Molybdenum Boride

W-B: 3628-3672 K → Tungsten Boride

Conclusion

TMB nanoparticles were successfully synthesized by induction thermal plasma.

- Mo and B react more easily than W and B. The products of W-B system showed greater deviation from the phase diagram.
- Induction thermal plasma can provide a high efficient way to synthesize TMB nanoparticles to apply to large-scale industrial production.

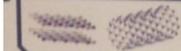
Synthesis of Few-walled Boron Nitride Nanotubes using Triple Thermal Plasma Jet System with Hydrogen Injection

Minseok Kim¹, J.-H. Oh¹, B. I. Min¹, Y. H. Lee¹, S. H. Hong¹, T.-H. Kim^{2*}, and S. Choi^{1,2*}

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Introduction

1994 years



- Firstly proposed
- Boron Nitride Nano Tubes (BNNT) might be formed from hexagonal boron nitride (h-BN) [1]

1995 years



- Firstly synthesized
- BNNTs are synthesized for the first time by Zettl and coworkers [2]

1998 - 2004 years

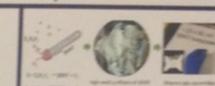
1. Young's modulus = Stress / Strain
 2. Thermal stability
 3. Oxidation resistivity
- Filing various properties
 - Wide band gap = 5 eV
 - The elastic Young's modulus of BNNT over 1 TPa
 - It was revealed BNNTs are stable at 700 °C in air
 - It was demonstrated shortest temperature for oxidation of BNNTs is 800 °C

2009 years



- A noteworthy advance
- Ultrafine BNNT were produced using laser ablation
- The production rate was 60 mg of BNNTs during 30 minutes

2014 years



- Impressive BNNT mass production
- Highly crystalline small diameter BNNT are synthesized and at an unprecedentedly high rate approaching 20 g/h without ferrous catalysts

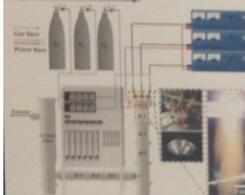
HYPOTHESIS AND SYNTHESIS

PROPERTIES

MASS PRODUCTION (PRESENT GOAL)

Experimental set up

Experimental Set-up



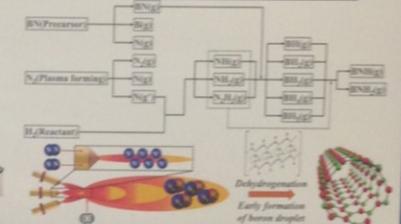
Experimental Condition

Chamber pressure (kPa)	Plasma forming gas (slpm)	Carrier gas (slpm)	Reactant gas (slpm)	Ar current [A]	Ar voltage [V]	Starting material
0.1	4(C ₂) and N ₂	0(Ar)	0(BN ₂)	100	(1) 70-120 kV (2) 70	B and h-BN

Analysis: FE-SEM, FE-TEM

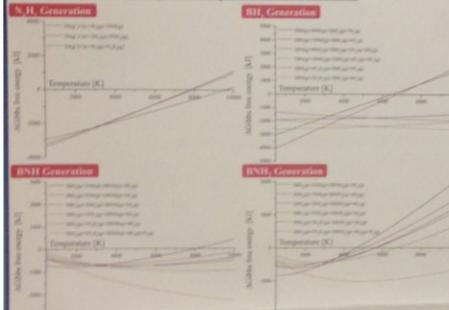
Thermal equilibrium equation: $\Delta T \propto \text{Chemistry}$

Hypothesized Chemical Path to be Grown into BNNT



Results and Discussion

The results of thermodynamic equilibrium calculation



The macroscopic, SEM, and TEM images of the formed BNNT



Comparison with other works

Method	Input power(kW)	Production range(g)	Production rate per power(g/kW)	Inputs gas(NL/PM)	Production rate per nitrogen power(g/LN/PM)	Reference
Laser ablation	1	0.12	0.12	Ar-0.1, N ₂ , O ₂	0.48	Smith, M. W. et al.
Chemical vapor deposition	10	0.010	0.001	Ar-0.1, N ₂ , O ₂ , H ₂	0.03	Huang, T. et al.
Inductively coupled plasma	60	20	0.33	Ar-75, H ₂ , O ₂ , N ₂ , H ₂	0.36	Kim, K. S. et al.
Inductively coupled plasma	40	10	0.25	N ₂ , H ₂	0.7	Faloutsos, A. et al.
Triple DC thermal plasma	20	12.4	0.62	Ar-12, H ₂ , N ₂ , H ₂	0.820	Present work

Super heating area

- The nitrogen molecules are circumstanced in the strong electrical field which is sufficient to ionize them.
- The formed radicals react with hydrogen molecules to produce N₂H₂ gases.

Quenching area

- In the process of quenching, the formed N₂H₂ gases combine with BN₂ gases to form assorted BNH₂ gases.
- Among the BNH₂ gases, BNH₂ and BNH₂ gases continuously combine with N₂H₂ gases during the cooling process to form BNH and BNH₂ gases.

Conclusion

IMPORTANT Triple DC thermal plasma jet provides appropriate environment for synthesis of BNNT with hydrogen

- The N₂ gas as plasma forming gas was circumstanced in the strong electrical field which is sufficient to ionize them, which leads forming N₂H₂ gases with H₂ gas in plasma flame.
- The formed N₂H₂ gases reacts with BN₂ gas as precursor to generate B-N-H intermediates which are eventually grown into BNNT.

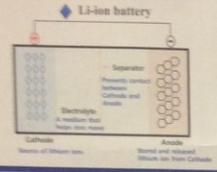
IMPORTANT The thin cotton appearance material in macroscopic scale was successfully formed and validated for BNNT

- The TEM analysis validated the fabric material from the reactors has highly crystalline tubular structures which are straight and parallel to the axis of the tube, and these tubular structure have diameters below 5 nm without drawback.
- As a result, 12.6 g of the BNNT was produced with input power of 21.4 kW, which was a superior yield.

Synthesis of Si-MWCNT nanocomposite using triple DC thermal plasma jet system

Seung-Hyun Hong¹, Tae-Hee Kim², Jeong-Hwan Oh¹, Minseok Kim¹ and Sooseok Choi^{1,2*}
¹ Department of Nuclear and Energy Engineering, Jeju National University, 102 Jejudachak-ro, Jeju 63243, Republic of Korea
² Institute for Nuclear Science and Technology, Jeju National University, 102 Jejudachak-ro, Jeju 63243, Republic of Korea

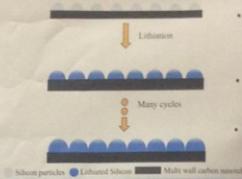
Introduction



Advantage of silicon as an anode electrode

Materials	Carbon (current anode material)	Silicon
Lithiated phase	LiC ₆	Li ₁₅ Si ₄
Specific capacity (mAh/g)	372	4200
Volume change (%)	12	420

Role of MWCNT in Si-MWCNT anode material



- Silicone anode material has high specific capacity but difficult to commercialize due to significant volume expansion.
- The high tensile strength of MWCNT prevents the volume expansion of silicon.
- We propose synthesis of Si-MWCNT according to the mass ratio.

Experimental set-up

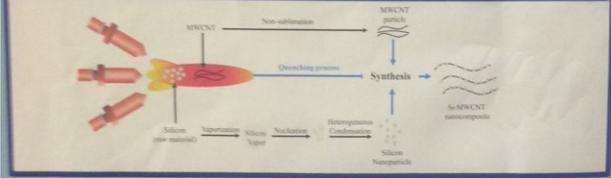
Thermal plasma system used for Si-MWCNT synthesis consists of a power supply, triple plasma torch, powder feeder, reactors and cyclone filter. The mixed powder of micron sized Si and MWCNT was injected into the triple plasma jet as raw material. The detail of experimental condition is presented in the right Table.

Experimental Condition

Exp. no.	Exp.1	Exp.2	Exp.3
Total input power (kW)	18.6	19.1	19.9
Feeding rate (g/min)	0.32	0.31	0.5
Plasma forming gas (L/min)	N ₂ (6), Ar (4)		
Mass ratio of powder (Si: MWCNT)	2 : 1	5 : 1	1 : 2

◆ All experiments were carried out in atmospheric pressure

Synthesis process using triple DC thermal plasma jet system



Results and discussion

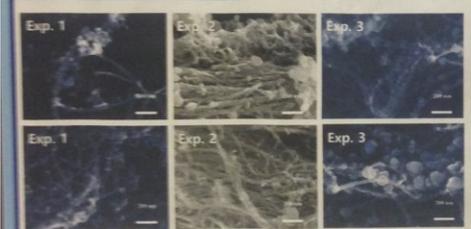


Fig 1. FE-SEM images of synthesized powder in Exp. 1, 2, and 3.

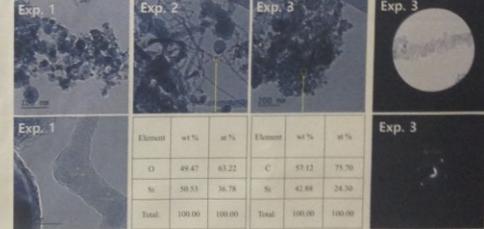


Fig 2. FE-TEM images and SAED patterns of synthesized powder in Exp. 1, 2, and 3. Elemental composition of nanowire (Exp. 2) and nanoparticles (Exp. 3) by EDS analysis

Table 1. Average diameter of synthesized nanomaterial in Exp. 1, 2, and 3.

	Exp. 1	Exp. 2	Exp. 3
Silicon (nm)	62.84	100.67	53.52
MWCNT (nm)	18.09	19.11	20.57

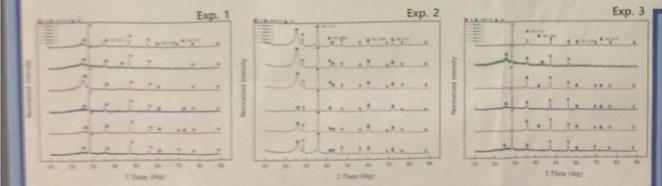


Fig 3. XRD patterns of synthesized product in Exp. 1, 2 and 3 according to the separated source.

Summary and future plan

- Si-MWCNT nanocomposite synthesis experiments were conducted according to the mass ratio of Si and MWCNT as raw material.
- For the high mass ratio of MWCNT (Exp. 3), the peak intensity of silicon carbide was strongest in the XRD and Si-MWCNT nanocomposite structure was observed relatively well in FE-SEM analysis.
- When the mass ratio of Silicon was high, large circular silicon particle and silicon nanowire structure are observed and the diameter of the silicon particles was large. (Exp. 1, 2).

➢ Silicon nanoparticles and MWCNT were mainly observed in FE-TEM analysis. Some MWCNT was sublimated by injection into high temperature and synthesized silicon carbide nanoparticles.

➢ In order to enhance the synthetic process for Si-MWCNT nanocomposite synthesis, two powder feeding system will be applied to separately introduce the Si and MWCNT powder. Si powder should be injected into the high temperature of plasma flame to evaporate and produce Si nanoparticles, MWCNT should be introduced into relatively low temperature region of plasma jet tail to prevent sublimation and provide active site to nucleate Si.





Pure Silicon Nanoparticle Synthesis using Tandem Type of Induction Thermal Plasmas with Simultaneous Controlled Modulation of Upper- and Lower-Coil Currents

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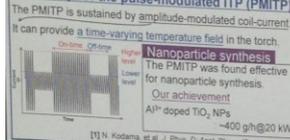
ISPC24
June 13, 2019
Naples, Italy

1. Introduction

The Induction Thermal Plasma (ITP) is widely used in materials processing from the following advantages:

- Extremely high gas temperature (~10,000 K)
- High density of chemical active species
- Contamination-less process (No electrode discharge)

In addition to the above features, we have developed a pulse-modulated ITP (PMITP) system. The PMITP is sustained by amplitude-modulated coil-current. It can provide a time-varying temperature field in the torch.



In order to increase production rate of NPs, more heavy load feeding of feedstock is necessary. However, the PMITP is weak against a large disturbance. To enhance the stability of the PMITP,

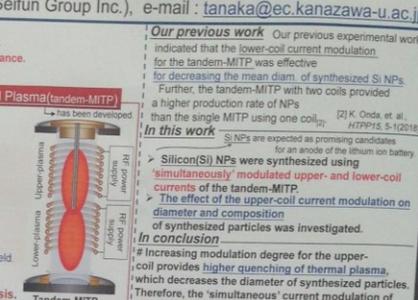
Tandem Type of Modulated Induction Thermal Plasma (tandem-MITP)

It has two separate coils and two RF power supply.

Advantages of the tandem-MITP

- Complete evaporation of feedstock is expected from its axially long high temperature field.
- Tempo-spatially varying temperature field can be offered by modulating upper- and lower-coil currents.
- Stable processing is expected by the two coils:
 - The upper-coil is used to maintain the ITP.
 - The lower-coil is used to obtain a larger varying temperature field.

These advantages can offer more efficient and stable nanoparticle synthesis.



Our previous work Our previous experimental work indicated that the lower-coil current modulation for the tandem-MITP was effective for decreasing the mean diam. of synthesized Si NPs.

Further, the tandem-MITP with two coils provided a higher production rate of NPs than the single MITP using one coil. [2] K. Onda et al., ITP'19, 5-1(2018)

In this work

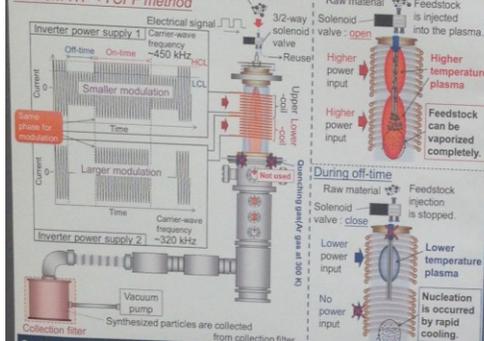
- Si NPs are expected as promising candidates for an anode of the lithium ion battery.
- Silicon(Si) NPs were synthesized using 'simultaneously' modulated upper- and lower-coil currents of the tandem-MITP.
- The effect of the upper-coil current modulation on diameter and composition of synthesized particles was investigated.

In conclusion

Increasing modulation degree for the upper-coil provides higher quenching of thermal plasma, which decreases the diameter of synthesized particles. Therefore, the 'simultaneous' current modulation of tandem-coils enhances the efficiency of NPs process.

2. Experimental setup

Tandem-ITP + TCF method



3. Experimental condition

Common conditions		Modulation conditions	
Time-averaged input power	Upper: 10 kW Lower: 4 kW	Cond (1)	Cond (2)
Pressure	300 torr	100%	100%
Sheath gas flow rate	Ar: 90 L/min	0%	0%
Carrier gas flow rate	Ar: 4 L/min	100%	0%
Feedstock	Si(97% purity) mean diam. (d) = 26 μm	0%	0%
Valve open/close	6 ms / 9 ms	2.80	1.51
		2.99	2.93
		2.64	

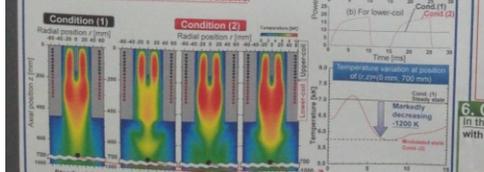
Definition of modulation degree SCL
SCL_{low} = Lower current level (LCL) [A]
SCL_{high} = Higher current level (HCL) [A]
Note: 0% SCL is most high modulation degree, which corresponds to zero current amplitude during off-time.

The solenoid valve was controlled for feedstock to be synchronically supplied into the MITP just during on-time. Quenching gas was not used for fundamental study.

5. Discussion (Temperature field from numerical simulation)

A thermo-fluid field in a tandem-MITP was computed without considering a powder injection.

Numerical conditions were set to the same for the experiment. For cond. (1) and (2) simulation and comparison were done. Powder injection was neglected for simplicity. The power of only a lower-coil was modulated.

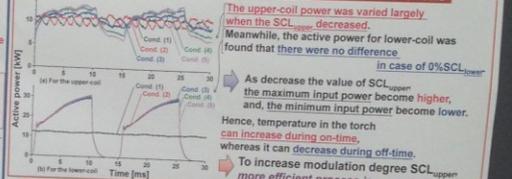


The temperature increases during the on-time. The modulated evaporation may provide and decreases during the off-time effectively completely evaporation during on-time and efficient cooling during off-time are expected.

It is found that a larger modulation of the tandem-MITP is effective for nanoparticles synthesis.

4. Experimental results for nanoparticle synthesis

Responses of the active power of the upper- and lower-coils



SEM images of synthesized particles collected from the filter



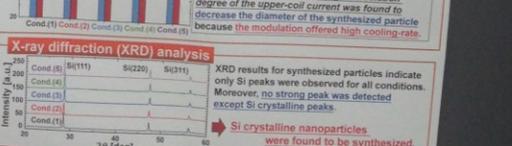
These figures indicate that spherical nanoparticles were successfully fabricated using the tandem-MITP with current amplitude modulation. These morphologies imply that the synthesized particles grew up in a vapor phase to have sphere shapes.

Particle size distribution (PSD)



In case of cond. (5), a high yield ~91% for synthesized particles and a smaller diameter ~59 nm were obtained despite of no quenching gas condition. From the PSDs estimated, a high modulation degree of the upper-coil current was found to decrease the diameter of the synthesized particle because the modulation offered high cooling rate.

X-ray diffraction (XRD) analysis



6. Conclusion

In this study, pure silicon nanoparticles were synthesized using tandem-MITP with 'simultaneous' modulation of an upper- and lower-coil currents.

- The power variation of the modulation.
- Morphologies and size distribution of the obtained particles.
- Compositions of the particles.

Result: 1. Decreasing SCL_{upper} for upper-coil current raised a max. power and reduced 2. Larger modulation with a 'simultaneous' modulation raised a min. power for both upper and lower-coil enhanced a yield of the fabricated particles. 3. Pure silicon nanoparticles were successfully obtained with ~70 g/h@20 kW even without quenching gas/ currents provides a efficient nanoparticle synthesis.

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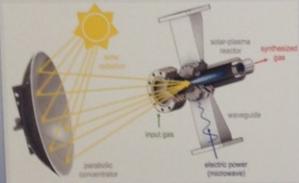
Abstract

The conversion of CO₂ using renewable energy can help mitigate environmental emission and address global fuel needs. Solar thermochemical processes have the greatest sustainability potential, but are limited by the low reactivity of CO₂ and the intermittency of solar radiation. In contrast, plasma processes have the potential for high efficiency and continuous operation. The synergistic combination of microwave plasma and concentrated solar is investigated as a novel approach for greater viability CO₂ conversion.

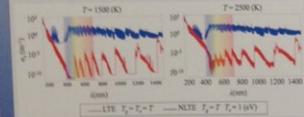
1. Introduction

Solar Enhanced Microwave Plasma (SEMP)

- Microwave plasmas have potentially the highest energy efficiencies for molecular dissociation via effective step-wise vibrational excitation
- Solar thermochemical synthesis processes directly utilize the solar energy as a most abundant form of renewable energy.
- Solar enhanced microwave plasma (SEMP) is motivated by the potential for synergistic effects from the interaction between solar photons and plasma-generated species [1, 2]



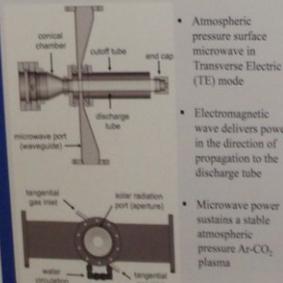
- Potential for synergism suggested by higher absorption of solar energy by CO₂ in non-Local Thermodynamic Equilibrium (NLTE) – potential for greater reactivity



Absorption coefficient of CO₂ in LTE and NLTE computed with the SPARTAN code [1]

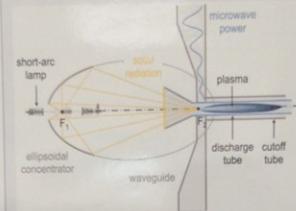
2. Reactor Design

SEMP reactor components



- Atmospheric pressure surface microwave in Transverse Electric (TE) mode
- Electromagnetic wave delivers power in the direction of propagation to the discharge tube
- Microwave power sustains a stable atmospheric pressure Ar-CO₂ plasma

Solar concentrator - SEMP reactor set-up



- High-flux solar simulator: 6.5 kW short-arc Xe lamp
- The center of the electric arc inside the short-arc lamp and the plasma generation point are located at the focal points F₁ and F₂, respectively

3. Experimental setup

SEMP reactor, Solar simulator, delivery and diagnostics systems



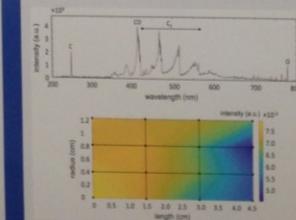
- Components: magnetron, waveguides, solar-plasma reactor, high-flux solar simulator, gas delivery system, water circulation, power monitoring, emission spectrometer, and gas chromatography

SEMP reactor under operation



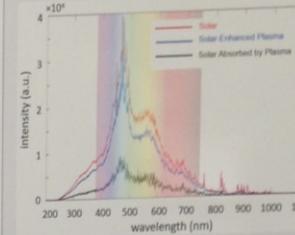
- Conical aperture – concentrated solar flux reception
- Vortex inflow – prevent deposition over aperture, enhanced stability of plasma
- Tapered waveguide – power concentration
- Cutoff tube – mitigate electromagnetic losses

Plasma emission spectra (off-solar characterization)

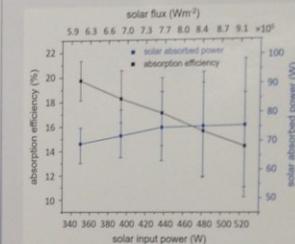


Atmospheric pressure operation with 100% CO₂ shows strong emission in the C₂ Swan bands - indicate of significant decomposition

4. Solar Radiation Absorption

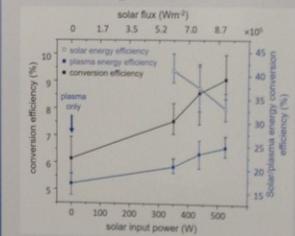


Lower intensity of solar radiation at the outlet of the reactor indicates the absorption by microwave plasma



Higher absorption efficiency and less absorbed power for higher solar power input

5. CO₂ Decomposition



Higher conversion and plasma conversion energy efficiency of CO₂ for higher solar power input

6. Summary and Conclusions

- Enhancement of microwave plasma process by solar radiation: increased sustainability, efficiency and resiliency of chemical synthesis
- Absorption of up to 20% of incident concentrated solar radiation by the plasma at the lowest solar input power
- Conversion and plasma energy conversion efficiency increase with increasing solar power input, achieving up to 9% and 25%, respectively

Acknowledgements

Financial support provided by the U.S. National Science Foundation award CBET-1552037

References

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- Nagassou, D., Mohsenian, S., Bhatta, S., Elahi, R., Trelles, J.P., 2019. Solar Energy, 180, 678-689
- Lim da Silva, M., Lopez, B., Espinho S. (2013) SPARTAN 2.5

Investigation of an atmospheric pressure 2.45 GHz microwave CO₂ plasma source: comparison of pulsed and CW operation

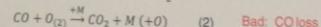
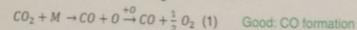


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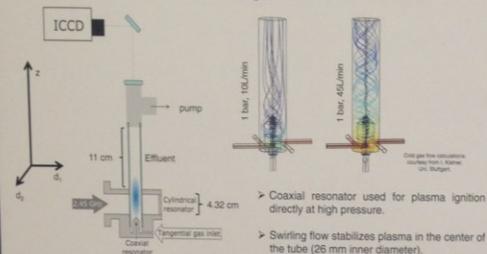
Introduction

How to improve CO₂ conversion?



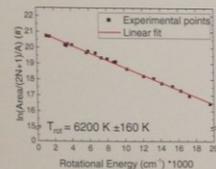
Electron temperature, gas temperature, cooling rates and flow dynamics are believed to be the limiting processes to improve (1) and minimize (2).

→ Spectroscopic diagnostics used for probing T_{gas} and plasma emission volume.

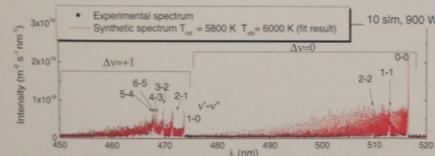


- Coaxial resonator used for plasma ignition directly at high pressure.
- Swirling flow stabilizes plasma in the center of the tube (25 mm inner diameter).

OES characterization of the plasma (T_{gas})

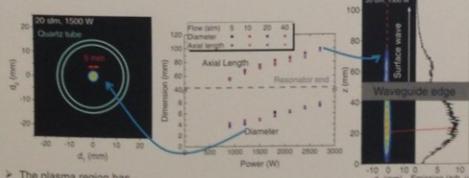


- Emission spectrum dominated by C₂ Swan Band d³Π_g → a³Π_u.
- Rotational levels of C₂(d³Π_g) are Boltzmann distributed.
- Emission spectra fit with massive OES [1] and line database [2] gives T_{rot} and T_{ob}.



The rotational and vibrational levels of C₂(d³Π_g) are Boltzmann distributed within statistical errors. Rotational energy transfer rates of C₂(d³Π_g) are consistent with assumption that T_{rot} = T_{gas}.

Power deposition profile



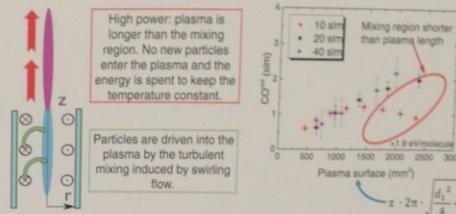
- The plasma region has been defined as the region where the light intensity is above 15% of the maximum intensity.
- Plasma extends in the effluent due to coupling of surface wave onto the plasma surface.

Cross section and axial length of plasma emission do not depend on CO₂ gas flow.

Conclusions and Outlook

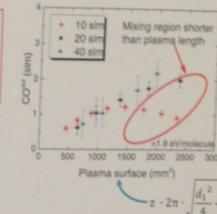
- The CO₂ conversion is dominated by thermal conversion both in CW operation and in kHz pulsed plasma.
- The flow dynamic completely dominates the conversion of CO₂.
- The C₂ density behavior in the plasma afterglow can be described by temperature decay at thermal equilibrium.

Thermal CO₂ conversion and flow dynamics



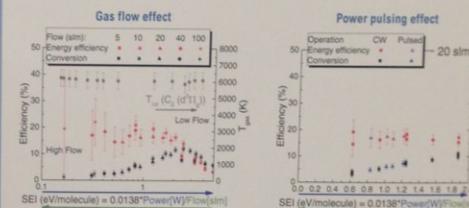
High power: plasma is longer than the mixing region. No new particles enter the plasma and the energy is spent to keep the temperature constant.

Particles are driven into the plasma by the turbulent mixing induced by swirling flow.

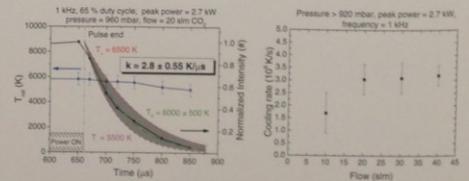
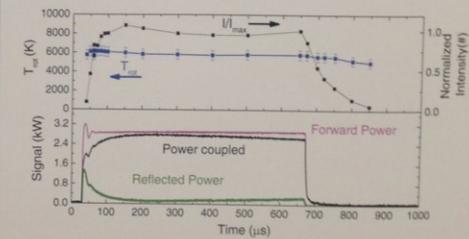


The influx of particles into the plasma region determines the CO out flux, that does not depend on the input flow (between 10 and 20 s/m).

Does MW pulsing change something?



Conversion in pulsed operation is equivalent to the conversion in continuous mode (CW) with Power = duty cycle · Peak Power



- Using a thermodynamic model (NASA-CEA code [3]) based on minimization of Gibbs free energy $G(p, T) = H - TS$ → decay of C₂ state density can be described using the decay of T_{gas}.
- The cooling rate weakly depends on the CO₂ flow and saturates to a value of 3 K/μs for flow higher than 20 s/m.

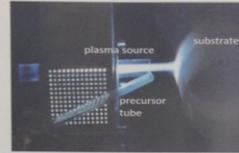
[1] J. Moril and P. Snyek, "Batch processing of overlapping molecular spectra as a tool for spatial-temporal diagnostics of power modulated microwave plasma jet", Plasma Source Science and Technology 2017, doi:10.1088/1361-6595/aa660d
 [2] J. A. Brooks, "Line strengths and updated molecular constants for the C₂ Swan system", Journal of Quantitative Spectroscopy and Radiative Transfer 2013, 124, 11–20
 [3] Gordon, Searles and McBride, Bureau J. New reference publication, 1911 (1984).

MOTIVATION

A microwave (MW) plasma torch operated at atmospheric pressure at a frequency of 2.45 GHz is currently studied for multi-component doping of silica preforms.

The determination of the plasma parameters in the region of plasma-precursor interaction is of primary importance for the technological application since

- the plasma parameters in the plume depend on the conditions inside the plasma source
- the source is hardly accessible by diagnostics methods.



CONCLUSIONS AND OUTLOOK

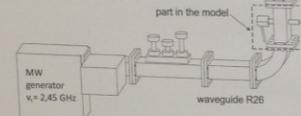
The gas temperature was determined in the MW plasma source and in the plume by means of self-consistent modelling, emission spectroscopy and thermography.

Since gas temperatures are still not determined in oxygen-containing mixtures with the admixture of any precursor materials, future studies will be extended to such application-oriented plasmas. Additionally, the influence of the deposition target on the plasma and its temperatures will be investigated in more detail.

PHYSICAL BACKGROUND

Experimental arrangement

The plasma source consists of a standard waveguide R26 and a quartz tube traversing at the position of maximum electric field of the fundamental mode TE₁₀. Argon/oxygen mixtures are employed as working gas. The plasma jet is directed towards a rotating substrate



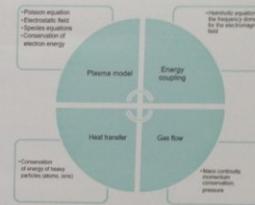
Equipment: optical emission spectrometer (a 500 nm imaging spectrograph SP-2556 by Roper Acton is combined with an intensified CCD camera PI-MAX4:1024I-RB by Princeton Instruments); thermographic camera VarioCAM by InfracTec.

Operation conditions

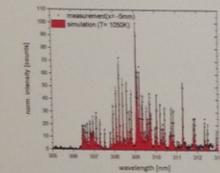
pressure: 1.01 10⁵ Pa
 working gas: Ar/O₂ - mixtures,
 flow rate 10-20 slm
 frequency: 2.45 GHz,
 power: 1-2 kW in continuous operation,
 tube: made of quartz,
 inner radius 6.1 mm,
 tube length outside the resonator: L_{out}=15-38 mm,
 distance from the tube end to the target: 20-50 mm

Self-consistent modelling approach

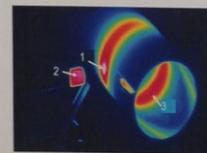
The model is based on a hydrodynamic approach. Its equations describe self-consistently the gas flow, the plasma kinetics, the heat transfer, and the microwave field in the waveguide [1].



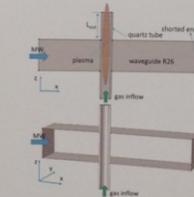
Example of measured and calculated OH-spectra in the argon jet without substrate



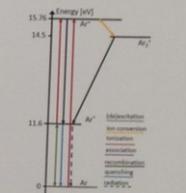
Thermography at the place of deposition



Schematics of the MW plasma source

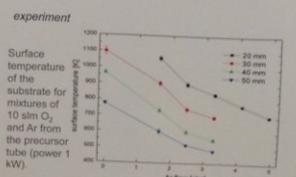
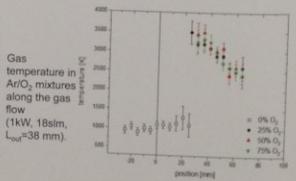
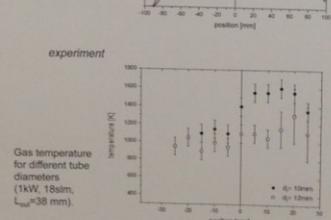
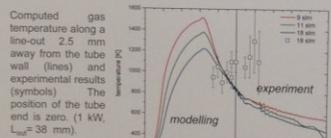
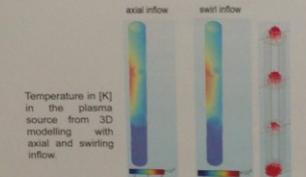
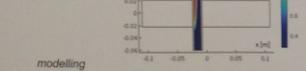


Energy and reaction scheme



EXPERIMENTAL AND MODELLING RESULTS

Two-dimensional distribution of the gas temperature in the plasma source and in the plume (incident power 1 kW, flow rate 8 slm).



References:
 [1] M Baeva, F Hempel, H Baier, T Trautvetter, R Foest, D Loffhagen, J Phys D: Appl Phys 51 (2018) 385202

Acknowledgments
 This work was supported by the Leibniz-Gemeinschaft: SAW-2017-4PH-T-1. The technical support by Daniel Köpp is greatly acknowledged.

Abstract: Hydroxyl radical is measured as function of distance, flux and microwave power in atmospheric pressure argon microwave plasma expanding in air. Employing mass spectrometry and optical emission spectroscopy the plasma jet was characterized and the conditions for maximum production of OH were determined. The kinetics of OH was discussed and its relationship with other radicals like as H_2O_2 , H_2O , H_3O and NO , was addressed.

1. Introduction

In this work the production and loss channels of OH in an atmospheric pressure plasma jet generated by a Surfatron launcher expanding in air was studied. A microwave power generator of 2.45GHz was employed to feed a Surfatron surface-wave launcher. The power was varied between 30W and 100W, flux of 2.5 SLM and 5.0 SLM and the gas used to produce the discharges was argon. Employing mass spectrometry measurements, the main neutral and positive ions along the jet are measured as function of operating parameters of the plasma. Axial variation of plasma parameters n_e , T_e , and T_g in was measured by optical emission spectroscopy (OES).

2. Experimental apparatus

The experimental set-up used for OES diagnostics was detailed in a previous publication [1]. As shown in figure 1, the experimental apparatus includes the plasma source, the mass spectrometer and data acquisition system for measurements.

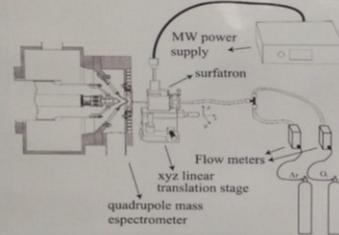


Figure 1. Arrangement employed in mass-spectrometer diagnostics.

3. Results

The understanding of the kinetics of the intermediate short-lived radical OH and the stable H_2O_2 depends not only on the knowledge of other species such as H_2O , but also on the subsequent chain and end reactions.

Figure 2 shows the density of OH, H_2O , H_2O_2 , H_3O and NO as function of distance when the plasma is excited by 100W of microwave power. The OH intensity initially decreases after Surfatron exit until a minimum at 2.5 mm growing after to a maximum at ~11 mm, corresponding the maximum density of electrons. As n_e maximum is at ~11 mm, electron-ion recombination should be the most important mechanism for OH production in this region, while at the Surfatron exit the electric power density is high and electron dissociation may also be an important reaction for production of hydroxyl radical.

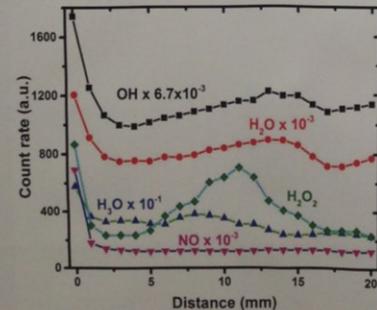


Figure 2. Mass flux of neutral radicals as function of distance; microwave power of 100 W and flux of 5.0 SLM. OH (filled square), H_2O (filled circle), H_2O_2 (filled diamond), H_3O (up filled triangle) and NO (down filled triangle).

In figure 3 it can be seen that maximum of OH count rate for power of 100 W occurs at 5 mm from the Surfatron exit while for 150 W the intensity continuously grows until distance of 10 mm after which a small decrease is observed.

In figure 4 the flux was varied from 2.5 to 7.5 SLM. As the flux increases the maximum intensity of the OH moved to higher distances. This occurs because the point of turbulence development gets closer to the jet nozzle as the flux increases favoring the injection of the H_2O into the plasma.

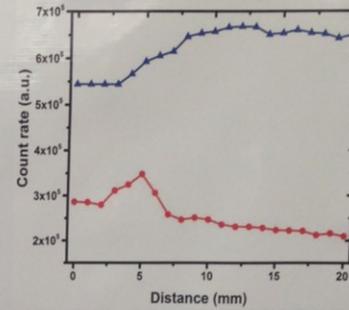


Figure 3. OH as function of distance; flux of 2.5 SLM, 100 W (filled circle) and 150 W (up filled triangle).

This effect improves the mixing of ambient air particles with the effluent plasma jet in the region near the nozzle forming H_2O^+ and H_3O^+ ions but the position of maximum electron density gets closer to the plasma tip as the flow increases. The resulting net balance of ionization and dissociative electron attachment is the profile presented in figure 4.

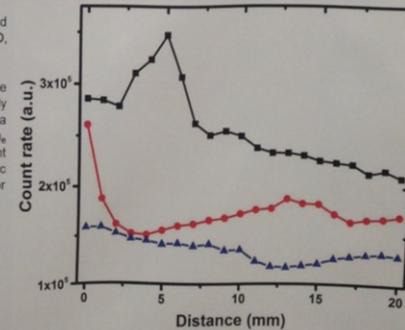


Figure 4. OH as function of distance; power of 100 W and flux of 2.5 SLM (filled square), 5.0 SLM (filled circle) and 7.5 SLM (up filled triangle).

4. Conclusion

It was shown that hydroxyl radical mass flux intensity initially decreases after Surfatron exit until a minimum at 3 mm growing after to a maximum at ~11 mm corresponding the maximum density of electrons. OH intensity tends to increase like the electron density and gas temperature, in the range of powers and fluxes investigated. Electron-ion recombination is the most important mechanism for OH production in this region.

References

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Introduction

Low pressure and low temperature plasma is a non-thermal technology. The absence of toxic components and the large volume treatment capacity provide a good alternative to the conventional spices decontamination methods [1].

The process optimisation requires an excellent understanding and control of plasma characteristics. This includes the fundamentals plasma parameters (n_e , T_e , FDEE...), the type of created species (photons, reactive species...), the gas temperature, the substrate influence on the plasma for example.

In this work, the plasma chemistry has been investigated by optical emission spectroscopy. Probes measurements have been performed first, to study the plasma parameters in several sustained conditions, and next, to understand the heating process of the substrate by the ionized gas.

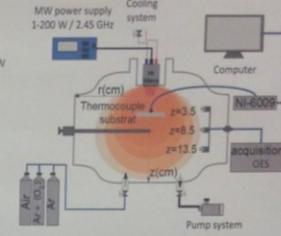
Experimental set-up

Set-up:

- Chamber volume: 40 L
- Gas: Ar, Ar-O₂ (2%), Air
- Source: Hi-Wave 2,45GHz (SAREM [2])
- Microwave power supply: $1 < P_{\text{MWS}} < 200$ W
- Pressure: $10 < p < 60$ Pa
- Radial axis: $0 < r < 18$ cm
- Axial axis: $Z = 3.5, 5.5, 8.5$ cm

Plasma diagnosis:

- Optical Emission Spectroscopy (OES)
- Boltzmann Plot (BP)
- Langmuir Probe (LP)
- MicroWave Interferometry (MWI)



Determination of T_e by the Boltzmann Plot and Langmuir Probe

Boltzmann Plot (BP): Calculation of T_e by inverting the slope of the following logarithmic functions:

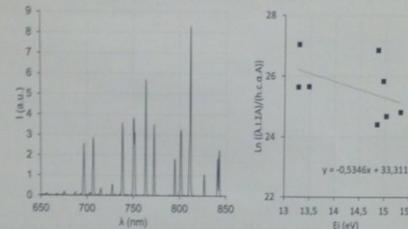
$$\ln \left(\frac{A_{ij} I_{ij} \sum_{k,j} A_{kj}}{h c \nu_{ij} A_{ij}} \right) = \frac{-E_i}{k_B T_e} + D$$

Requirements:

- Assuming the Corona model described by Fujimoto [3].
- Argon plasma characterisation by Optical Emission Spectroscopy: λ_{ij} and I_{ij} in our study ($\lambda_{ij} = 751.46, 750.38, 731.60, 731.17, 714.70, 706.87, 687.95$ and 516.22 nm).
- Literature data (NIST or [4]): A_{ij} , h , c , ν_{ij} , E_i and k_B .

Plasma conditions:

- Gas: argon
- Microwave power: 150 W
- Pressure: 15 Pa



Langmuir probe (LP): Calculation of T_e from the $I(V)$ curve measured with the probe at $Z = 8.5$ cm.

Plasma conditions:

- Gas: argon
- Microwave power: 150 W
- Pressure: 15 Pa

Diagnostics	T_e (eV)
Boltzmann plot	1.9 ± 0.5
Langmuir probe	1.4 ± 0.3

Determination of n_e by Langmuir Probe and MicroWave Interferometry

MicroWave Interferometry (MWI): Determination of n_e from the microwave beam phase shift crossing the plasma area [5].

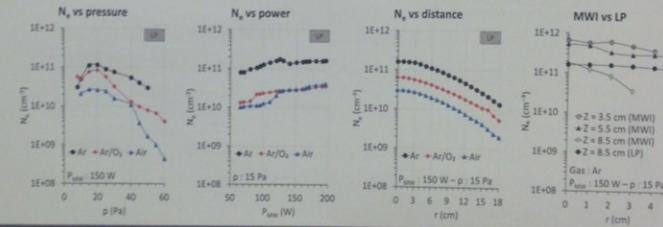
$$(n_e) = \frac{n_p \lambda_p}{\lambda} [\Delta\phi]$$

Requirements:

- Large reactor windows to avoid microwave reflexion (> 5 cm).
- Plasma length (> 6 cm).
- Homogeneous plasma.

Differences with Langmuir probe (LP):

- Non-invasive diagnostic.
- Suitable for etching or depositing plasma applications.
- Give the average electron density in the line of sight.



Substrate temperature measurements

P_{sub} is the microwave power quantity transferred to the substrate. Two methods have been used to calculate P_{sub} .

A. By deducing P_{sub} from temperature measurement

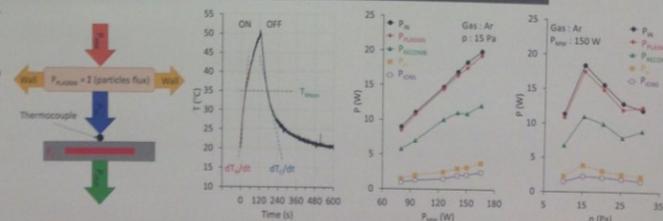
1. Establish the balance power provided by the generator.
2. Measure the substrate temperature variation in the plasma ON/OFF phase using a type K thermocouple.
3. Resolve the following equation:

$$P_{\text{th}} = P_{\text{p}} + P_{\text{cool}} = C_p \left(\frac{dT_{\text{sub}}}{dt} - \frac{dT_{\text{amb}}}{dt} \right) T_{\text{sub}} \quad [\text{W}]$$

B. By calculating P_{sub}

$$P_{\text{th}} = P_{\text{microwave}} = P_{\text{e}} + P_{\text{ionization}}$$

Details are given in [4] and [6].



Conclusion

$1.9 < T_e$ (eV) < 2.0 : Boltzmann plot method can be an alternative to Langmuir probe measurement but high resolution spectrometer is strongly recommended to minimize optical data deviation.

$3.00 \times 10^9 < n_e$ (cm⁻³) $< 3.50 \times 10^9$: MicroWave Interferometry is complementary to probe measurement. It can reach plasma zone inaccessible to Langmuir probe.

$P_{\text{sub}} = 12\%$ of P_{MWS} at $Z = 8.5$ cm: Both methods show a good correlation. Others experiments would be done closer to the source.

References and acknowledgements

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