Plateforme Nationale de Frittage Flash

Geoffroy CHEVALLIER

GFDM-FACE

Groupe Francophone de Densification de Matériaux par Frittage Assisté sous Champ Électromagnétique

Programme de la Journée

9h30-10h Accueil des participants - Café

10h-10h25 « Présentation des activités FACE au Centre Inter-universitaire de Recherche et d'Ingénierie des Matériaux » (Geoffroy CHEVALLIER, C. ESTOURNES, CIRIMAT)

10h25-10h50 « Présentation des activités FACE au Laboratoire de Cristallographie et Sciences des Matériaux » (Jacques NOUDEM, CRISMAT)

10h50-11h15 « De l'optique à l'énergie: frittage SPS de verres, composés à clusters et intermétalliques à l'Institut des Sciences Chimiques de Rennes » (Mathieu PASTUREL, ISCR)

11h15-11h40 « Fabrication de pièces complexes Near Net Shape par SPS » (Arnaud FREGEAC, NORIMAT)

11h40-12h05 « Activités FACE à l'Institut de Chimie et de la Matière Condensée de Bordeaux » (U-Chan CHUNG, ICMCB)

12h05-12h30 "Bref aperçu des activités passées et actuelles en matière de densification par SPS et frittage flash au Centre de Recherches de l'Industrie Belge de la Céramique » (Jean-Pierre ERAUW, Vedi DUPONT, Laurent BOILET, CRIBC)

12h30-12h55 « Présentation des activités FACE à l'Institut de Chimie et des Matériaux de Paris-Est » (Judith MONNIER, ICMPE)

13h-14h30 Buffet

14h30-16h30 Assemblée générale

Création en 2004 à Toulouse : premier SPS en France

Accessible à tous les laboratoires

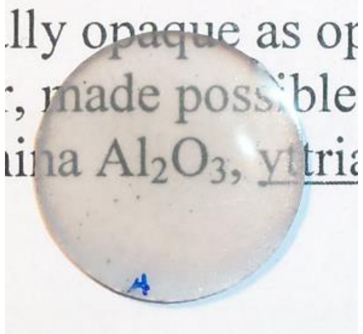
Mise en forme de tous types de matériaux

Plateforme Nationale de Frittage Flash

Création en 2004 à Toulouse : premier SPS en France

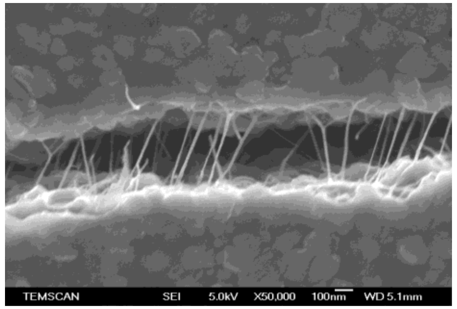
Accessible à tous les laboratoires

Mise en forme de tous types de matériaux

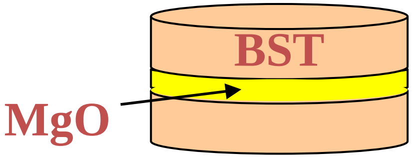


Céramiques

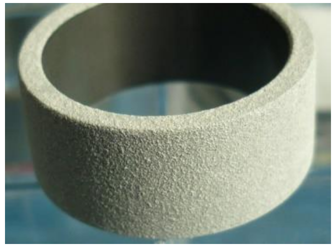
Métal



Composites [1]



Multicouches [2,3]



Revêtements

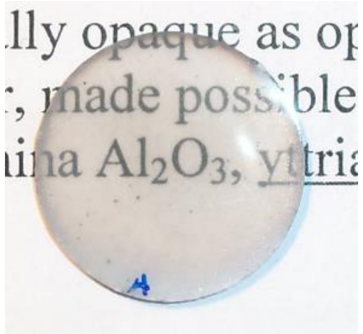
[1] A. Peigney, Carbon (2010)
[2] C. Elissalde, J. Am. Ceram. Soc. (2007)
[3] U-Chan Chung, Appl. Phys. Let. (2008)

Plateforme Nationale de Frittage Flash

Création en 2004 à Toulouse : premier SPS en France

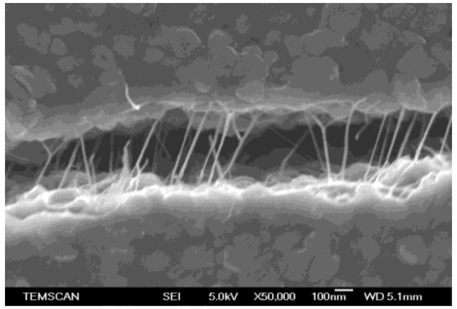
Accessible à tous les laboratoires

Mise en forme de tous types de matériaux

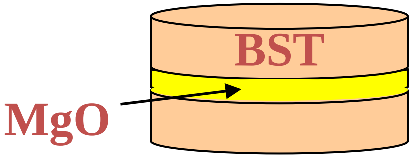


Céramiques

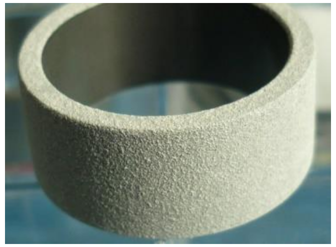
Métal



Composites (1)



Multicouches (2,3)



Revêtements

Plus de 27 000 échantillons

Contact : geoffroy.chevallier@univ-tlse3.fr

(1) A. Peigney, Carbon (2010)
(2) C. Elissalde, J. Am. Ceram. Soc. (2007)
(3) U-Chan Chung, Appl. Phys. Let. (2008)

Equipements

Fuji 632 Lx

Imax : 3000 A
Fmax : 60 kN
Atm : Vide (< 10 Pa) / Ar
Φmax : 30 mm

Equipements

Fuji 632 Lx

Imax : 3000 A
Fmax : 60 kN
Atm : Vide (< 10 Pa) / Ar
Φmax : 30 mm

Dr Sinter 2080

Imax : 8000 A
Fmax : 200 kN
Atm : Vide (< 10 Pa) / Ar / N_2
Φmax : 100 mm

Equipements

Fuji 632 Lx

Imax : 3000 A
Fmax : 60 kN
Atm : Vide (< 10 Pa) / Ar
Φmax : 30 mm

Tmax : 2200°C
Pmax : 150 MPa

Dr Sinter 2080

Imax : 8000 A
Fmax : 200 kN
Atm : Vide (< 10 Pa) / Ar / N_2
Φmax : 100 mm

Outillages

Graphite : Toyo Tanso ISO68

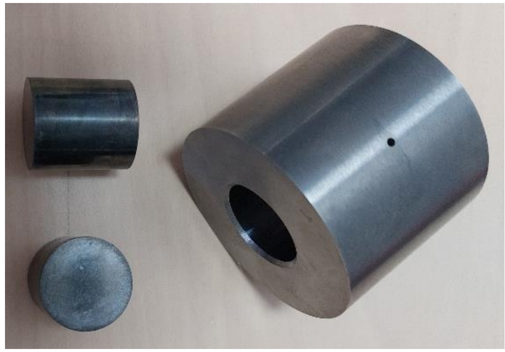
Tmax : 2200°C
Pmax : 150 MPa
Φmax : 100 mm

Outillages

Graphite : Toyo Tanso ISO68

Tmax : 2200°C
Pmax : 150 MPa
Φmax : 100 mm

WC/Co : Pedersen

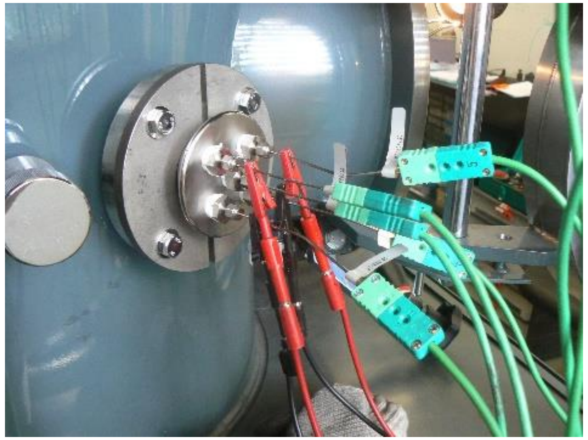


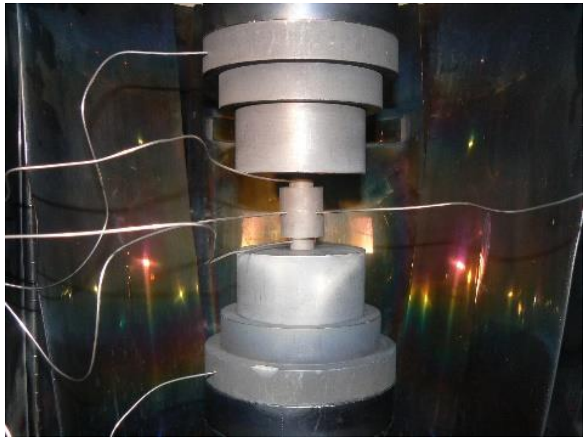
Tmax : 800°C
Pmax : 2000 MPa
Φmax : 30 mm
Essais sous air

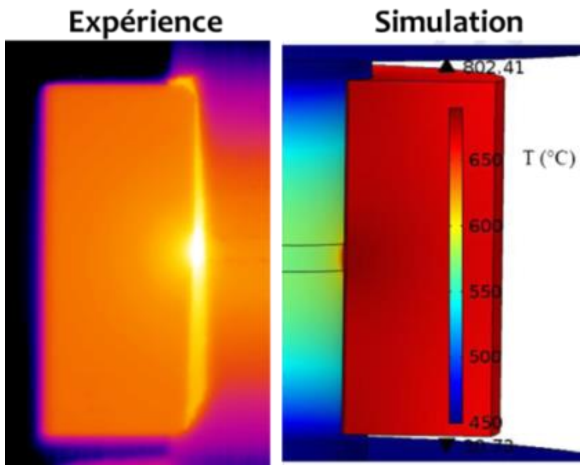
Instrumentation

Conception d’un passage étanche pour capteurs (température, courant, tension)

Mesures in-situ
Réalisation d’un programme informatique (LabView)
Alimentation d’un modèle numérique multiphysique





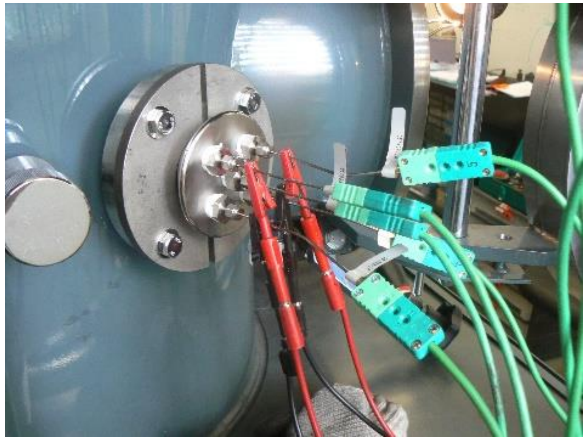


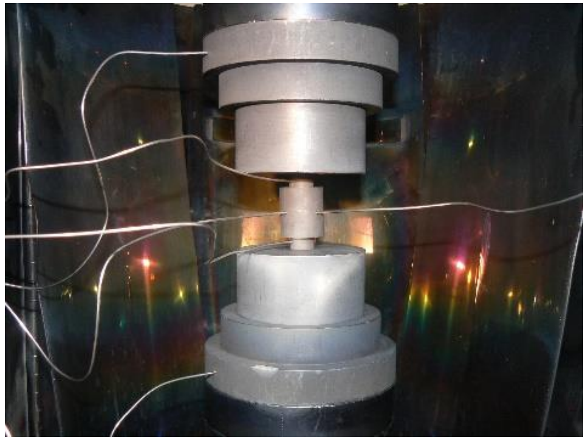
ANR Impulsé 2009 – 2014
Doctorat Pavia 2009 – 2012
Doctorat Manière 2012 - 2015

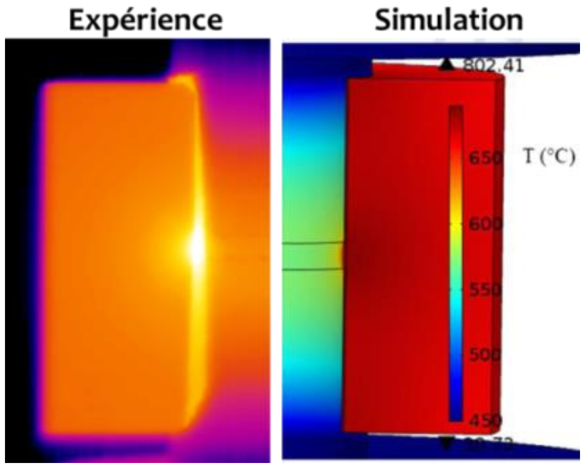
Instrumentation

Conception d'un passage étanche pour capteurs (température, courant, tension)

Mesures in-situ
Réalisation d'un programme informatique (LabView)
Alimentation d'un modèle numérique multiphysique

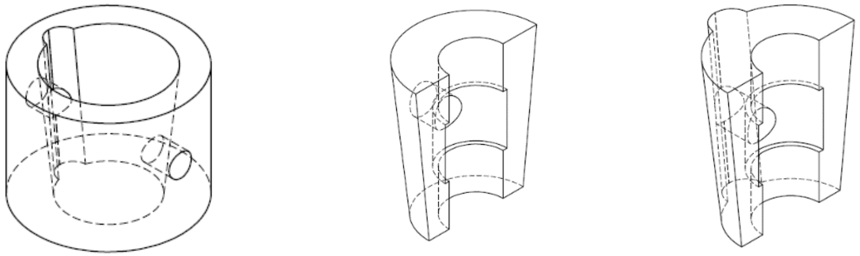


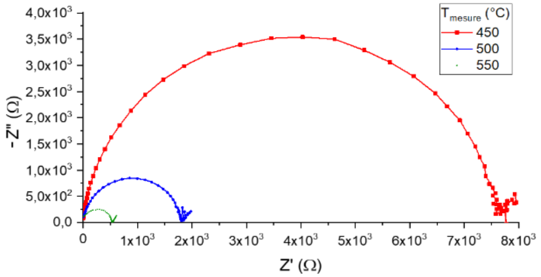




ANR Impulsé 2009 – 2014
Doctorat Pavia 2009 – 2012
Doctorat Manière 2012 - 2015

Conception d'un outillage pour mesures d'impédance *in situ*

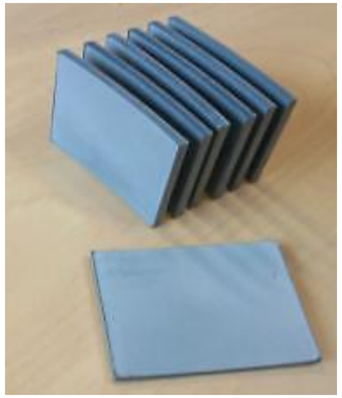




Doctorat A. Flaureau 2017 - 2020

Formes complexes

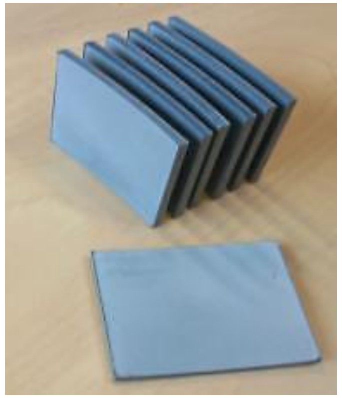
Conception d'outillages à la contre-forme (→ pièces directement aux cotes)



Contrats SAFRAN - 3 brevets

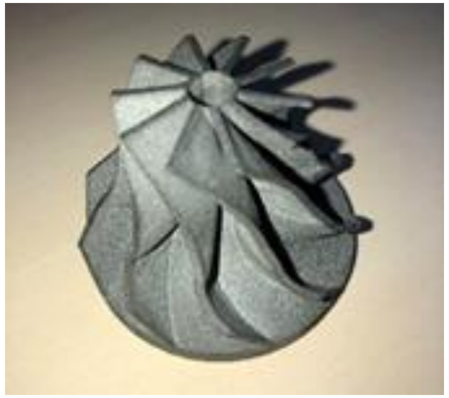
Formes complexes

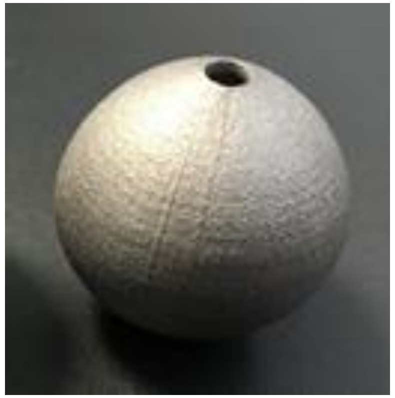
Conception d'outillages à la contre-forme (→ pièces directement aux cotes)



Contrats SAFRAN - 3 brevets

Couplage SPS - techniques additives (fusion laser, impression 3D céramiques)

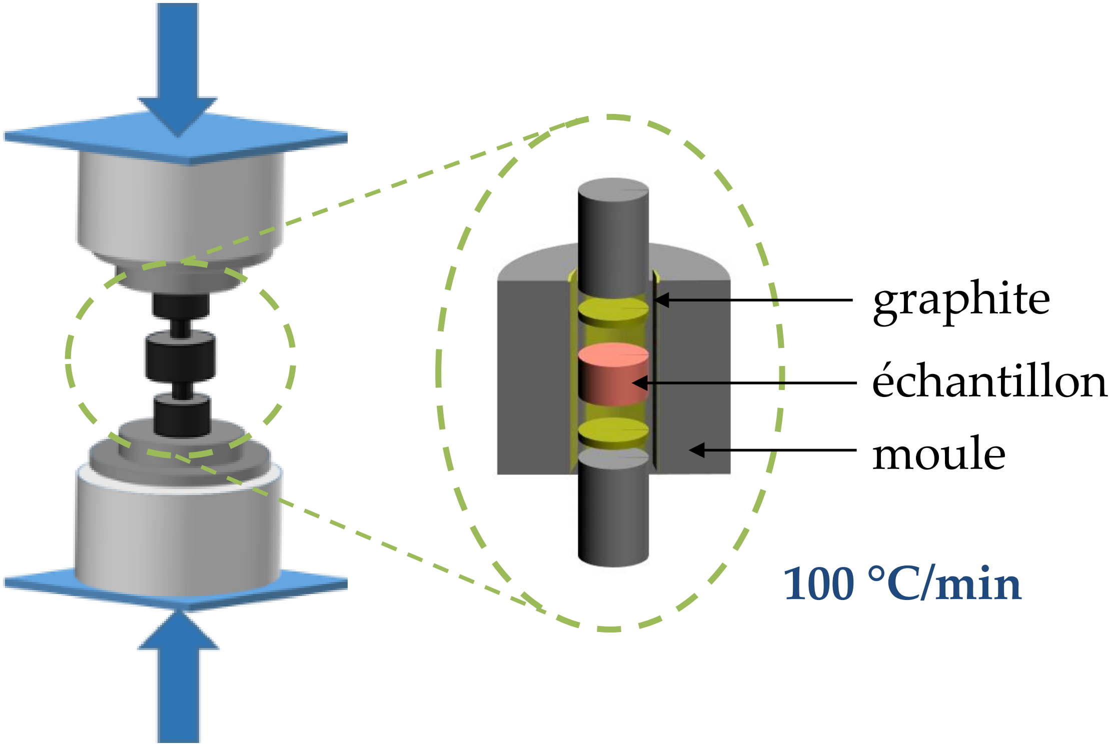




3 brevets CNRS/UPS

Développements

Pression + courant **SPS**



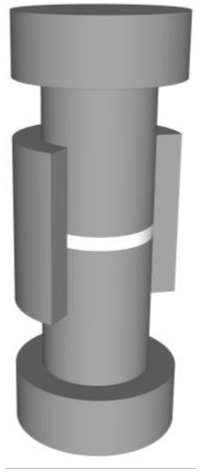
100 °C/min

FSPS

- Parois du moule fines (5mm)
- Puissance maximale machine

➔ **Rampes très élevées**

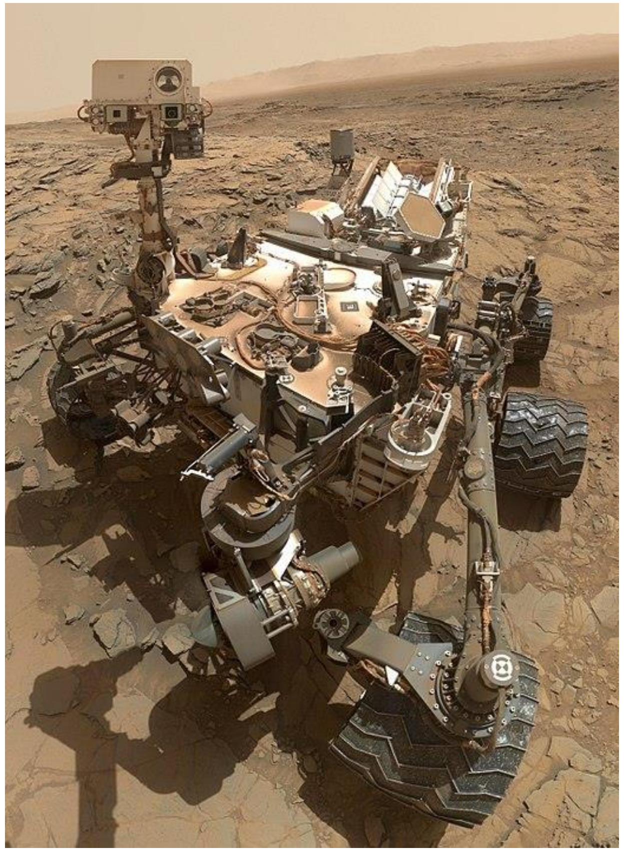
10 000 °C/min



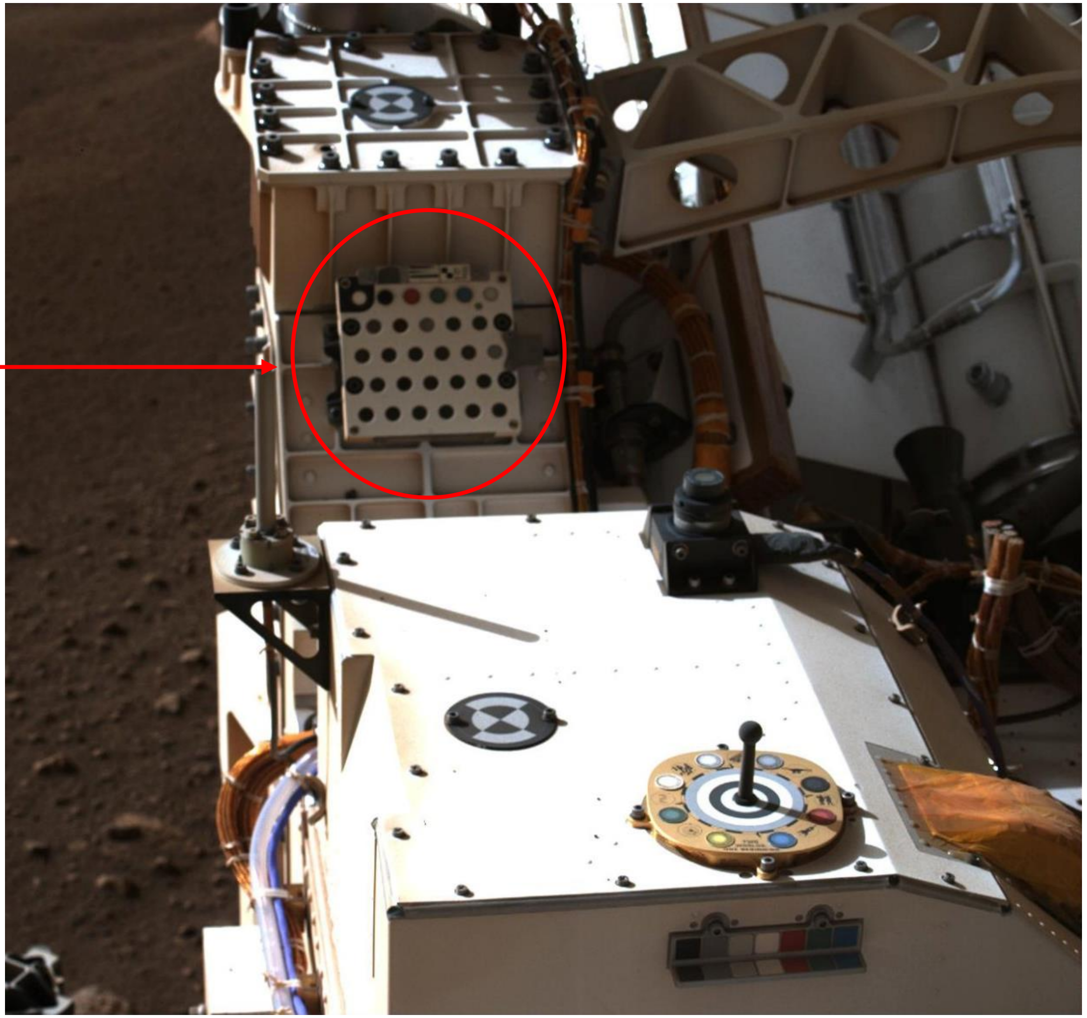
3YSZ : Impact sur microstructure [4]

[4] T. Hérisson de Beauvoir, J. Eur. Ceram. Soc. (2021)

Merci de votre attention



Cibles de calibration densifiées à la PNF² et embarquées sur Perseverance ***Mars2020***

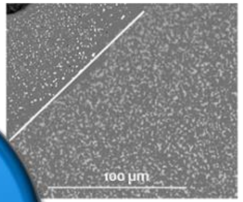


Activité au CIRIMAT

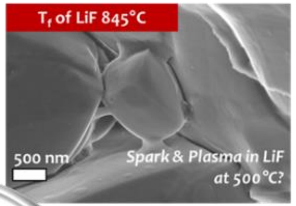
Claude ESTOURNES

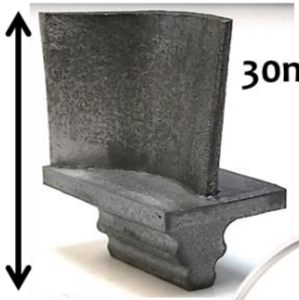
Activity of my team in the SPS field

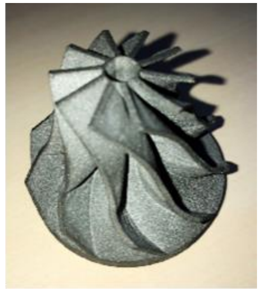
18 years of experience in the field
> 150 publications and 17 patents



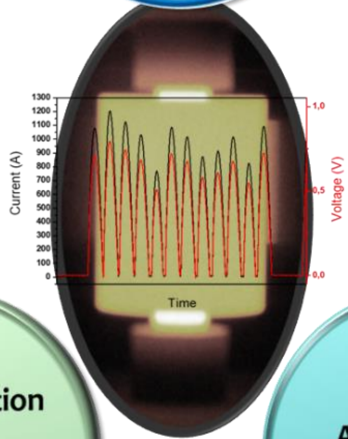
Densification, Consolidation, Reactive sintering



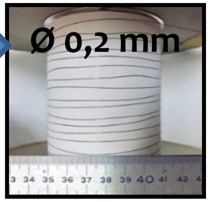


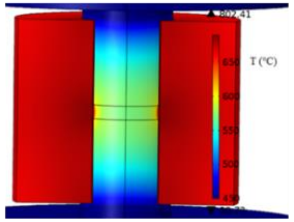


Complex Shapes and « Scale-up »



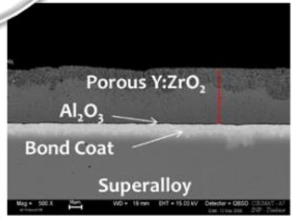
Sintering Mechanisms, Specific effects

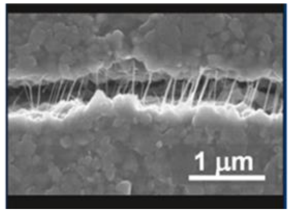




Instrumentation and Finite element Modelling

Association of Materials





Context

temperature

Kinetic

SINTERING

Thermodynamic

Relative control of the microstructures

Recent developments in sintering

Decreasing the **temperature** and/or **time** of sintering

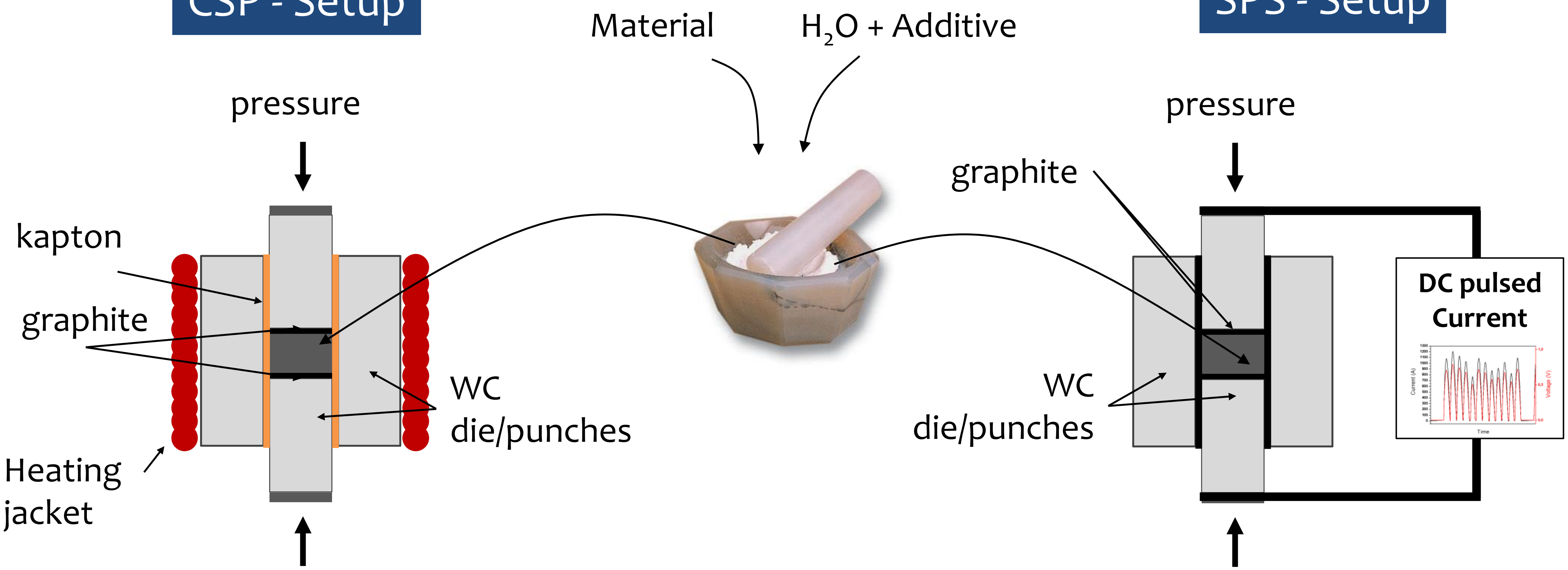
Low temperature Sintering Process
(Cold Sintering Process, Hydrothermal Sintering & Cold SPS : T<400°C)

time

CSP / Cold SPS

CSP - Setup

SPS - Setup



J. Guo et al. Angew Chem, 55, 2016, 11457-11461

C. Drouet et al., Adv. Sci. & Tech, 49 (2006), 45-50

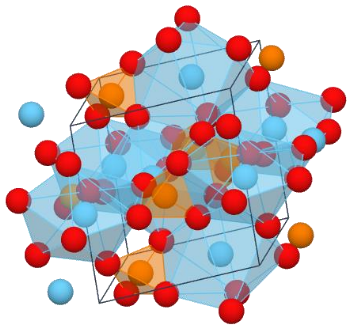
Transient liquid phase { Added / Generated in situ

Lanthanum phosphate

TBC applications — High Temperature lubricant

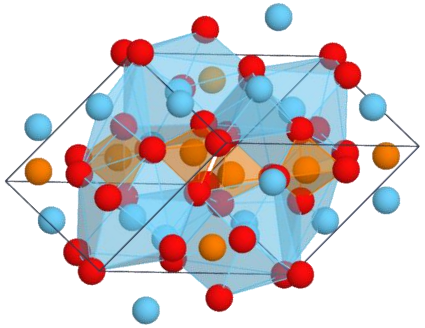
	T_f (°C)	λ (K^{-1})	σ_{therm} ($W.m^{-1}.K^{-1}$)	Microhardness (GPa)	E (GPa)
YSZ	2680	11.10^{-6}	2,2	12	210
$LaPO_4$ [1-4]	2072	10.10^{-6}	3,6	1,3 to 5,2	150

Thermal and chemical stability



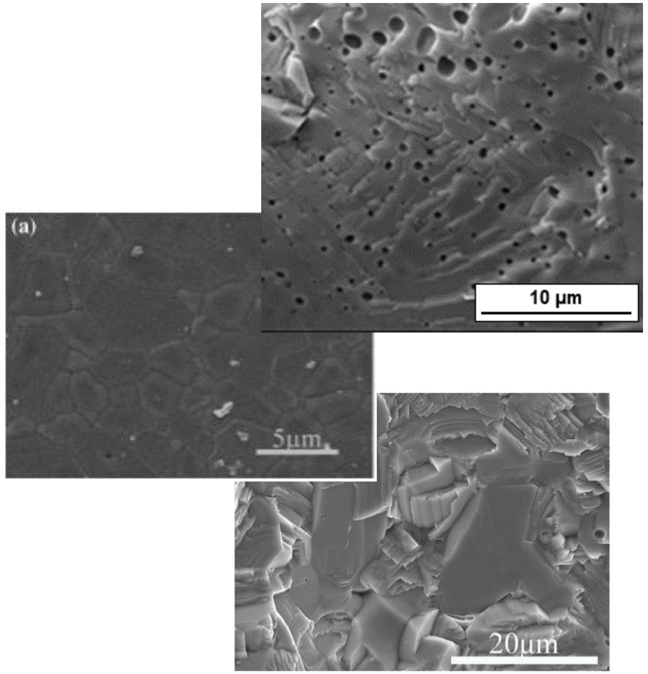
Hydrated phase
$LaPO_4.0,5H_2O$ Rhabdophane

Calcination →



Anhydrous high-temperature phase
$LaPO_4$ Monazite

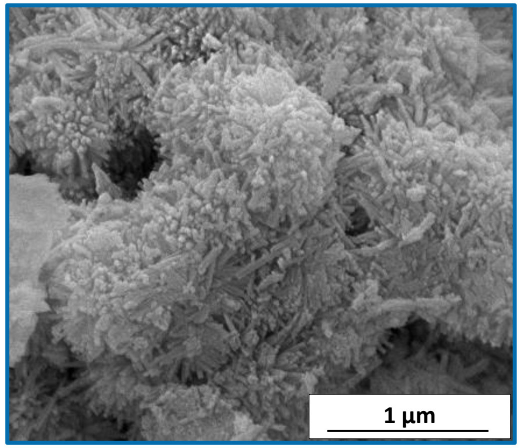
Sintering →
Conventional [3]
Pressure assisted [1&4]



[1] Luo Yongming & al., Mat. Chem and Phy. (2003); **[2]** D. Bernache-Assollant & al. J. Eu. Ceram. Soc. (2007); **[3]** S. Ananthakumar & al., Ceram. Int. (2014); **[4]** W. Pan & al., J. Am. Ceram. Soc (2010).

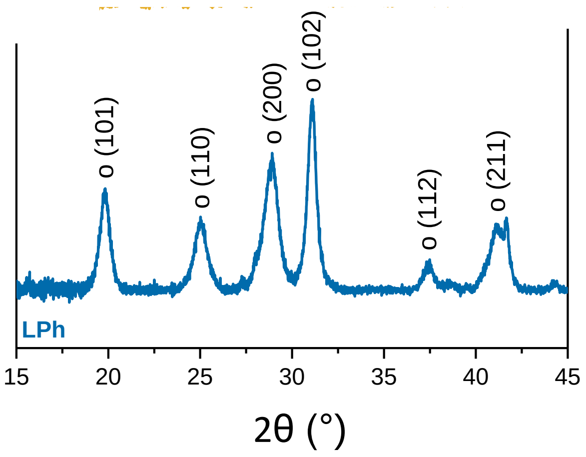
M. Rousselle *et al.* JECS. 41 (14) 2021, 7261-7268.

Structural and microstructural evolution

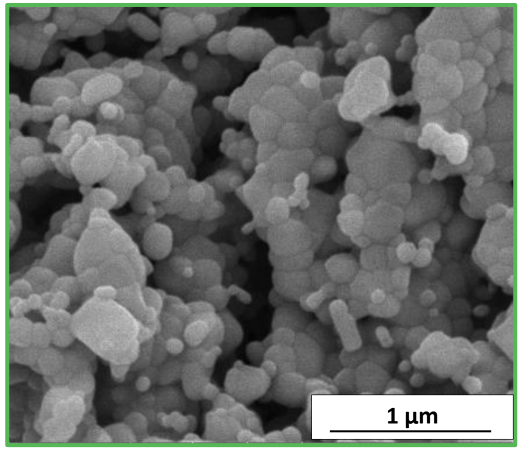


$LaPO_4 . 0.5H_2O$

TG – DTA
- Below 400°C dehydration
- Progressive phase transformation from 150 to 825 °C

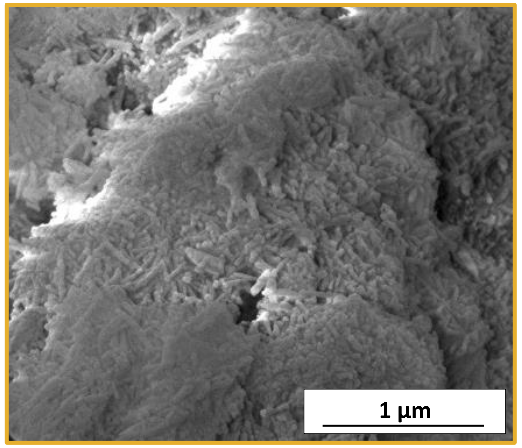


M. Rousselle *et al.* JECS. 41 (14) 2021, 7261-7268.



Grain ripening

Spherical particles

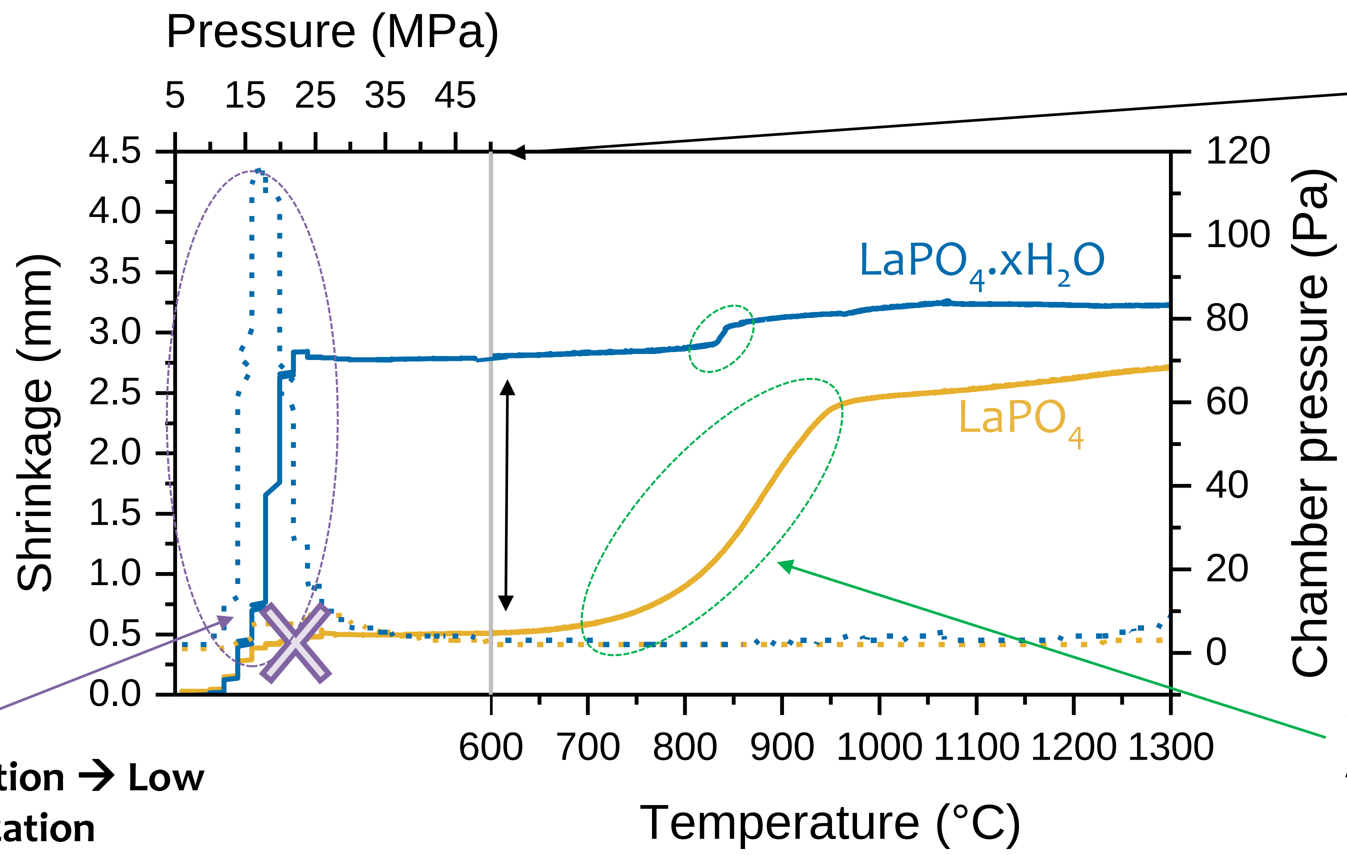


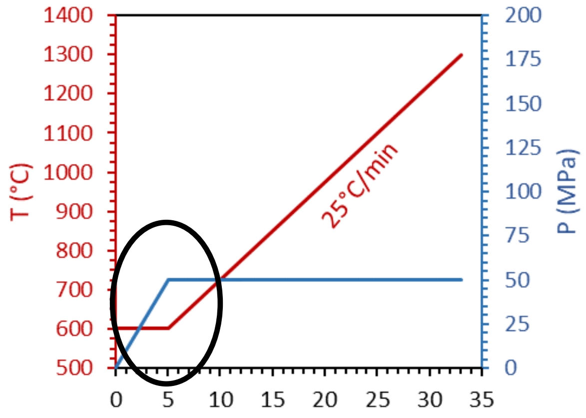
Nano-rods shaped particles

Anhydrous phase crystallization

Spark Plasma Sintering reactivity

In-Situ Spark Plasma Sintering dilatometry measurement – 600°C → 1300 °C - 50 MPa





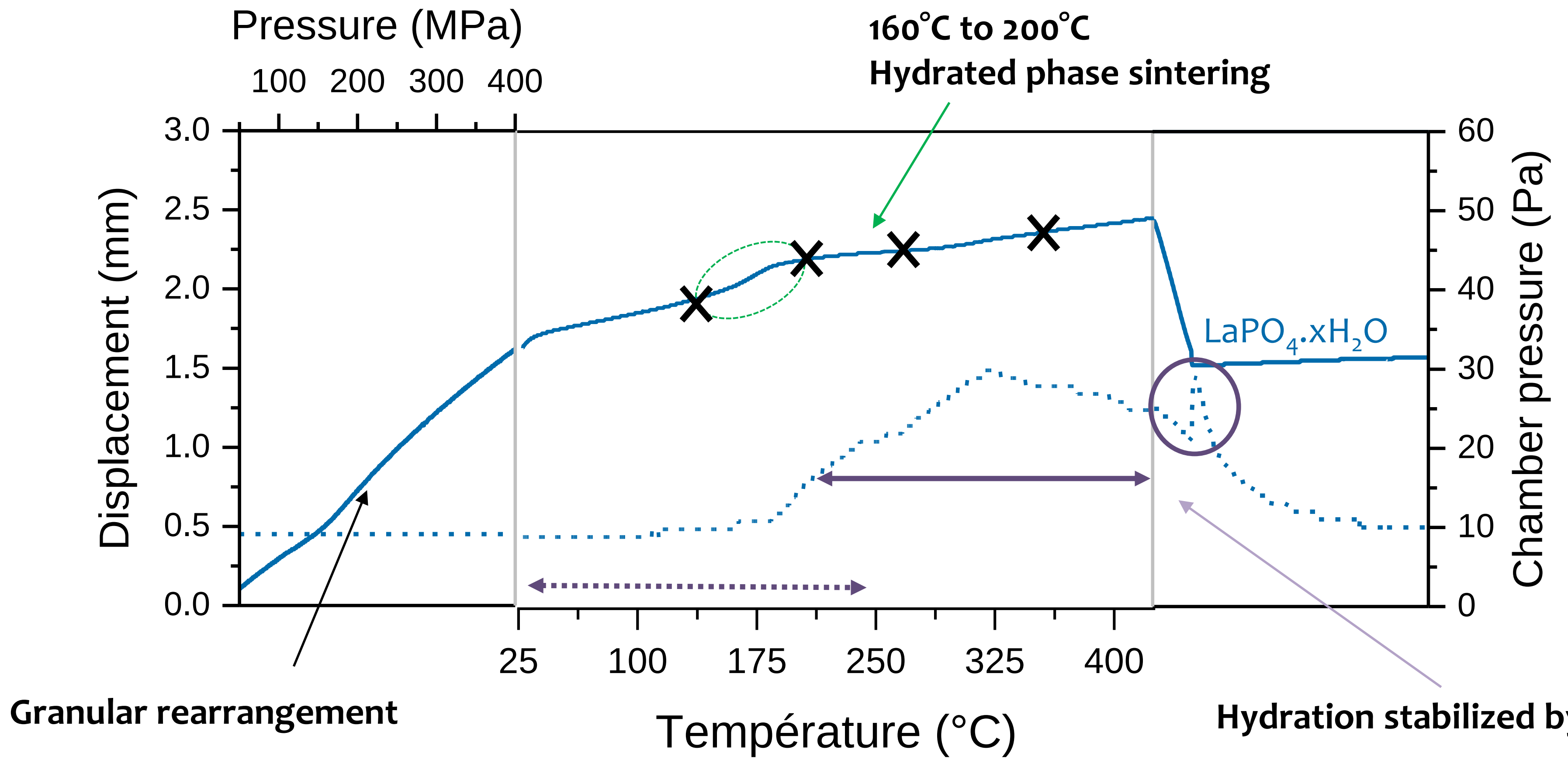
Shrinkage + dehydration → Low temperature densification

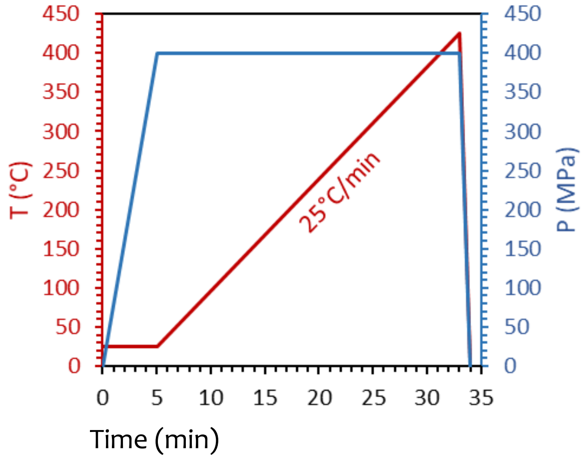
650°C à 1000°C Anhydrous phase sintering

M. Rousselle *et al.* JECS. 41 (14) 2021, 7261-7268.

Reactivity at low temperature

In-situ Spark Plasma Sintering dilatometry measurement– 25 → 425 °C - 400 MPa

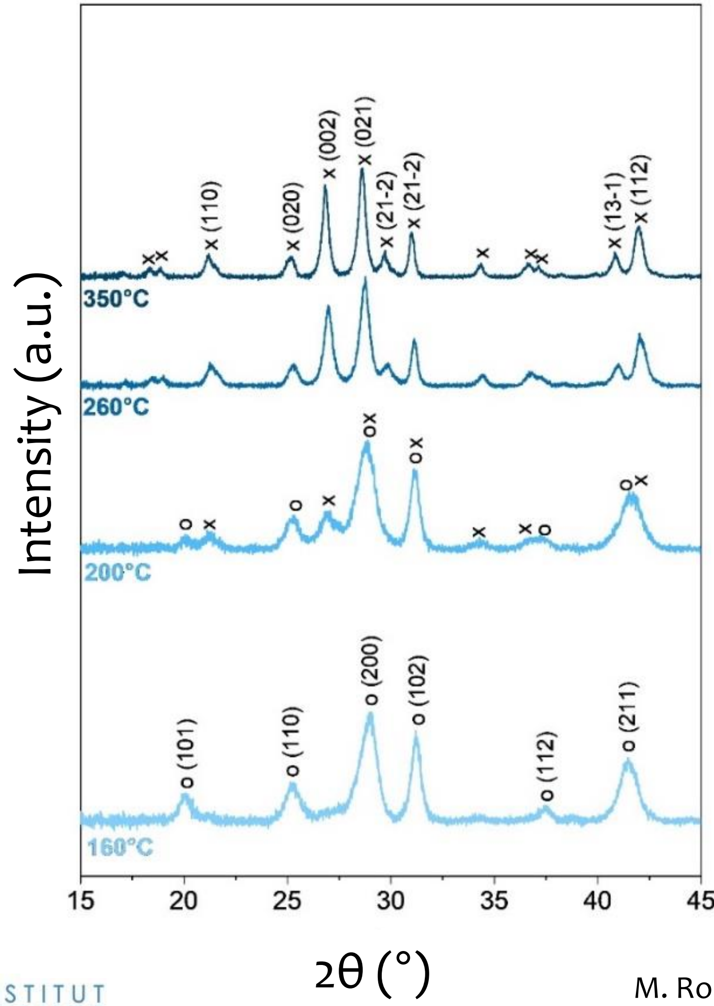




M. Rousselle *et al.* JECS. 41 (14) 2021, 7261-7268.

Lanthanum phosphate phases and structures

Low temperature SPS – T (°C) – 10 min – 400 MPa



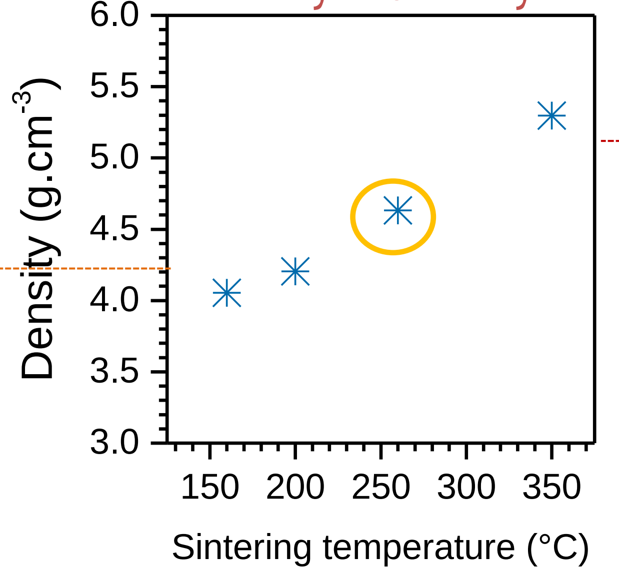
$LaPO_4$

$LaPO_4$ + amorphous

$LaPO_4 . xH_2O$ + $LaPO_4$ + amorphous

$LaPO_4 . xH_2O$ + amorphous

He Pycnometry



$LaPO_4$ 5.12 g.cm^{-3}

$LaPO_4.xH_2O$ 4.27 g.cm^{-3}

Anhydrous phase formation eased by applied pressure

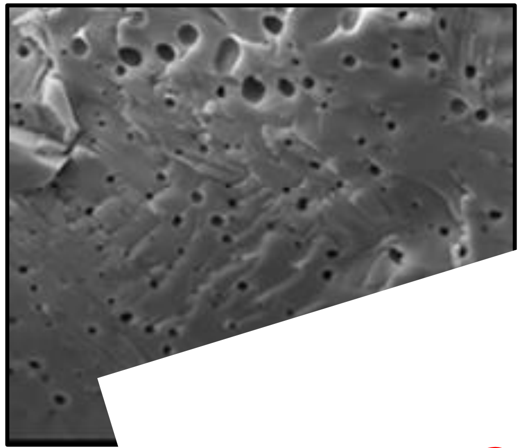
Crystallization of anhydrous phase at 350 °C

Intermediate amorphous phase

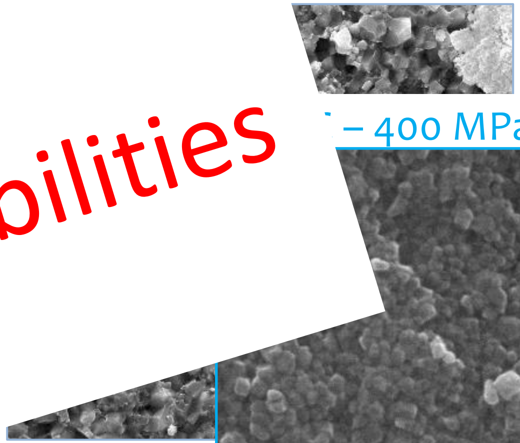
M. Rousselle *et al.* JECS. 41 (14) 2021, 7261-7268.

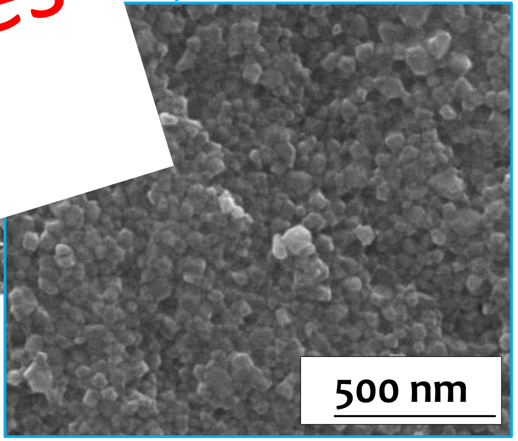
Lanthanum phosphate sintering

	Conventional Sintering	Spark Plasma Sintering	Low temperature SPS	
microstructure	1350°C – 3h	1150°C – 50 MPa – 10 min	…a – 10 min / … – 400 MPa – 10 min	
Relative density	[illegible]	96%	94%	86%
Grain size	[illegible]	3.5 ± 0,5 µm	0.9 & 0.09 µm	40 ± 0.3 nm
Microhardness	1.3 GPa	2.3 ± 0.4 GPa	2.5 ± 0.3 GPa	1.7 ± 0.3 GPa



[3] S. A… Ceram. …





Conclusion #1

Cold-SPS offers news possibilities to sinter materials

M. Rousselle *et al.* JECS. 41 (14) 2021, 7261-7268.

Context

SINTERING

temperature **Kinetic** ← SINTERING → **Thermodynamic**

Relative control of the microstructures

Recent developments in sintering

Decreasing the **temperature** and/or **time** of sintering

Flash-SPS

E. Olevsky *et al*, Sci. Rep. , 2016.
S. Grasso *et al*, *J. Am. Ceram. Soc.*, 2016.
B. Niu *et al*, *Scripta Mater.*, 2016.
C. Manière *et al*, Sci. Rep., 2017.

Cold SPS

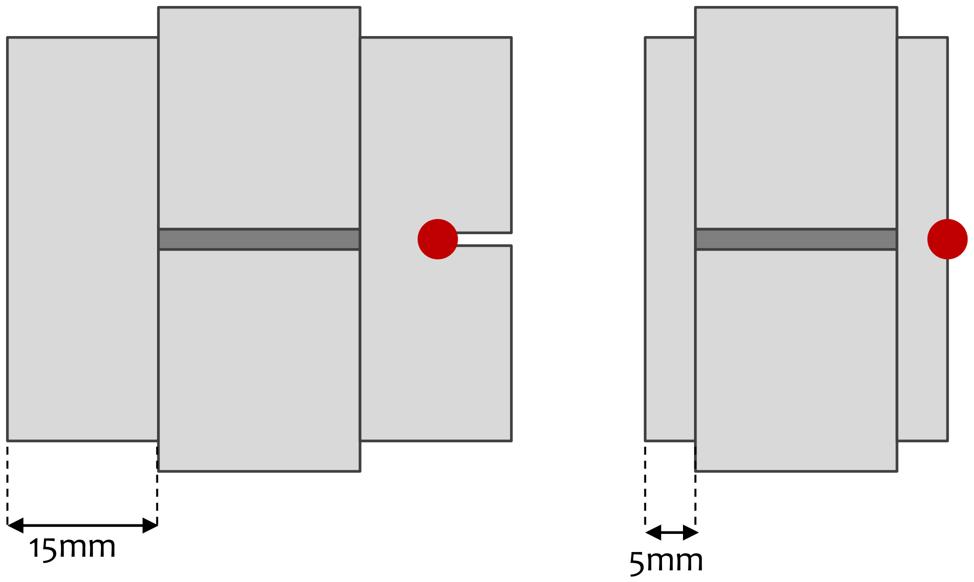
C. Drouet et al, Powder Tech., 2009
B. Dargatz *et al*, *JECS*, 2016.
T. Hérisson de Beauvoir *et al*, *J. Mater. Chem.*, 2018.
J. Gonzalez-Julian *et al*, *Acta Mater.*, 2018
T. Hérisson de Beauvoir *et al*, *Ceram. Int.*, 2019.
K. Nur *et al*, *JECS*, 2021.

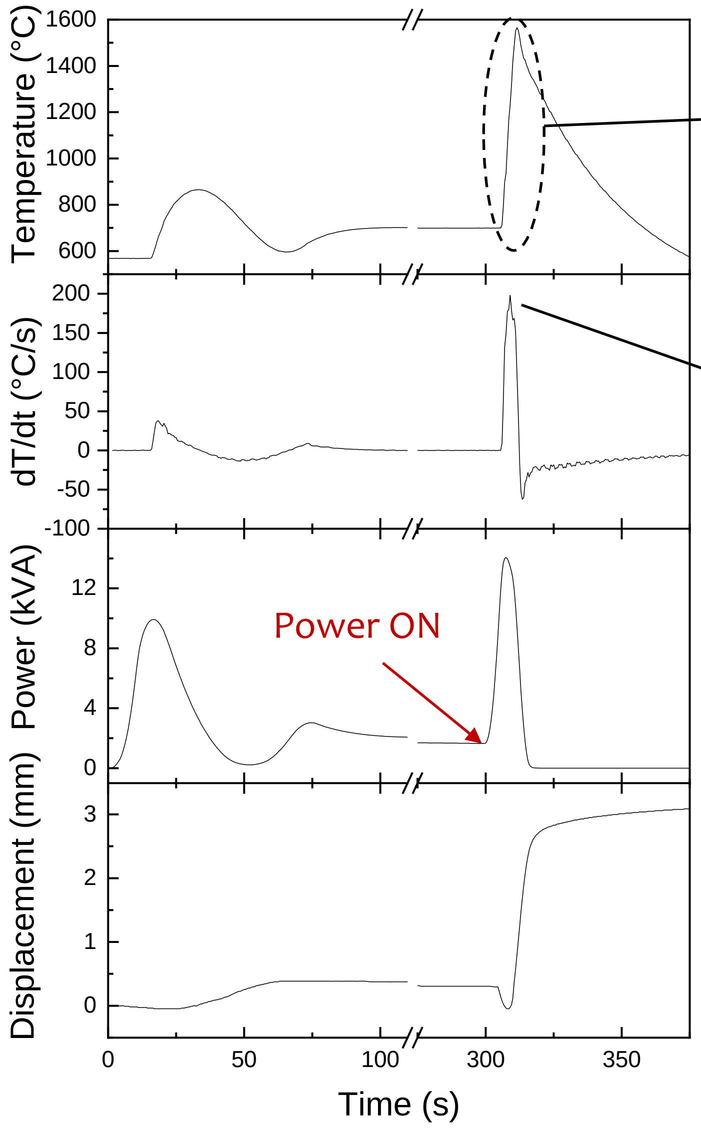
Low temperature Sintering Process
(Cold Sintering Process, Hydrothermal Sintering & Cold SPS : T<400°C)

time

Flash SPS Setup

Classic SPS setup | **Flash SPS**





> 850°C in 6s

T_{max} = 1560°C

No dwell time

→ Max 200°C/s

→ Average 144°C/s or ≈ 8 500 °C/min

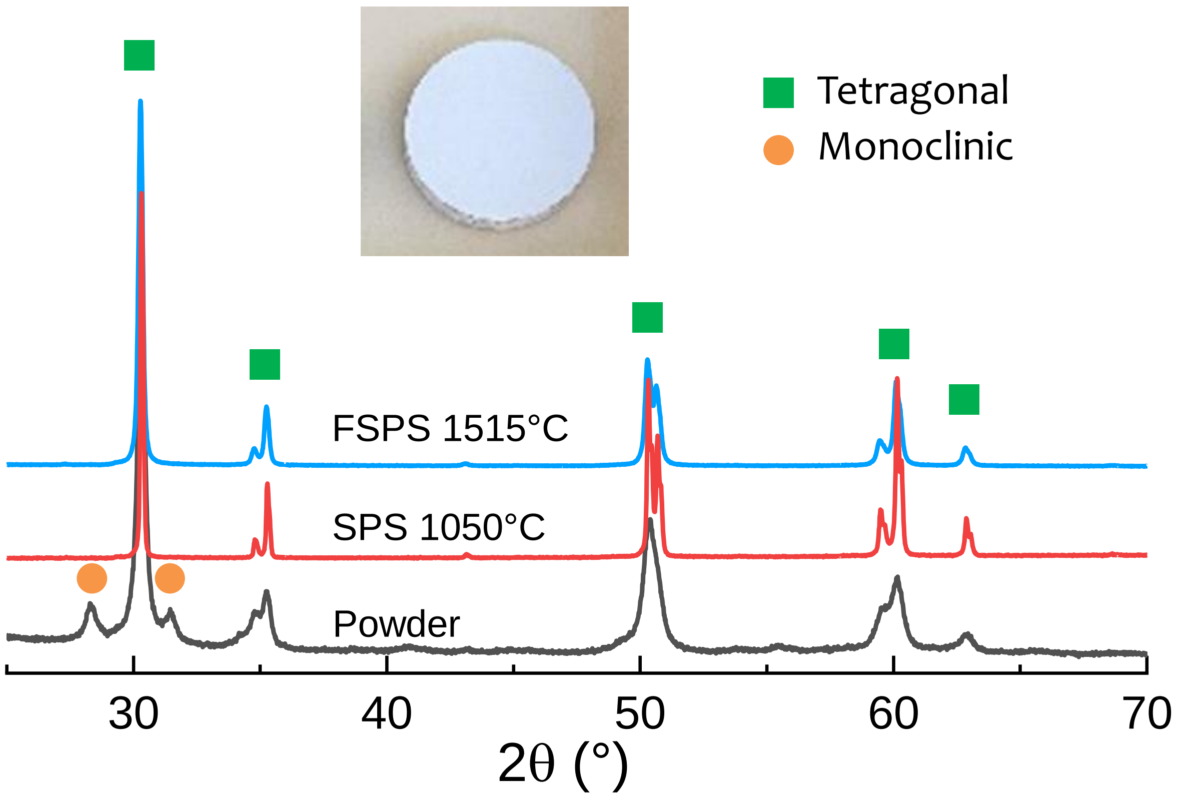
≈ 3mm in 6s

~~Sample~~ temperature → Apparent temperature

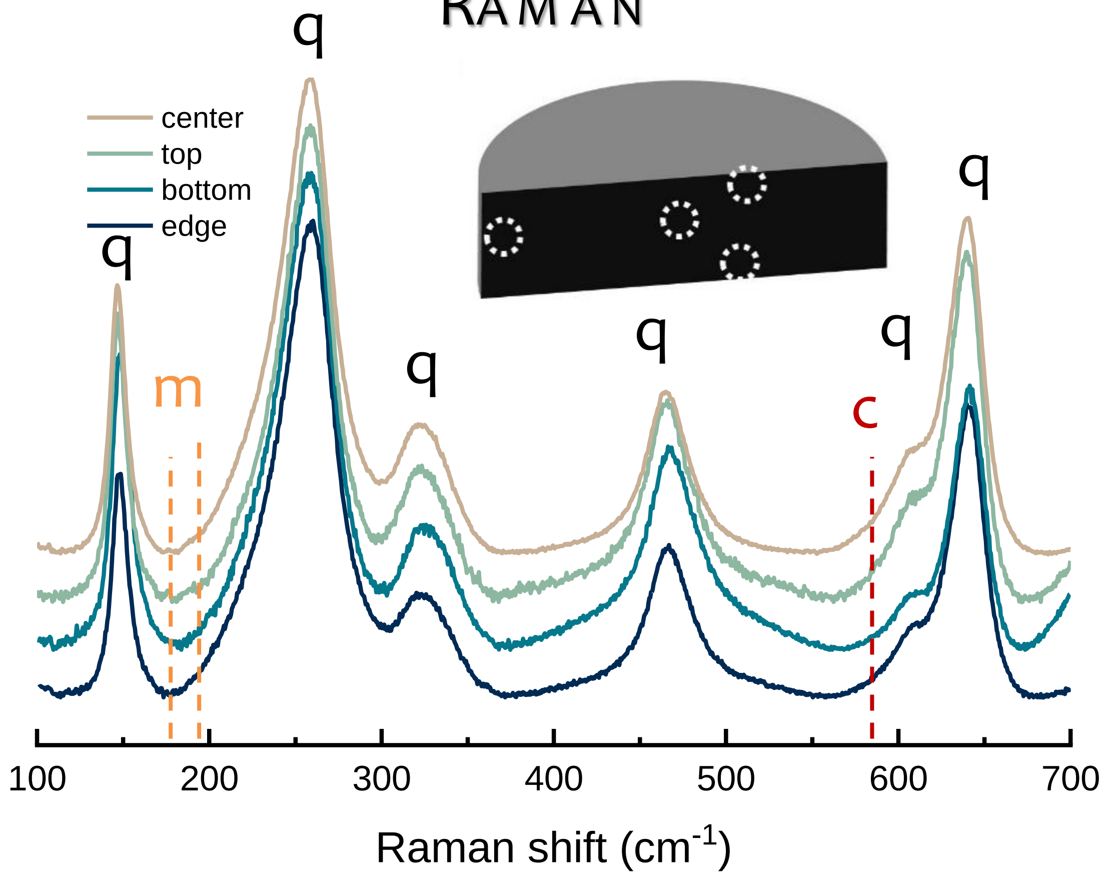
T. Hérisson de Beauvoir et al.- JECS. 41 (2021) 7762-7770.

Structure

XRD



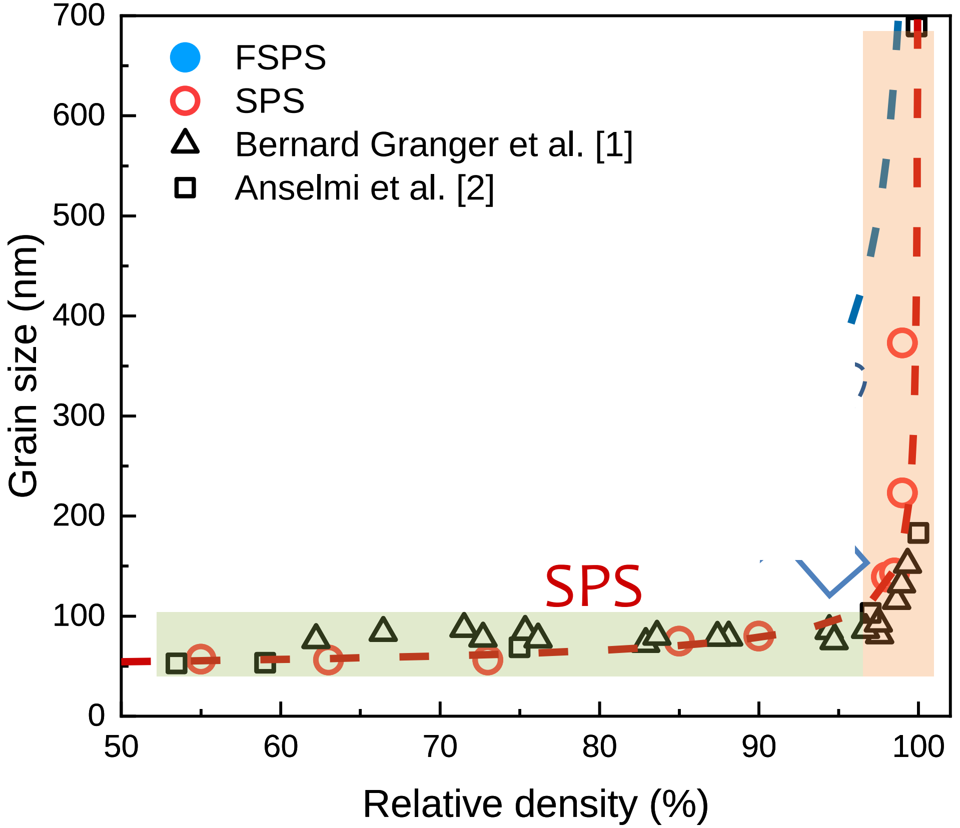
RAMAN



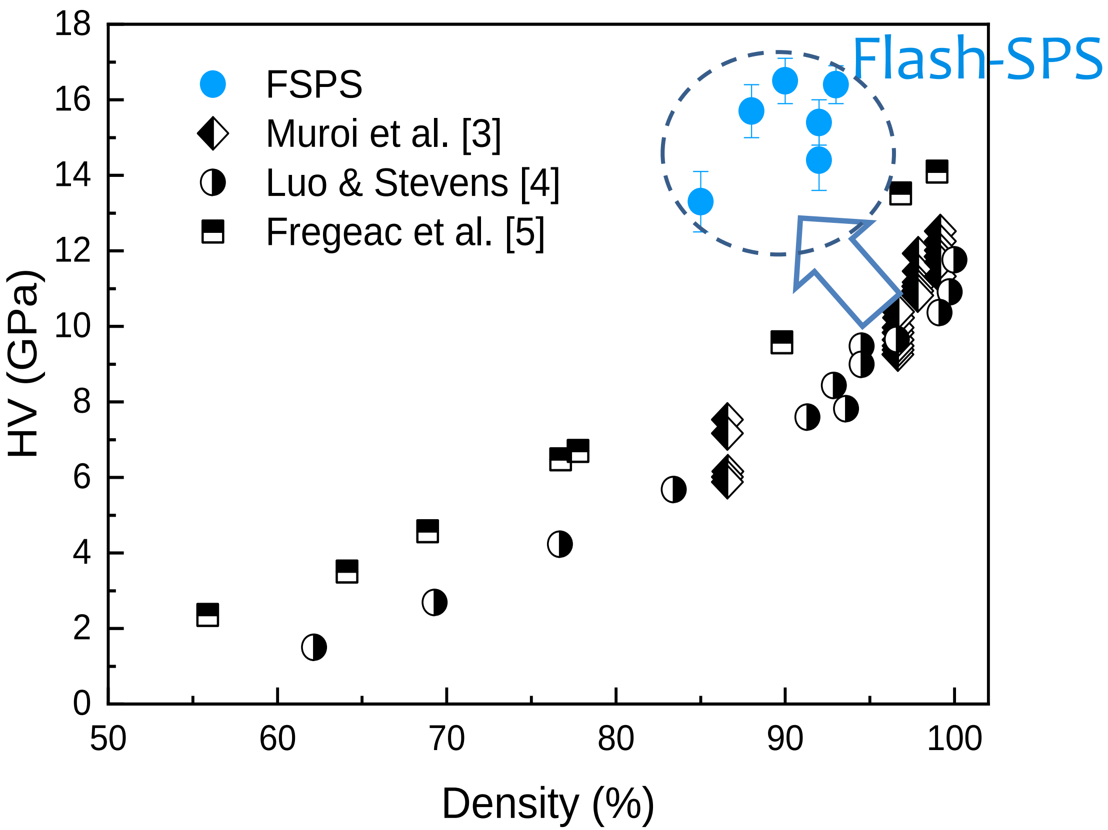
➔ Structural homogeneity

T. Hérisson de Beauvoir *et al.* JECS. 41 (2021) 7762-7770.

Sintering trajectories / Hardness



Vickers hardness

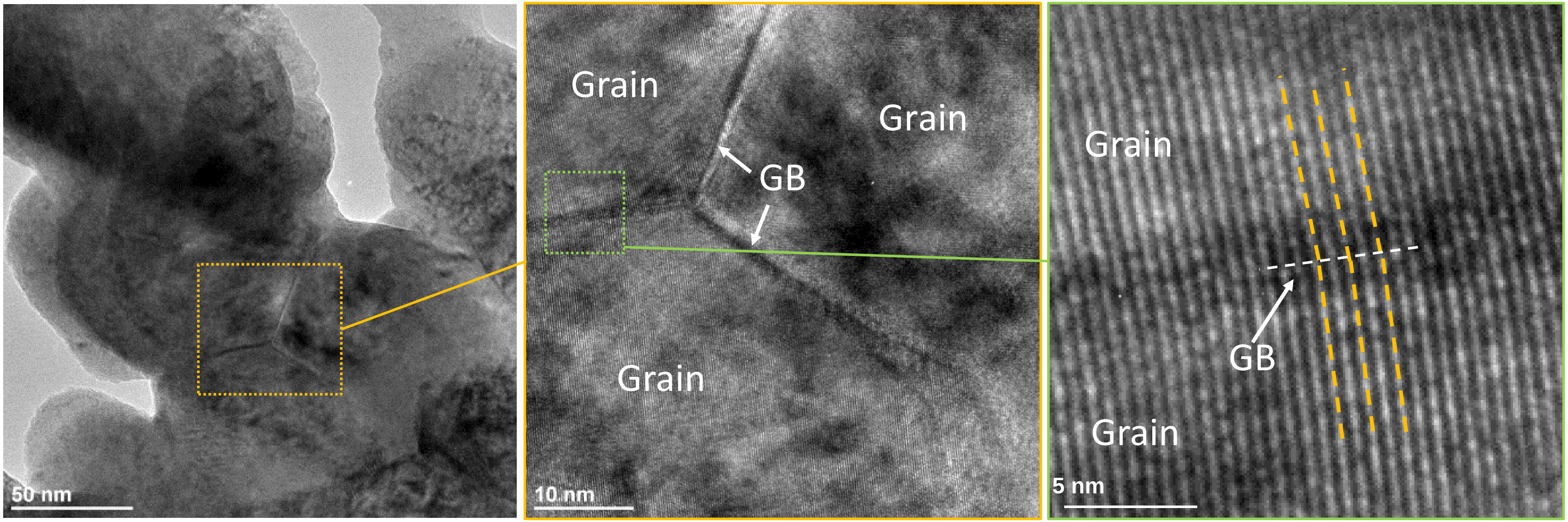


θ ⇨ non classical mechanisms ?

[1] *Acta Mater* 56 (2008) 4658-4672.
[2] *J. Mater. Res.* 19 (2004) 3255–3262.
[3] Randall German, *Sintering: From empirical observations to scientific principles* (2014) Butterworth-Heinemann.

[3] *J. Mater. Sci.*43 (2008) 6376-6384.
[4] *Cerm. Int.* 25 (1999) 281-286.
[5] *Ceram.Int.* 4 (2019)23740-23749.

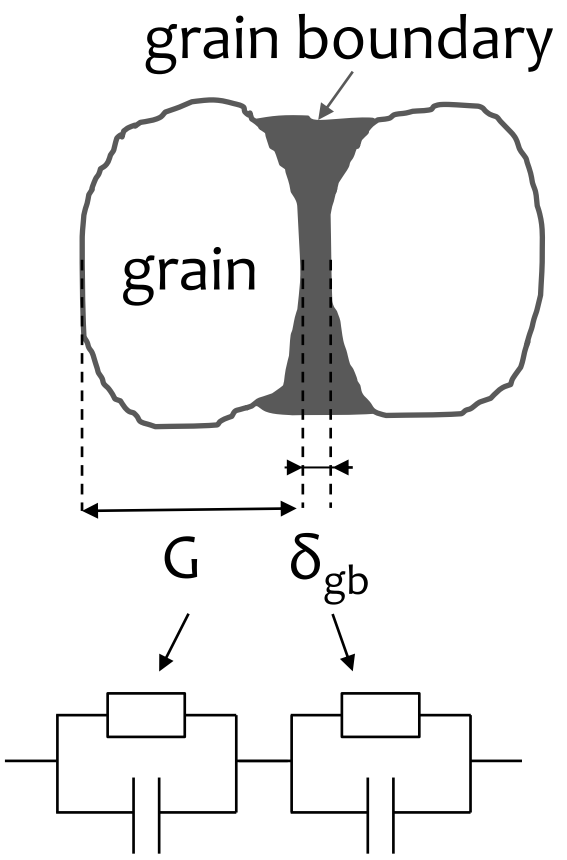
TEM observations



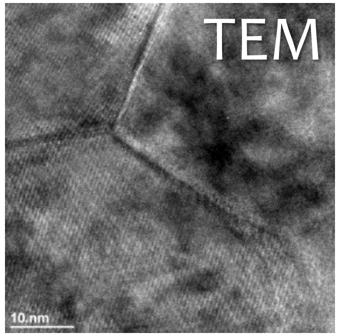
- Porosity
- Thin grain boundaries

T. Hérisson de Beauvoir *et al.* JECS 41 (2021) 7762-7770.

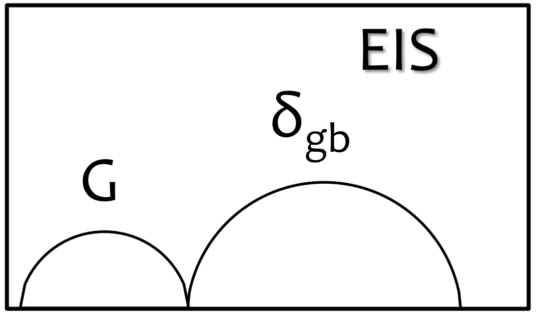
GB characterization

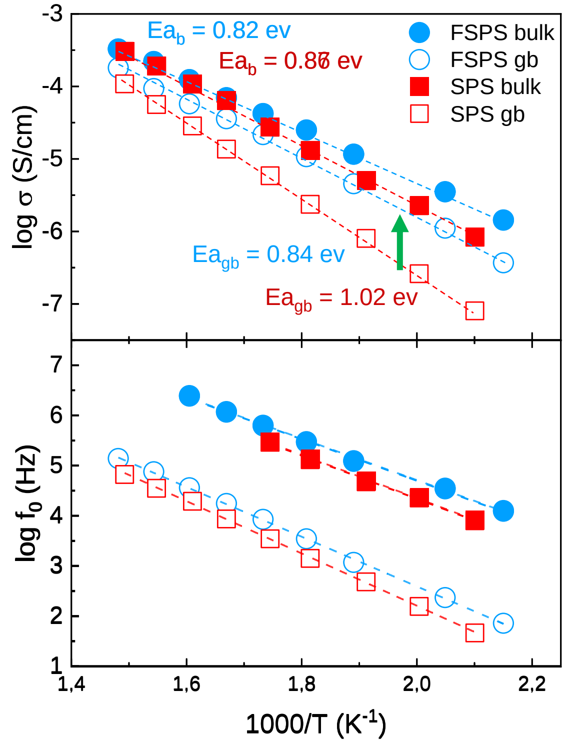


Local observation

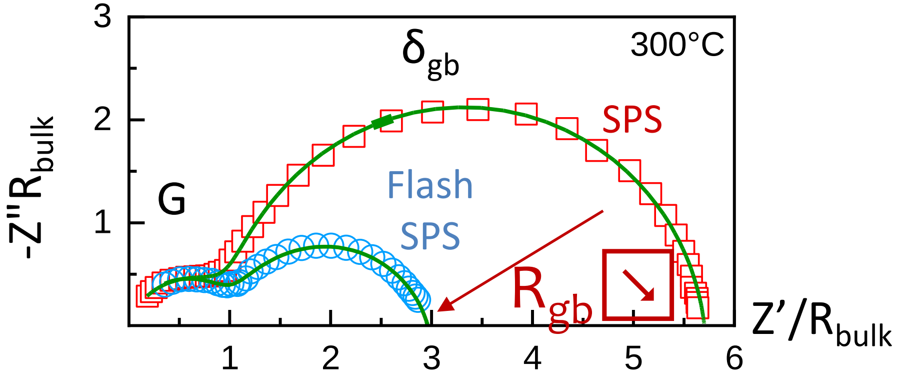


Global observation

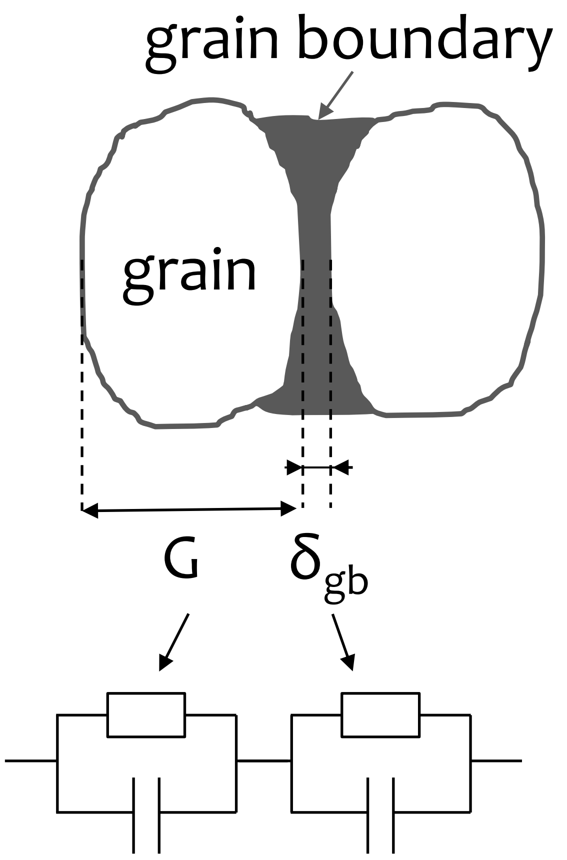


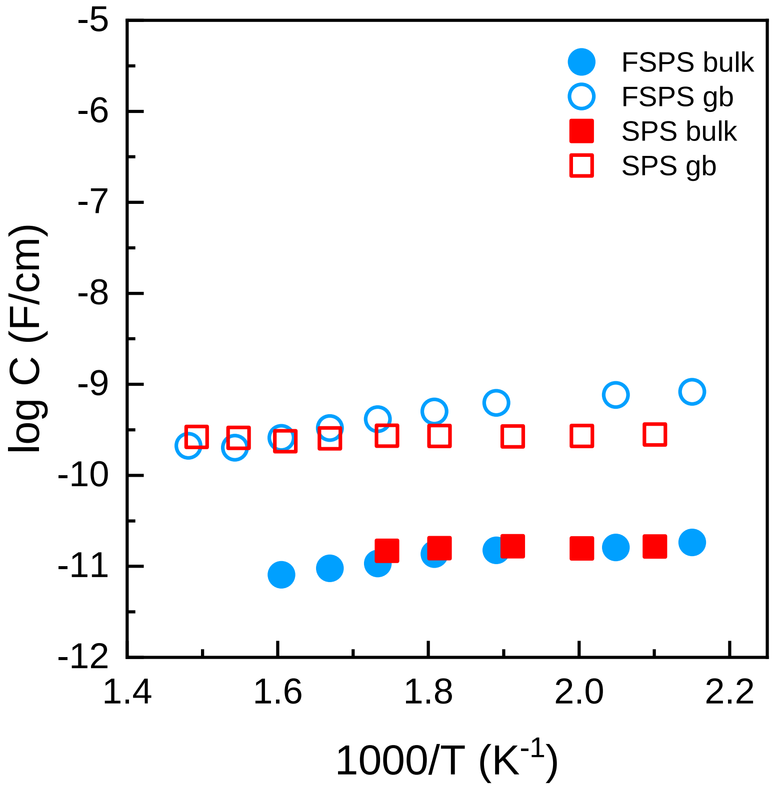


SPS & **FSPS**
Samples
same grain size
~220nm



EIS Measurements





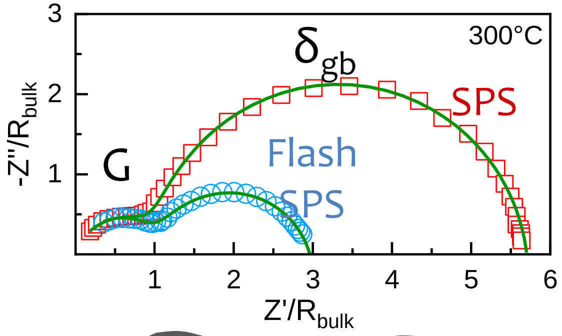
↘ grain ⇒ boundary thickness

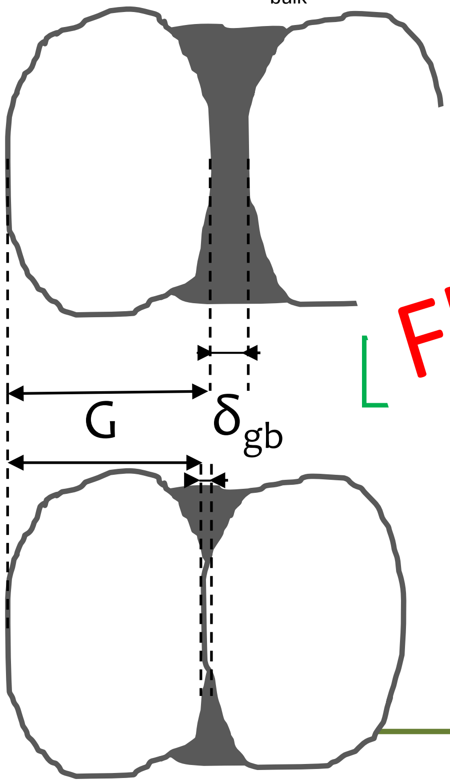
$$\frac{\delta_{gb}}{G} = \frac{C_{bulk}}{C_{gb}}$$

C_i : capacitance
δ_{gb} : GB thickness
G : grain size

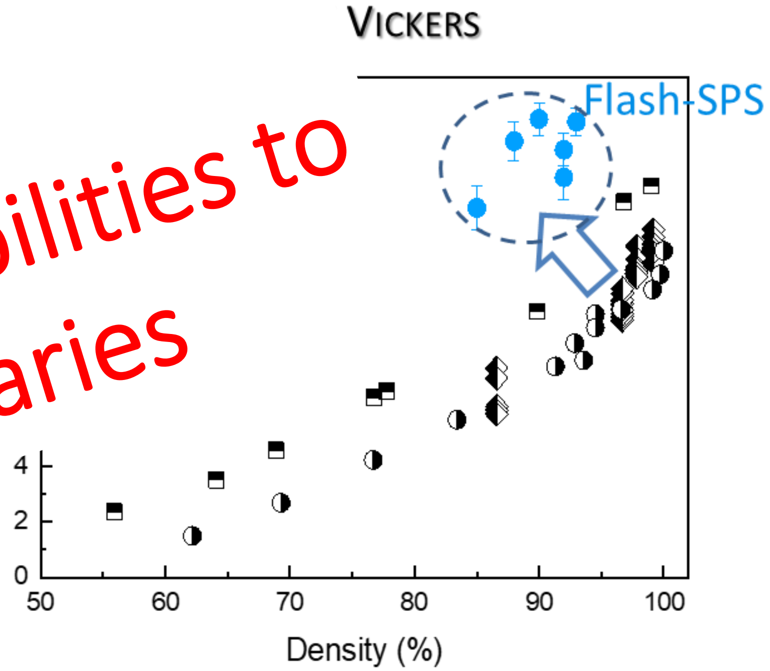
Summary

EIS - global → MET - local → Macro





Flash SPS

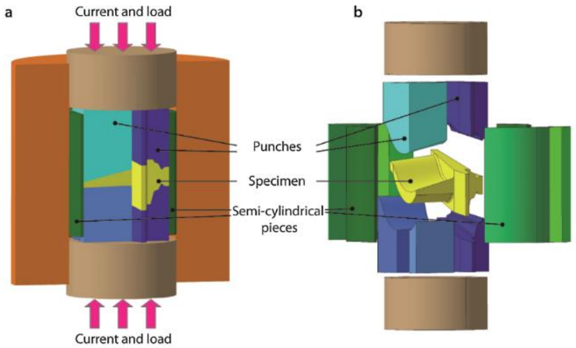


Conclusion #2

Flash-SPS offers news possibilities to engineer grain boundaries

Elaboration of complex shapes

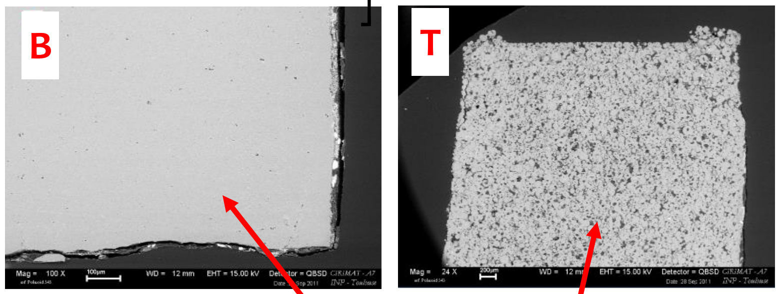
Use of complex tooling

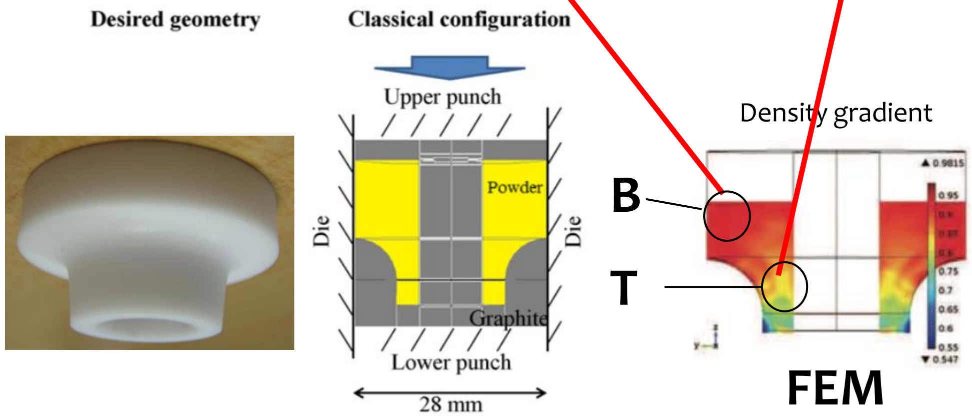


SPS tooling for the production of a turbine blade [1]

T . Voisin, *et al*, Adv. Eng. Mater., 2015

Images of the polished surfaces of the alumina part at points B and T





Targeted geometry and SPS configuration

C. *Manière et al*, Scripta Mat., 2016.
C. Maniere *et al*, Acta Materialia, 2016.

General description of the implied physics

Joule heating
Densification
} Electrical, Thermal, Mechanical Physics

Electrical model

Current Equation $\nabla.\vec{J} = 0$

FEM coupling

Thermal model

Heat Equation $\nabla.(-\lambda\nabla T) + \rho Cp\frac{\partial T}{\partial t} = \vec{J}\vec{E}$

Mechanical model (porous creep)

Olevsky model or Abouaf model

Stress tensor

$$\underline{\sigma} = \frac{\sigma_{eq}}{\dot{\varepsilon}_{eq}}\left(\varphi\underline{\dot{\varepsilon}} + \left(\psi - \frac{1}{3}\varphi\right)tr(\underline{\dot{\varepsilon}})\mathbb{1}\right) + P_l\mathbb{1}$$

$$\underline{\sigma} = \frac{\sigma_{eq}}{\dot{\varepsilon}_{eq}}\left(\frac{2}{3c}\underline{\dot{\varepsilon}} + \left(\frac{1}{9f} - \frac{2}{9c}\right)tr(\underline{\dot{\varepsilon}})\mathbb{1}\right)$$

Equivalent creep parameters

$$\dot{\varepsilon}_{eq} = \frac{1}{\sqrt{1-\theta}}\sqrt{\varphi\dot{\gamma}^2 + \psi tr(\underline{\dot{\varepsilon}})^2}$$

$$\sigma_{eq} = \sqrt{3cJ_2 + fI_1^2}$$

Functions of porosity

$$\varphi = (1-\theta)^2$$

$$\psi = \frac{2}{3}\frac{(1-\theta)^3}{\theta}$$

$$f = k\frac{(1-\rho)}{(\rho-\rho_{cr})}$$

$$c = 1 + a\frac{(1-\rho)}{(\rho-\rho_{cr})}$$

Microstructure evolution

Grain growth (Olevsky)

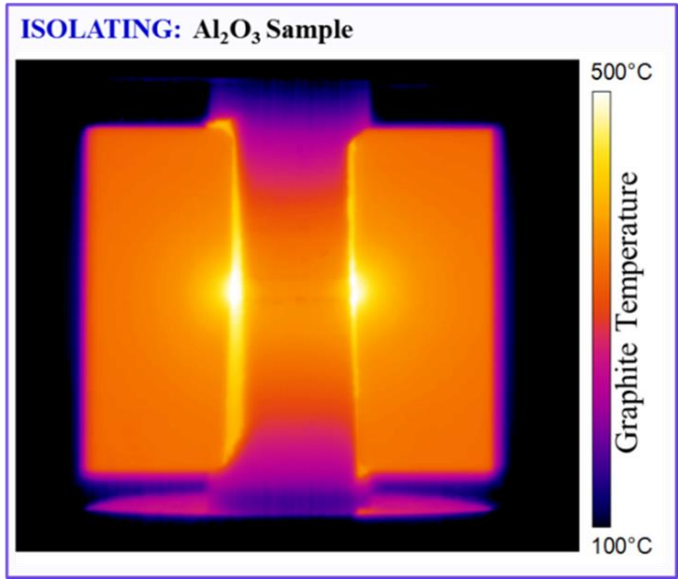
$$\dot{G} = \frac{k_0}{3G^2}\left(\frac{\theta_c}{\theta_c+\theta}\right)^{\frac{3}{2}} exp\left(\frac{-Q_G}{RT}\right)$$

Electro-Thermal Modelling

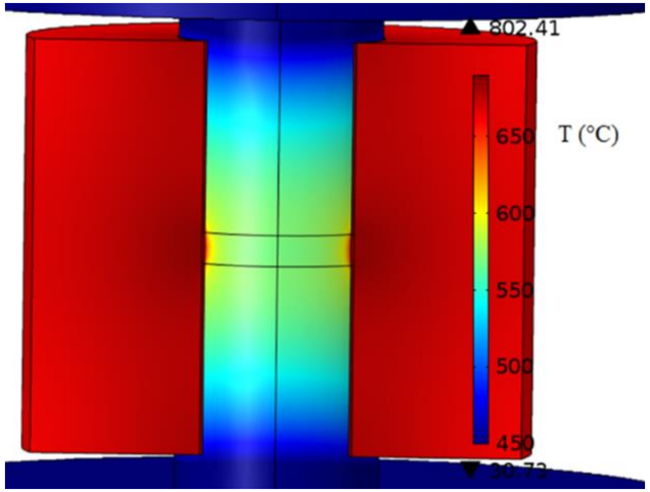
Adjusting by reverse analysis

- > Electric contacts : responsible for a global warming of the system
- > Thermal contacts : explains the localized heating of the papyex
- > Correct the thermal conductivity in plane of Papyex ⇨ hot spot.

Experimental



Modeling



1st Strategy : Calibration

C. Manière *et al*, EPSR, 2015
C. Manière *et al*, JECS, 2016

2nd Strategy : Reverse analysis via minimization

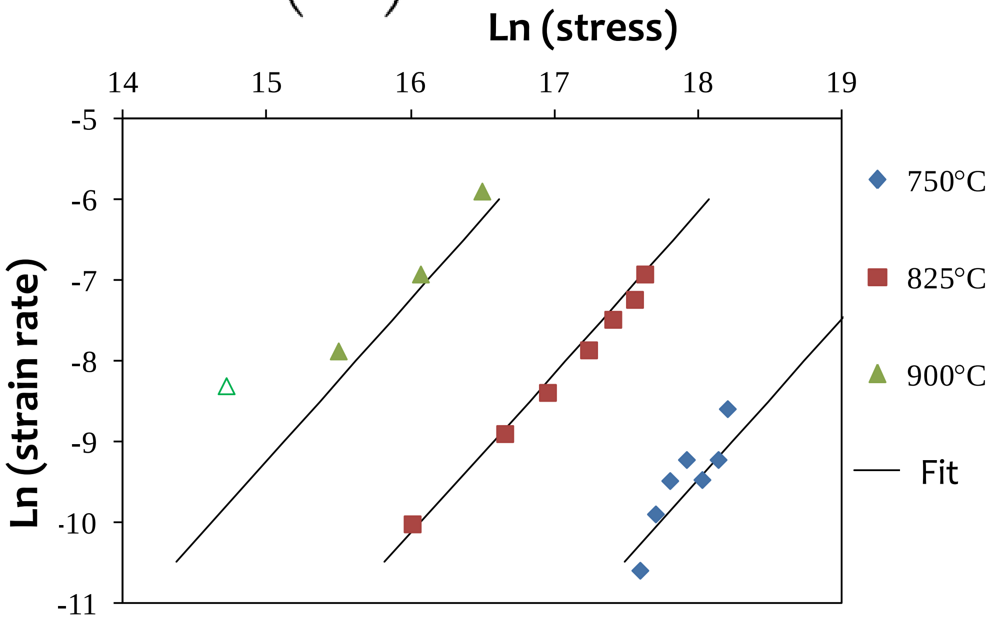
A. Van der Laan *et al*, JECS, 2021

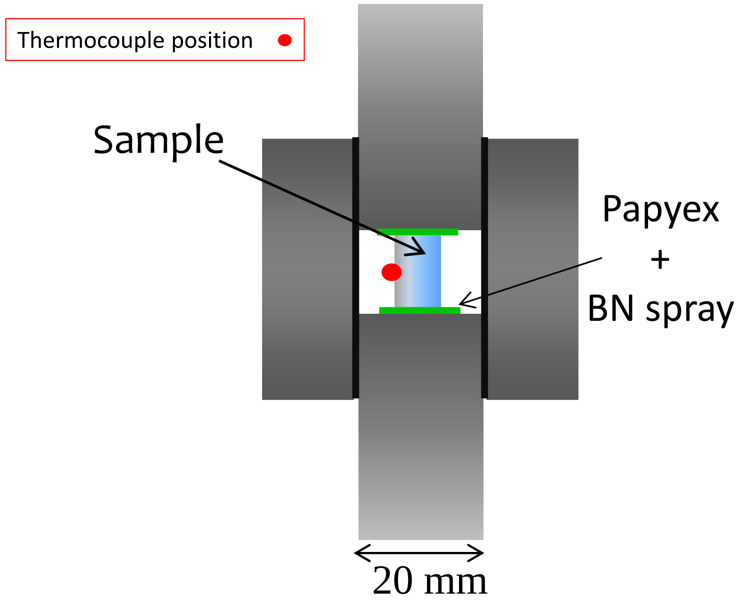
Mechanical Modelling

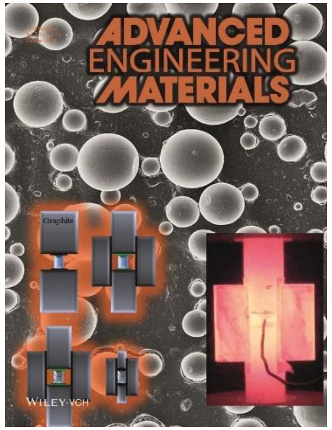
1st Strategy : experimental determination of creep parameters

Norton law $\dot{\varepsilon}_{eq} = A\sigma_{eq}^{n}$

With $A = A_0 \exp\left(\frac{-Q}{RT}\right)$







$$\dot{\varepsilon}_{eq} = 30{,}6 * exp\left(\frac{-4{,}16 * 10^{5}}{RT}\right)\sigma_{eq}^{2}$$

C. Manière et al., Adv. Eng. Mater., 2016.

2nd Strategy : creep parameter determination from densification curves by reverse analysis via minimization

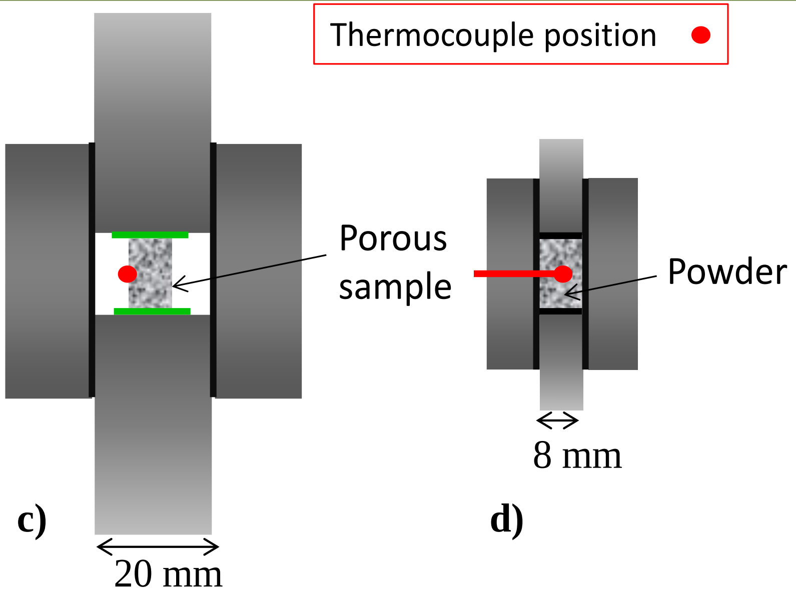
A. Van der Laan et al., JECS 2021 A. Van der Laan et al. Intermetallics 2022.

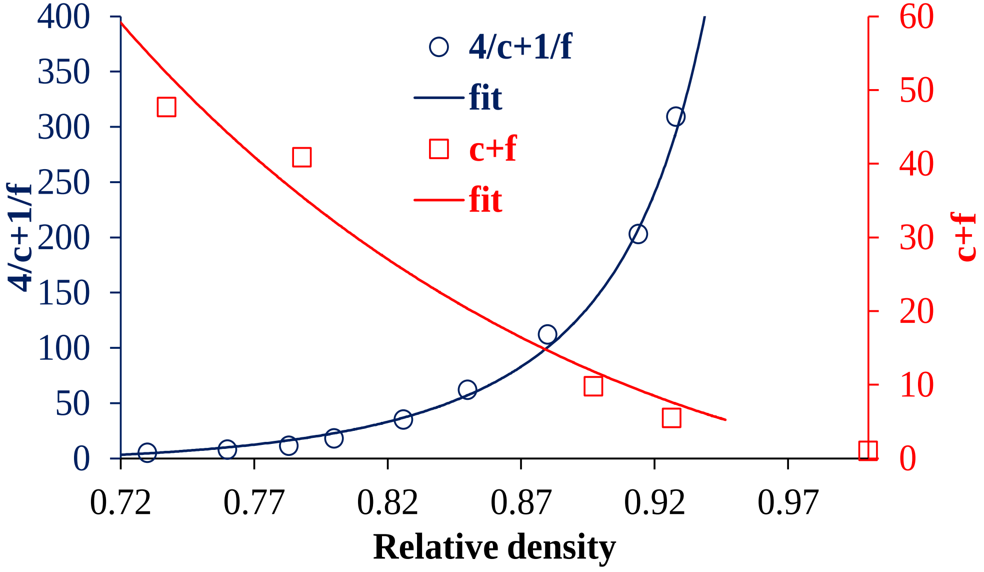
Mechanical Modelling

CIRIMAT Toulouse

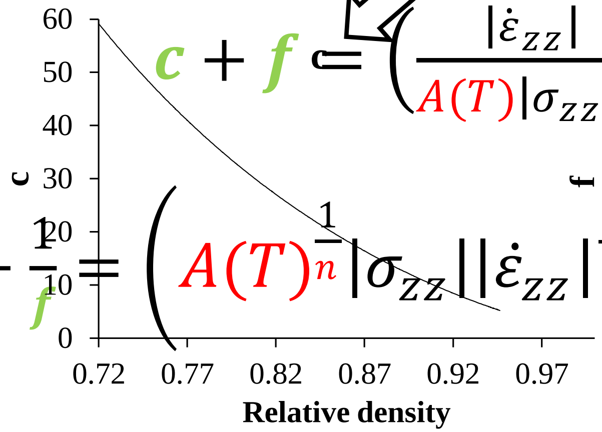
PNF2 PLATEFORME NATIONALE DE FRITTAGE FLASH TOULOUSE

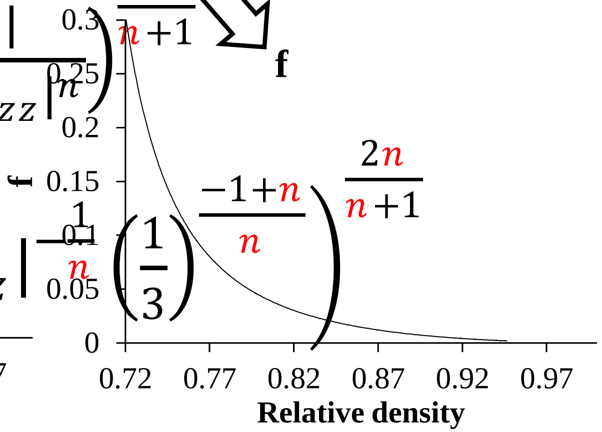
1st Strategy





$$\begin{cases} c + f = \left(\dfrac{|\dot{\varepsilon}_{zz}|}{A(T)|\sigma_{zz}|^{n}}\right)^{\frac{2}{n+1}} \\ \dfrac{4}{c} + \dfrac{1}{f} = \left(A(T)^{\frac{1}{n}}|\sigma_{zz}||\dot{\varepsilon}_{zz}|^{-\frac{1}{n}}\left(\dfrac{1}{3}\right)^{\frac{-1+n}{n}}\right)^{\frac{2n}{n+1}} \end{cases}$$





2nd Strategy :

creep parameter determination from densification curves by reverse analysis via minimization

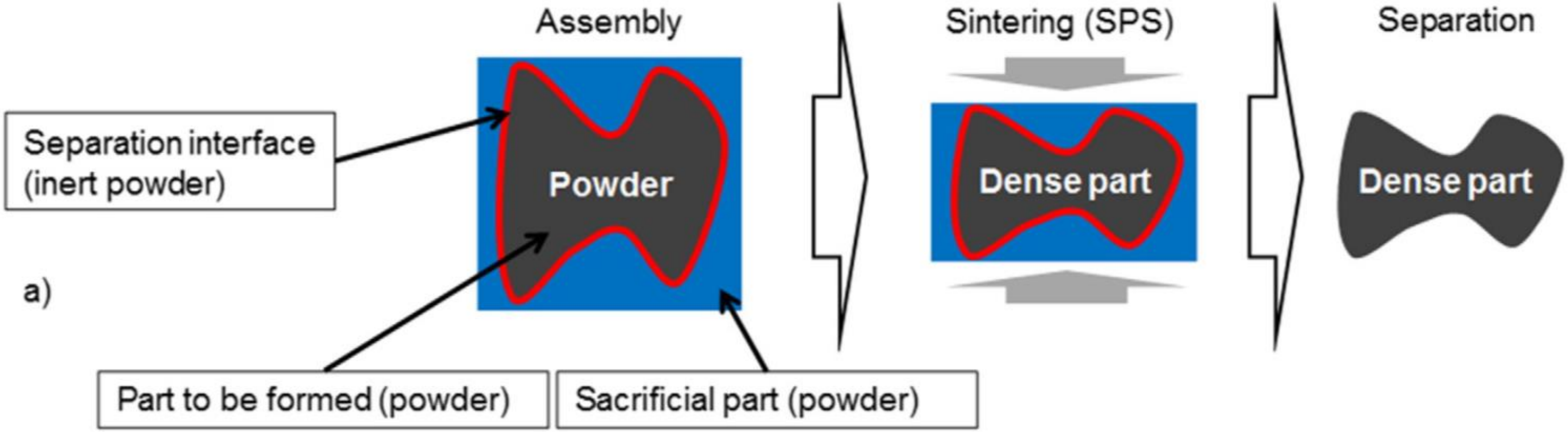
A. Van der Laan et al., JECS 2021
A. Van der Laan et al. Intermetallics 2022.

C. Manière *et al*, Adv. Eng. Mater., 2016.

INSTITUT CARNOT Chimie Balard Cirimat

Mobilint Strategy

State of the art: "Mobilint" strategy



Schematic of the "Mobilint" process

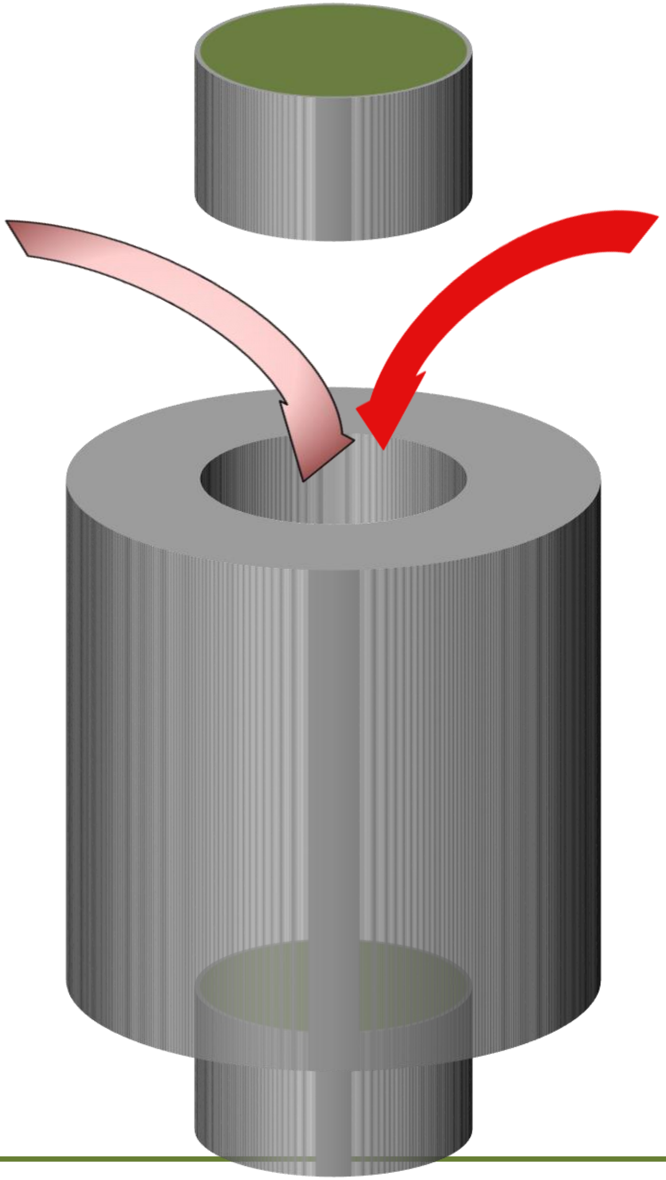
C. Estournes *et al*/ US 2018 / 0318931 A1   C. Manière *et al*, Powder Technology, 2017.

Mobilint Strategy

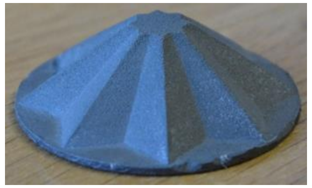
1st Strategy

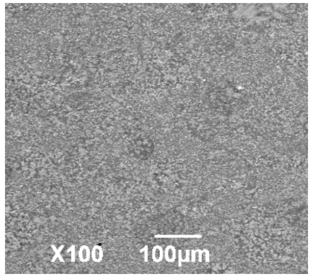
Porous
Counter part

Consolidated or
Partially sintered
obtained by
Free sintering
3D printing
Binder jetting
, SLM, FLD etc…



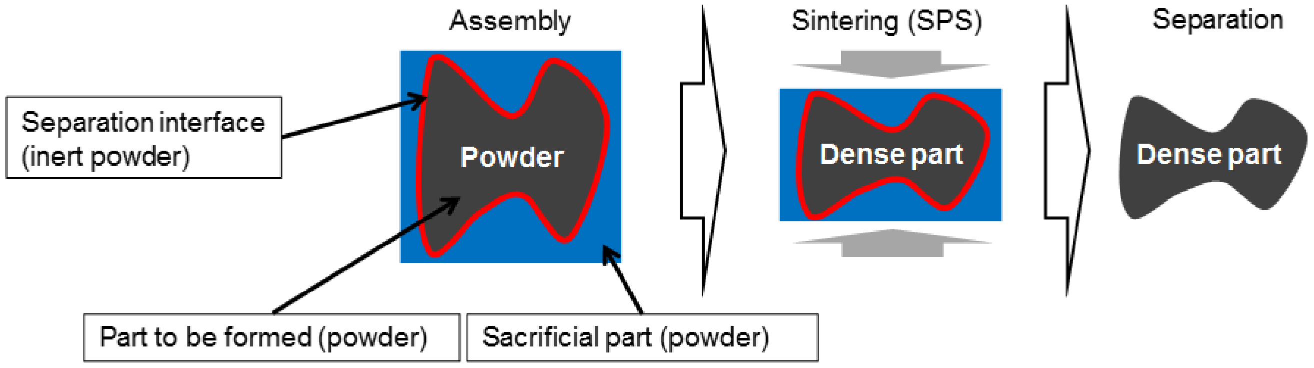
Ceramics
Metals
Alloys
Polymers
Composites





A star-shaped piece with homogeneous density and microstructure was successfully produced

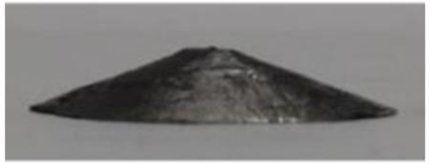
Mobilint Strategy



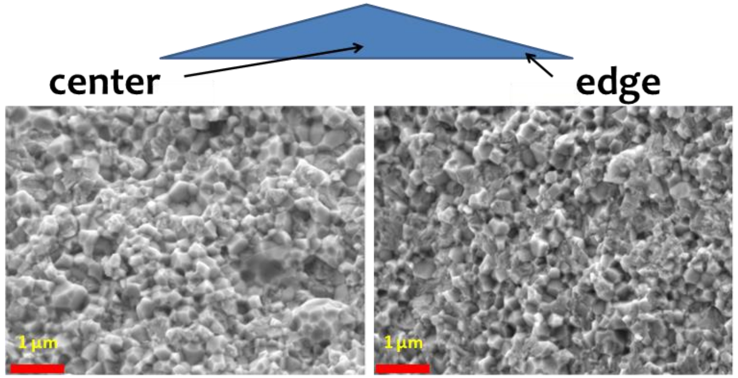
Polymers

PMMA d~100%

Ceramics

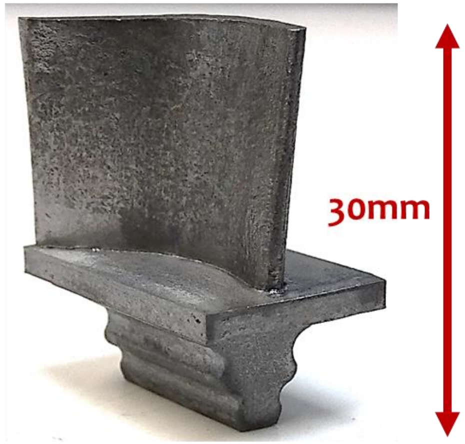


d=99% $4Y\text{-}ZrO_2$



Metals

Spark plasma sintered turbine blade



Ni superalloy

Compshape Strategy

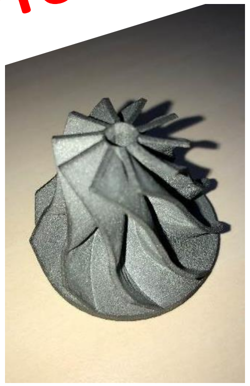
2nd Strategy

Preform

Porous prefrom
-
Partially consolidate
Fully Consolidated
zone on the perimete
of the object

3D printing Binder jetting
SLM,
etc…

Conclusion #3
SPS allows to elaborate
3D complex Near Net Shape Materials

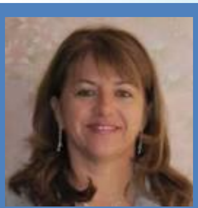


Fully dense parts with homogenous microstructures

C. Estournès *et al*, FR1860132A·2018-11-02
C. Estournès *et al*, FR1860133A·2018-11-02

Remerciements


Geoffroy Chevallier


Florence Ansart

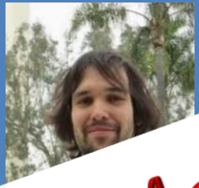

Christophe Laurent


Alicia Weibel


David Me


Thomas Herisson de Beauvoir


Antoine Lonjon




Simon Tardieu


Antoine Van der Laan


Mélanie Rousselle


Camille Estournès


Vincent Baylac

SAFRAN


rge elezneff


Guillaume Fradet

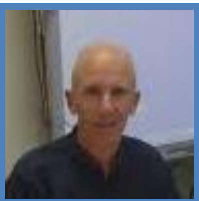
Lise Durand

icmcb institut de chimie de la matière condensée de bordeaux


Catherine Elissalde


Grazziella Goglio


Jérôme Majimel


Fabrice Mauvy


Mario Maglione


Michael Josse


U-Chan Chung


Matthew Suchomel

Merci de vôtre attention