Laser Pyrolysis Growth of ZrC, TiC, and SiC Nanopowders for Nanostructured Ceramics Elaboration

Yann Leconte, H. Maskrot, Nathalie Herlin-Boime,
Dominique Porterat, Cécile Reynaud.

Laboratoire Francis Perrin, Service des Photons Atomes et Molécules

DSM/DRECAM/SPAM - CEA Saclay

I – Interesting properties of nanostructured carbides

II – Laser pyrolysis technique

III – Carbide nanopowders synthesis

IV – Sintering of SiC and TiC nanopowders

V – Conclusion

Interesting properties of nanostructured carbides

➡ Refractory carbides : high temperature applications

➡ Nanostructure :

✓ *enhanced mechanical properties :*

- Hardness (R. Vassen, D. Stöver, *Phil. Mag. B*, 1997, vol. 76, no. 4, pp. 585-591.)

- Thermal shock resistance (A. Donato, E. Borsella, S. Botti, S. Martelli, C. A. Nannetti, M. R. Mancini, I. Morjan, *J. Nucl. Mater.*, 1996, vol. 233-237, no. 1, pp. 814-817.)

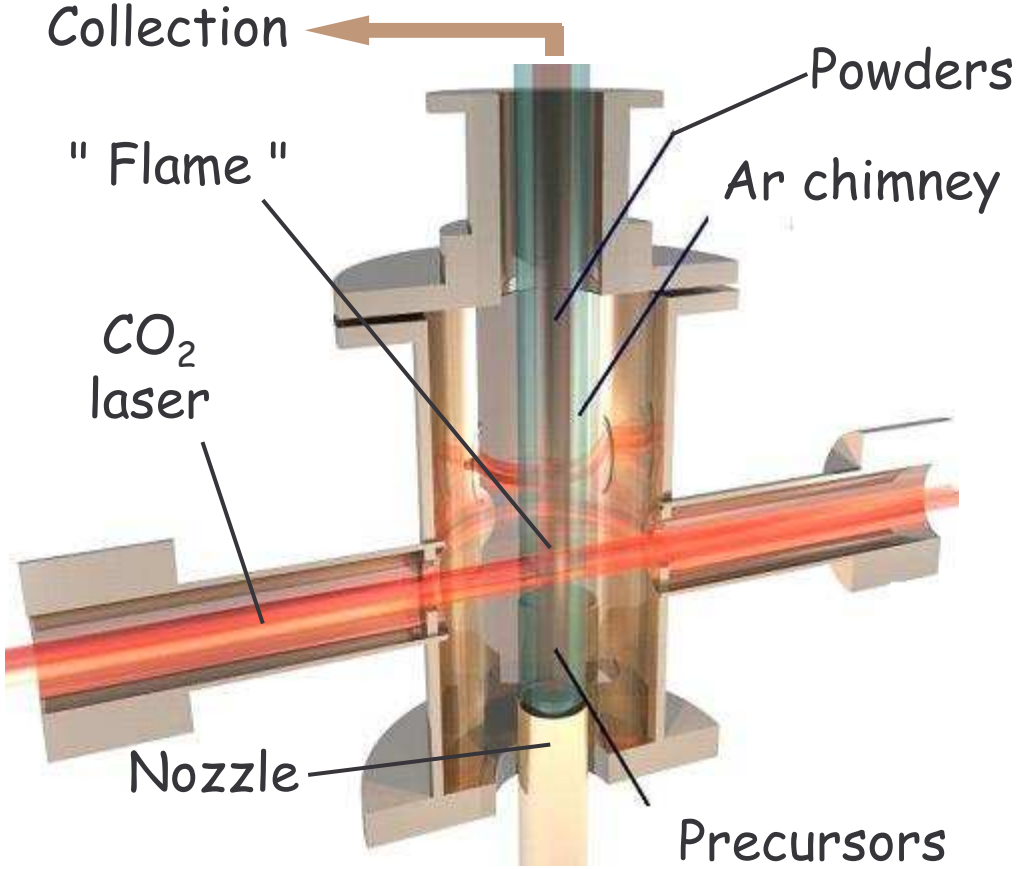
- Resistance to erosion (R. Vassen, A. Kaiser, D. Stöver, *J. Nucl. Mater.*, 1996, vol. 233-237, no. 1, pp. 708-712.)

✓ *behaviour under irradiation ?*

- high grain boundaries density = large amount of traps for defects

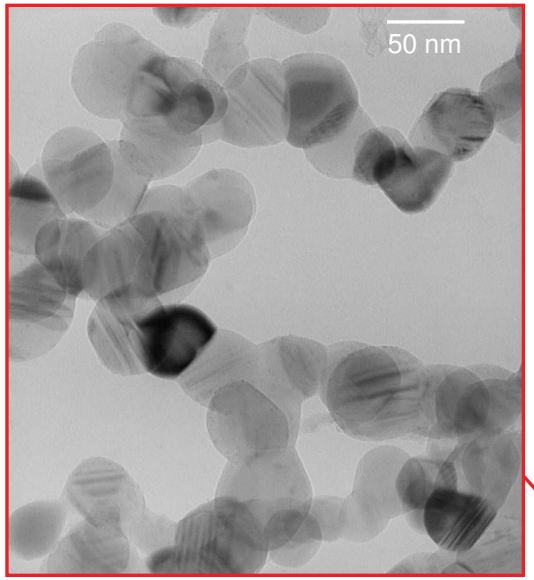
➡ Good candidates for next generation nuclear applications

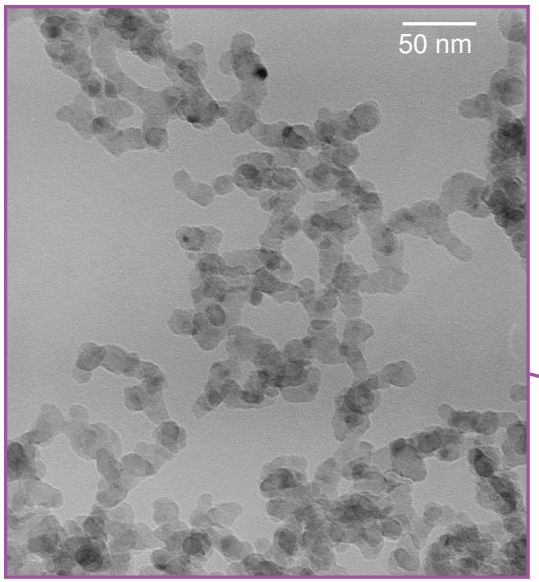
Laser pyrolysis technique



- No contamination by reactor walls
- Controlled grain growth
- Various precursors available (gas or liquid)
- Interesting for industrial purposes

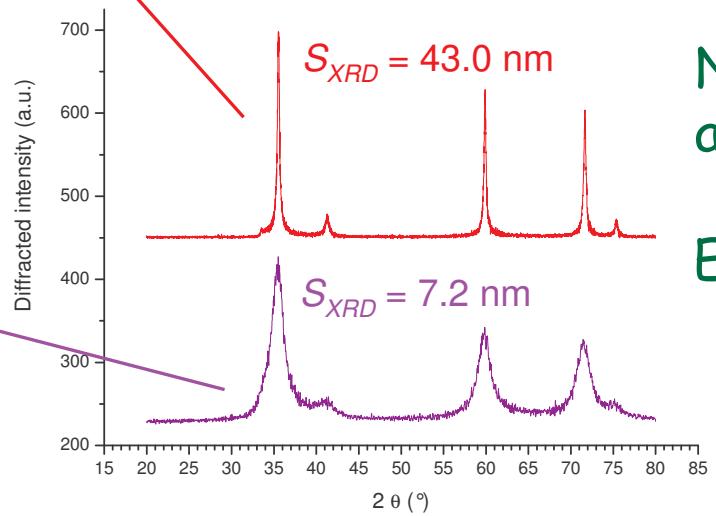
SiC nanopowders synthesis





Gaseous precursors : $SiH_4 + C_2H_2$ (+ He)

- β phase crystallization
- Density ~ 3.2
- Si/C (powder) = Si/C (precursor)
- chemical yield ~ 100 %
- Production = 100 $g.h^{-1}$ (lab.)



Narrow size distribution and controlled grain size

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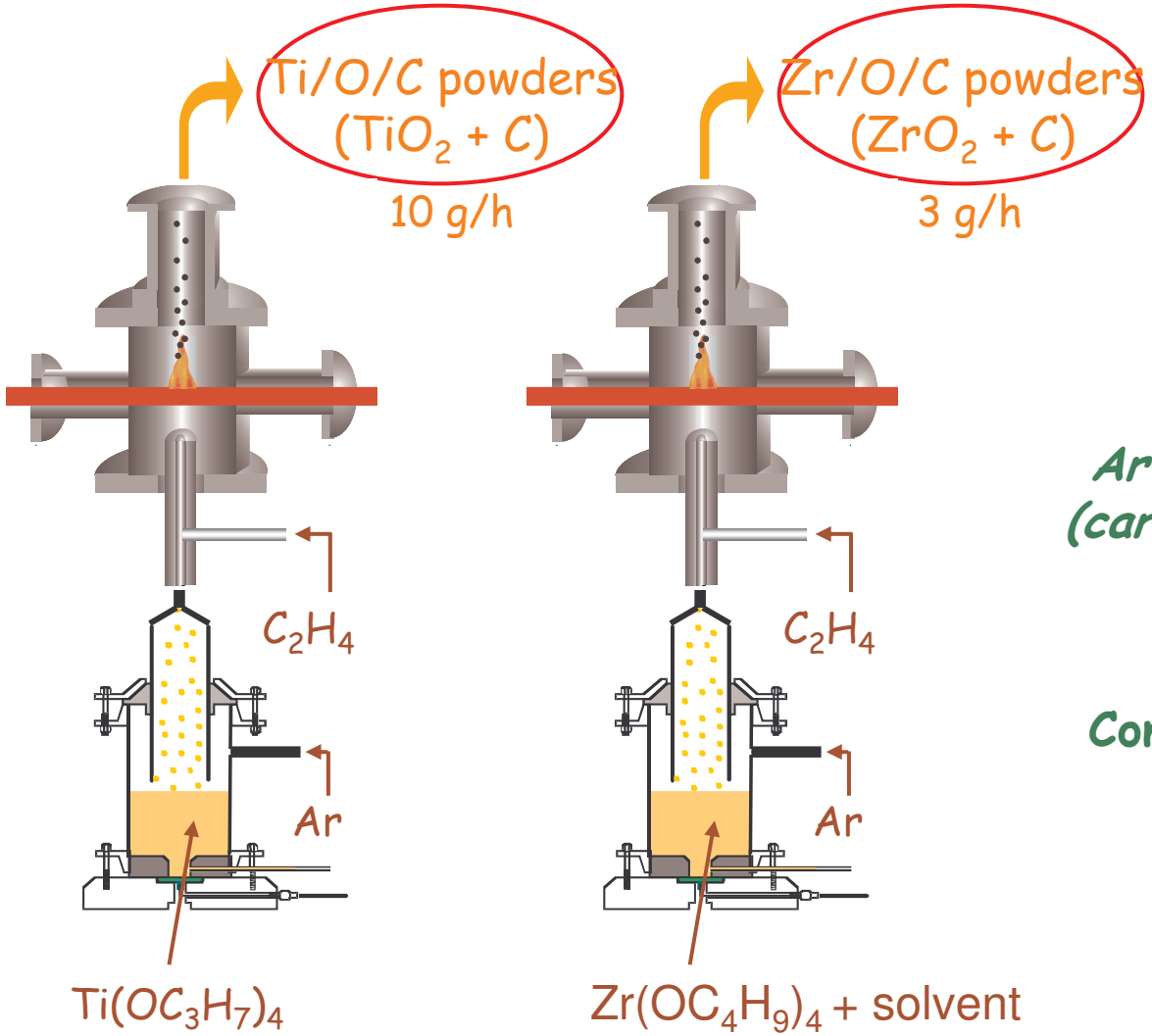
Enables the size effects study (densification, irradiation)

TiC and ZrC nanopowders synthesis

Ti/O/C et Zr/O/C powders synthesis from liquid precursors



Control of the oxide + C mixture composition

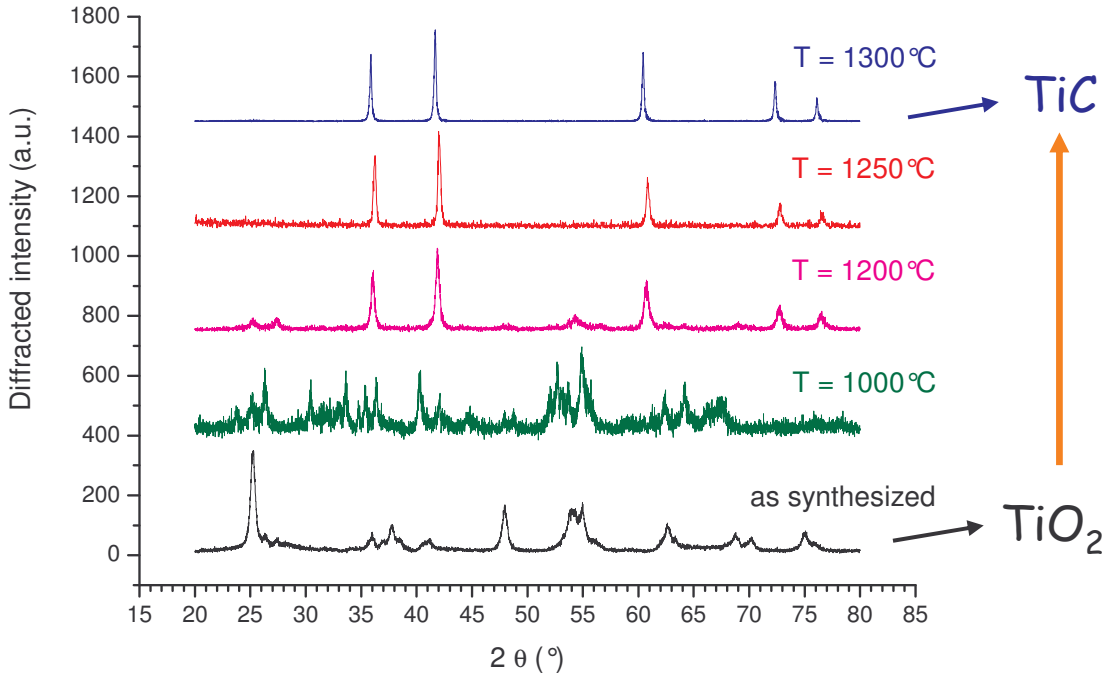
Ar annealing (carburization)

No additives

Control of the stoechiometry of the final carbide powder

TiC and ZrC nanopowders synthesis

Carburization study : TiC formation



$TiO_2 + 3\ C \rightarrow TiC + 2\ CO$

1h, Ar, no additives

Ref. a = 4,328 Å

T = 1300°C

⇩

Lower T than conventional carburization of raw TiO_2 + C black

T (°C)	Δm (%)	a (Å)	S_{XRD} (nm)
1200	29,7	4,296	33,1
1250	40,1	4,310	44,2
1300	44,4	4,331	82,0

J. Phys. Chem. B, 2005, in press

TiC and ZrC nanopowders synthesis

TiC stoechiometry study : C rich powder

	Powder	C (wt%)	Δm (%)	S_{XRD} (nm)	a (Å)
as synthe-sized	Ti/O/C (TiO_2 + C)	36,8	-	-	-
after carburi-zation	TiC	~ 14 % estimated	44,4	82,0	4,331

Very few oxygen

(Ref. a = 4,328 Å)

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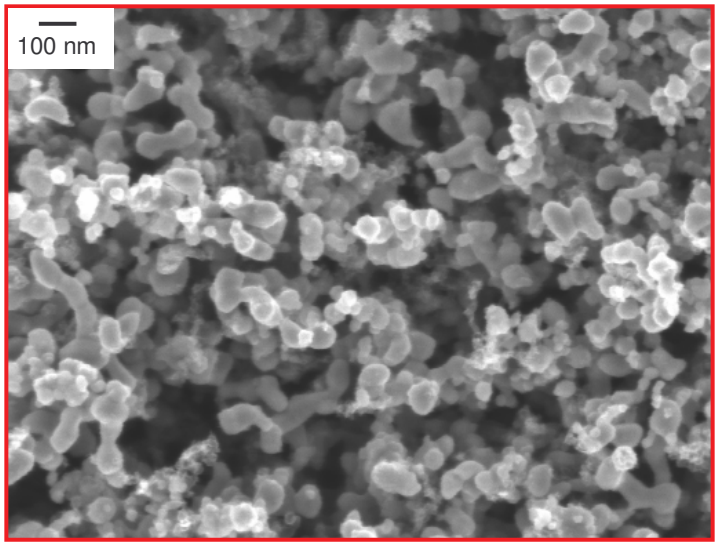
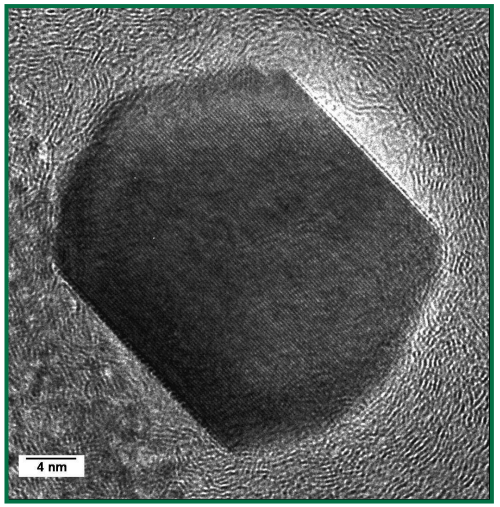


Homogeneous size distribution

SEM : HPRC Warsaw

TiC monocrystal surrounded by free C

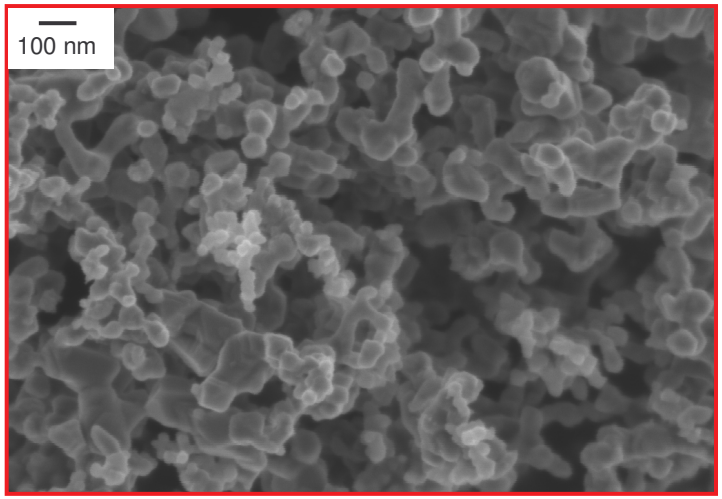


HREM : SIFCOM-ENSICAEN

TiC and ZrC nanopowders synthesis

TiC stoechiometry study : "stoechiometric" powder

	Powder	C (wt%)	Δm (%)	S_{XRD} (nm)	a (Å)
as synthe-sized	Ti/O/C (TiO_2 + C)	31,6	-	-	-
after carburi-zation	TiC	~ 1 % estimated	47,2	75,9	4,321



Oxidization in air : not protected by free C (Ref. a = 4,328 Å)

Wide size distribution (40 to 120 nm) : coalescence not inhibited by free C

SEM : HPRC Warsaw

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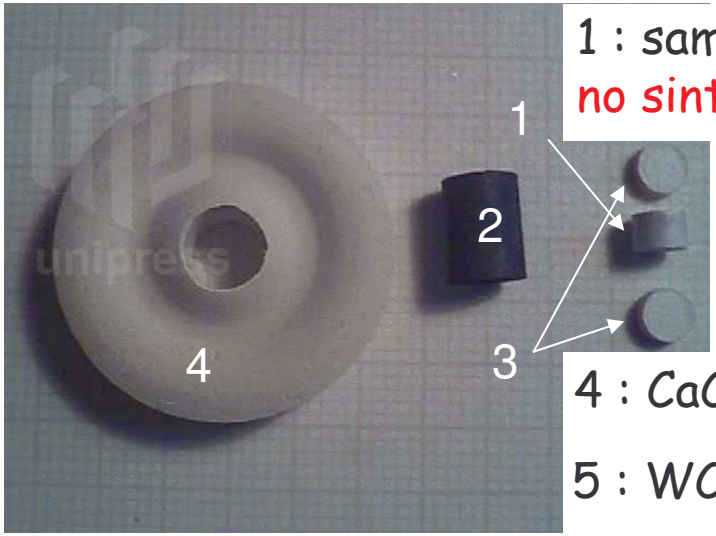
High pressure flash sintering (HPRC Warsaw)



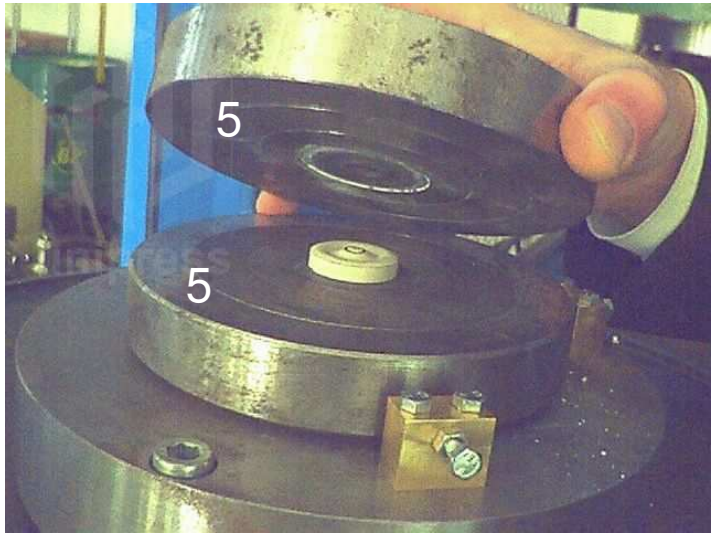
1 : sample (small amount)
no sintering additives

2 : graphite cylinder

3 : BN fillers

4 : $CaCO_3$ container

5 : WC anvils



- $P_s \leq 8$ GPa
- $T_s \leq 2000$ °C
- $t_s \sim 1$ to 10 min

SiC sintering

High pressure flash sintering (HPRC, Warsaw) :

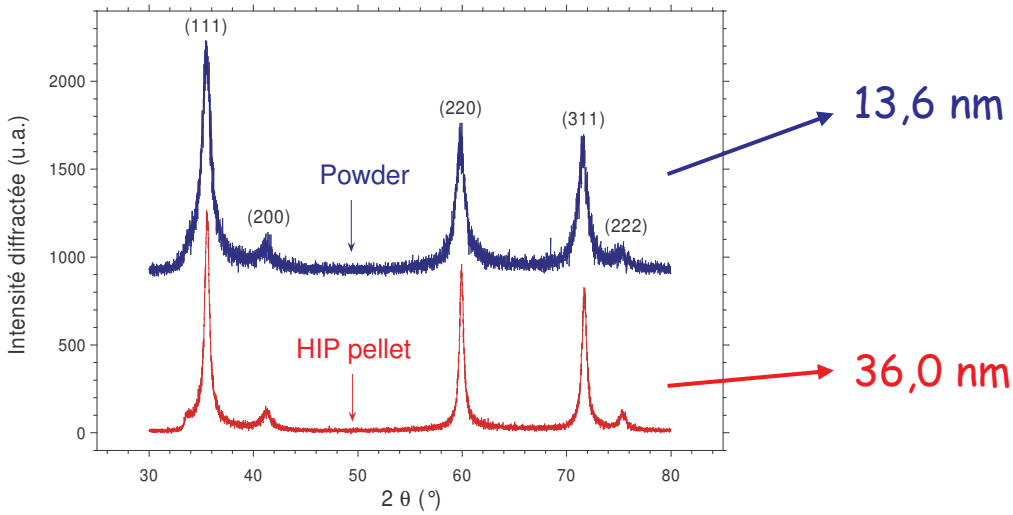
➢ P = 7,7 GPa, T = 1750 °C, t = 1 min

- no grain growth
- densification = 95 %
- strong residual stress

HIP sintering (DRT/LTMEX) :

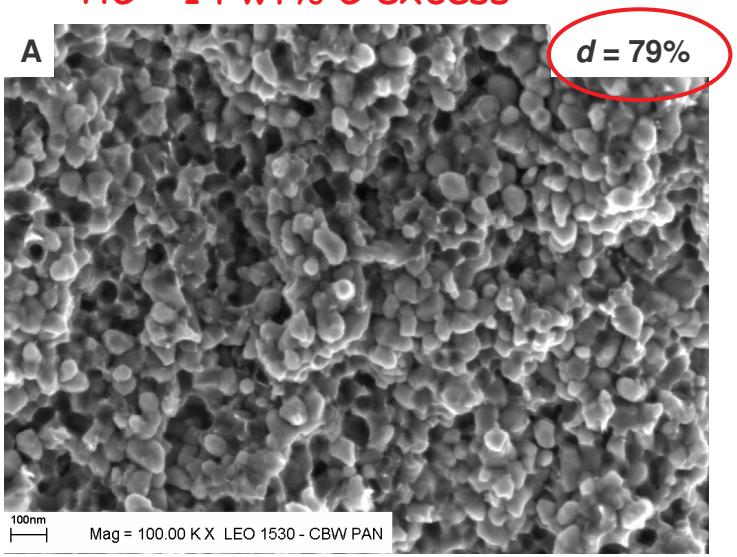
➢ P = 200 MPa, T = 1900 °C, t = 1 h

- occurrence of moderated grain growth
- densification = 92 %
- no (or few) residual stress



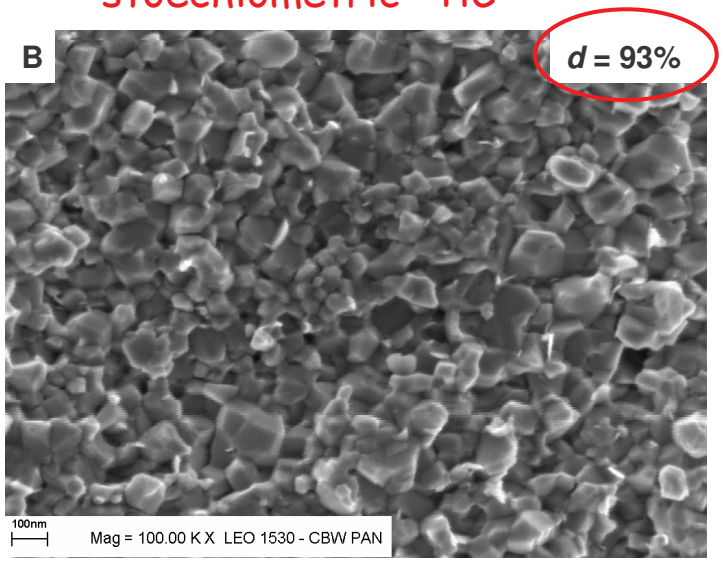
TiC high pressure flash sintering

TiC + 14 wt% C excess



- P_s : 8 GPa
- T_s : 1800 °C
- t_s : 2 min

"stoechiometric" TiC



SEM and density measurements : HPRC Warsaw

No grain growth, even without C excess

Effects of C excess :

- low densification
- inhibition of grain growth and coalescence
- protection from oxidization

J. Phys. Chem. B, 2005, in press

Conclusion

Conclusion :

✓ Synthesis of carbide nanopowders with controlled stoechiometry :

- SiC : accurate control of the grain size,
  high production rate and chemical yield
- TiC, ZrC : low carburization temperature

✓ Satisfying densification without grain growth during the additive-free sintering process

In progress :

- Synthesis : increased production, direct formation of the carbide phase for TiC and ZrC

- Ceramics : further investigations with different sintering techniques, in particular SPS (LRRS Dijon)

- Materials properties : behaviour under irradiation and mechanical tests.