CHARACTERIZATION OF SILICON CARBIDE AND PYROCARBON COATINGS FOR FUEL PARTICLES FOR HIGH TEMPERATURE REACTORS (HTR)

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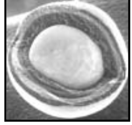
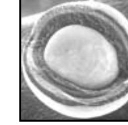
AGENDA



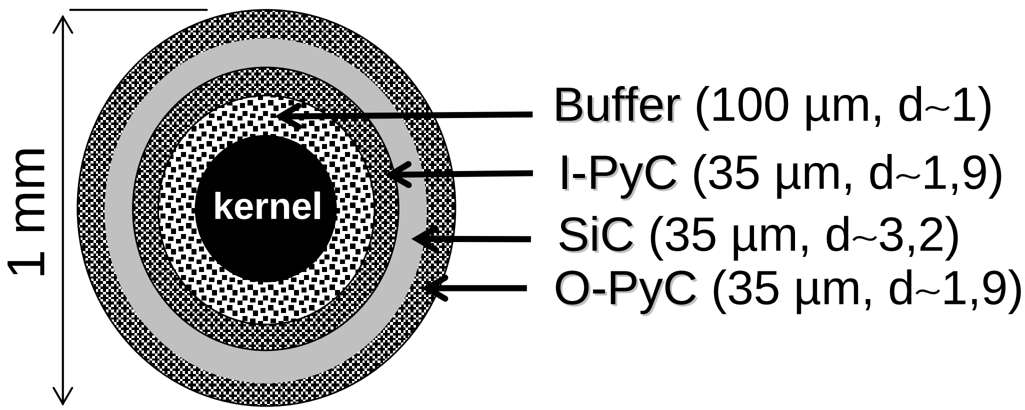
- Background
- SiC microstructure
- PyC microstructure
- PyC/SiC interfaces
- Concluding remarks

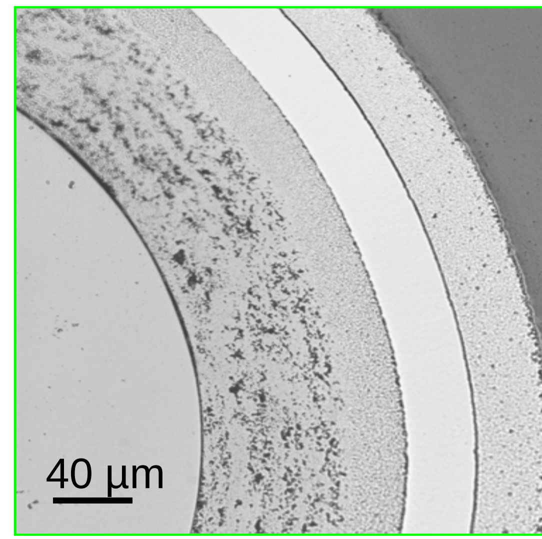


BACKGROUND

- Reviving interest worldwide for HTR technology (co-generation, safety, rentability)
- Fuel design = key element : 1st confinement barrier for fission products

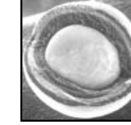
SiC/PyC multilayer coating





- Production and qualification of fuel particles are conducted by the CEA in collaboration with AREVA

BACKGROUND



PyC and SiC material challenges :

• *PyC* : gas-tight and perfect isotropic texture to improve performance under irradiation

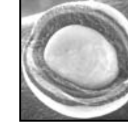
• *SiC* : β-SiC (cubic structure) to compensate the swelling effect due to irradiation and tight layer : fine-grained and strong grain boundaries to reduce the migration of fission products, less flaws as possible to sustain strain

• *PyC/SiC* interfaces : strong for mechanical synergy

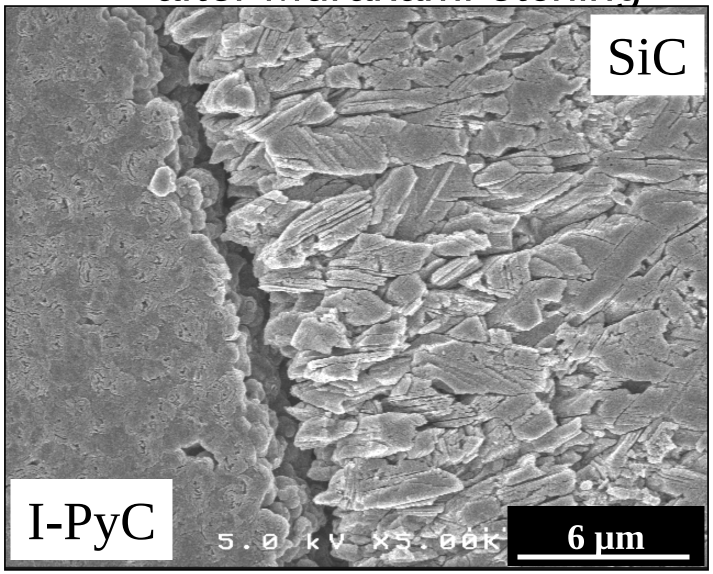
NEED FOR :

Developing analytical procedures
Characterising as-processed particles to improve process parameters
Comparing with analytic know-how developed in the 1970's

SiC MICROSTRUCTURE



SEM micrograph of SiC in cross-section after Murakami etching

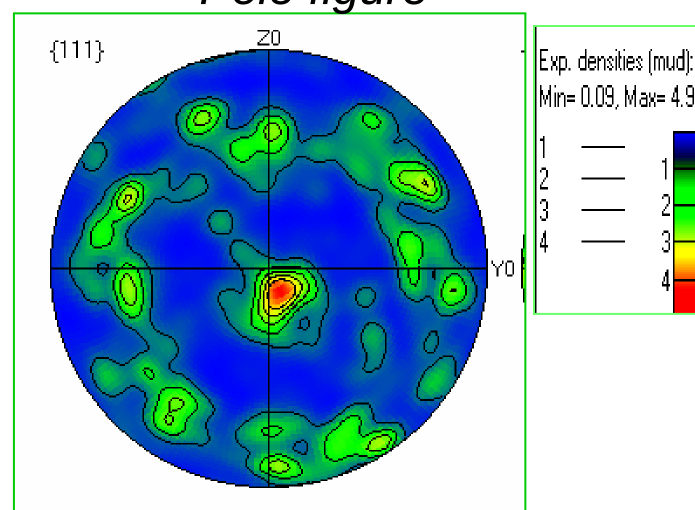


<u>Columnar grains</u> :

Thickness ~ 1 µm
Length ~ 4-5 µm

<u>Finer grains</u> in the beginning of the coating

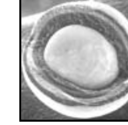
Pole figure



Exhibition of **<u>preferred orientation</u>** during growth
(Electron Back-Scattering Diffraction)

<111> pole parallel to the growth direction
XO normal to the particle

SiC MICROSTRUCTURE



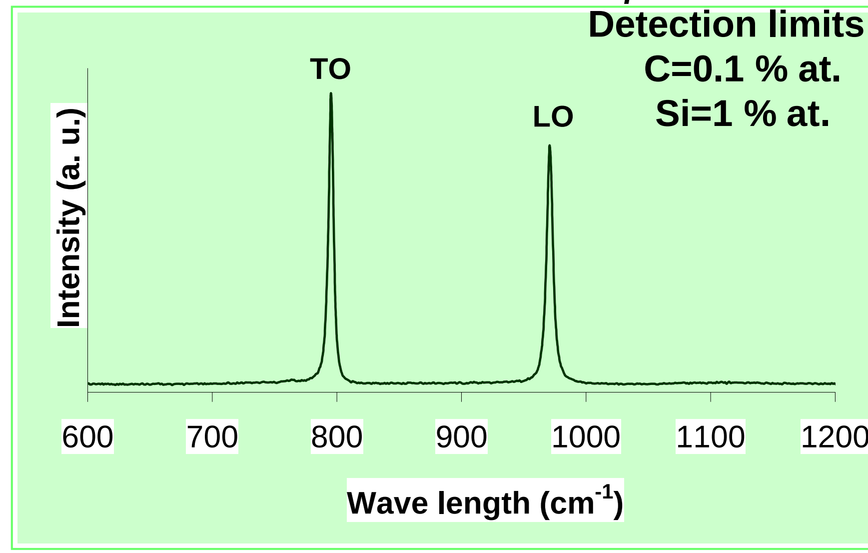
Crystallographic nature : **β-SiC (3C)**

No excess free carbon and silicon

SiC stoichiometric

Si/C=1.02 (Electron Probe Micro Analysis)

First-order Raman spectrum

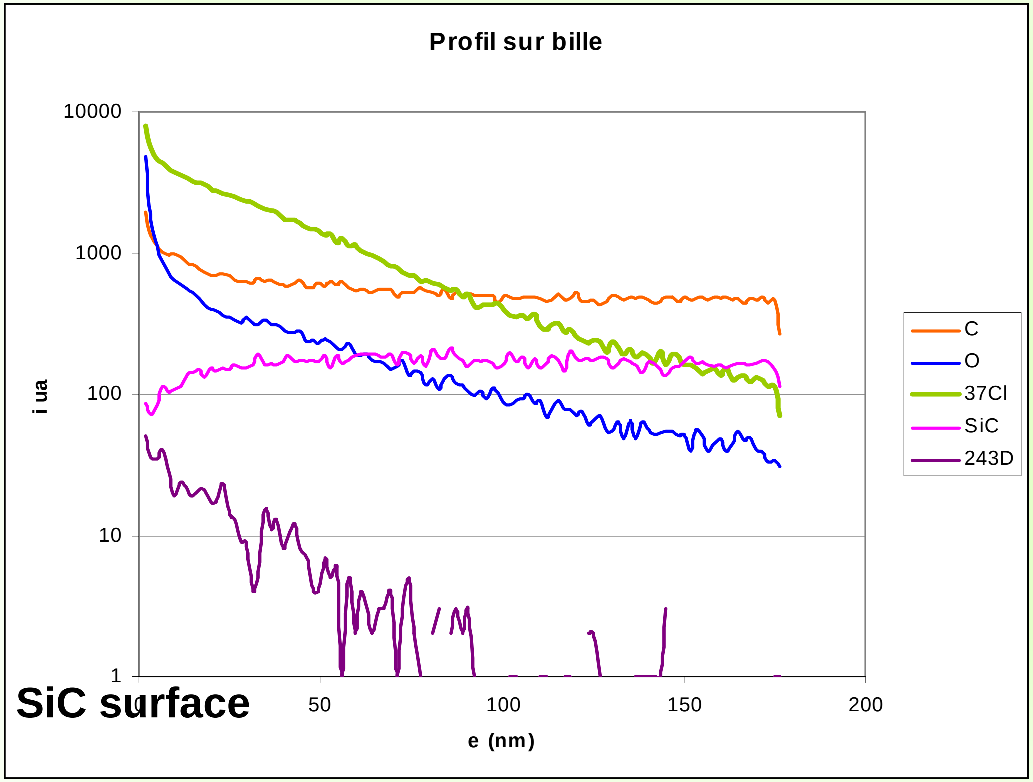


Detection limits :
C=0.1 % at.
Si=1 % at.

Measuring of chlorine :

- At the extreme surface concentration : 0.43 % at. (X-ray Photoelectron Spectrometry)
- In the core layer : **Cl<15 ppm** (EPMA)

SIMS DEPTH PROFILE :semi quantitative results



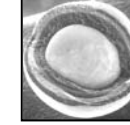
XPS analysis at :

C 83.24 %,

O 6.61 %,

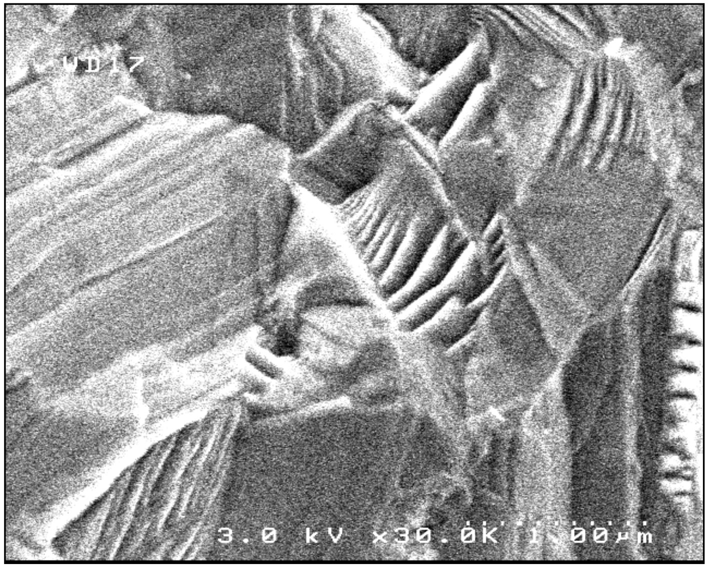
Si 9.72 %,

Cl 0.43 %



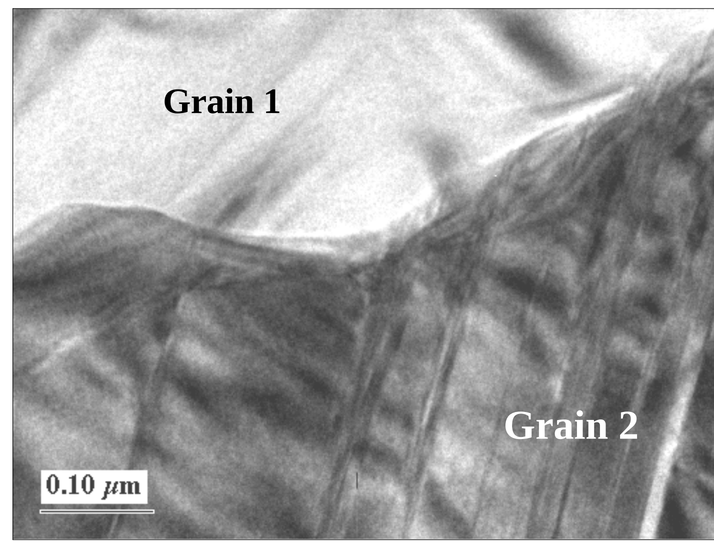
SiC MICROSTRUCTURE

SEM fractography



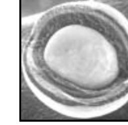
Predominantly transgranular cleavage

Bright field TEM image



No intergranular porosity

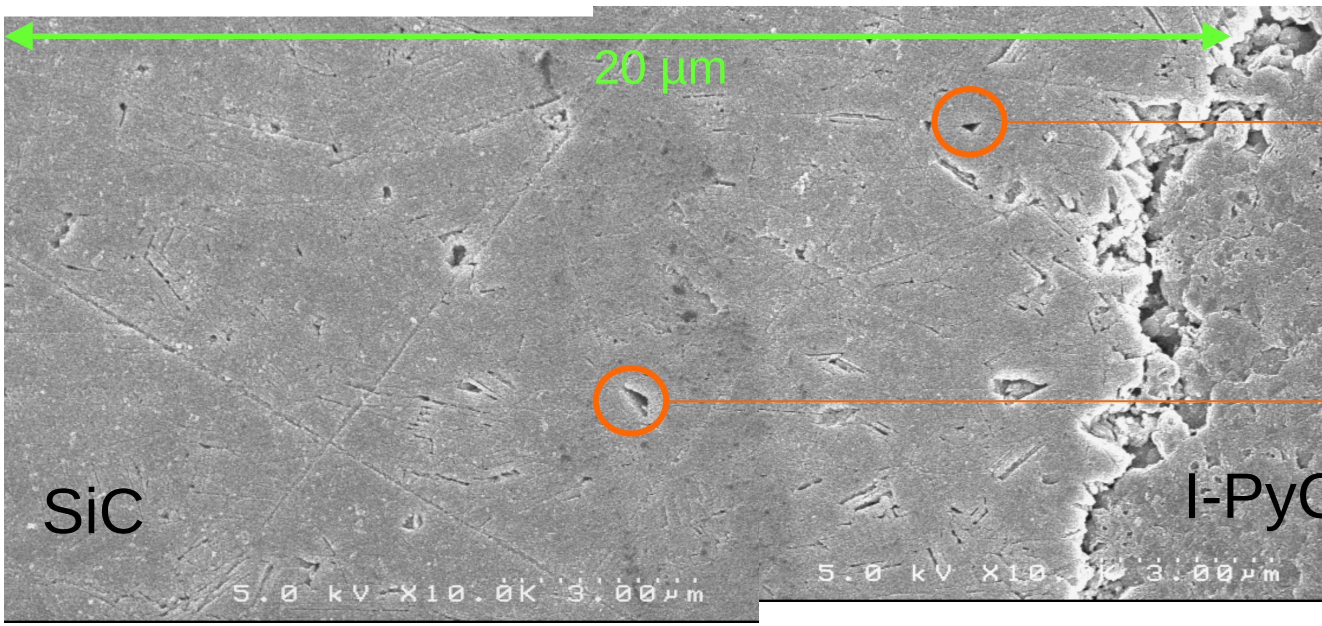
Strong grain boundaries
no free C,Si and Cl detected



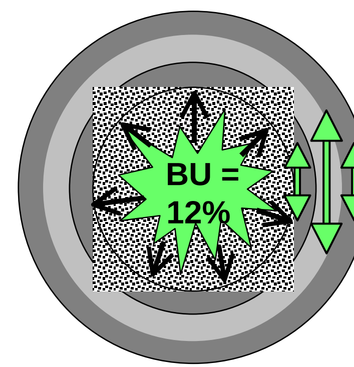
SiC MICROSTRUCTURE

Evidence of flaws by short etching on polished surface

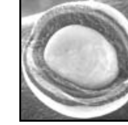
(reducing the SiC elastic limit)



Microcavities
= **Potential cracks initiators**



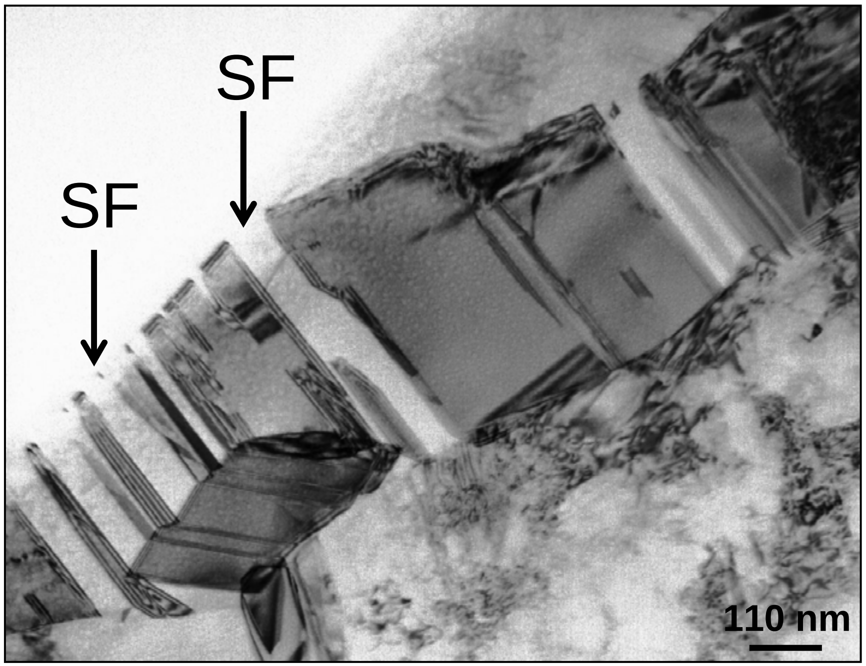
Prevision on the cracks apparition and propagation in the layer



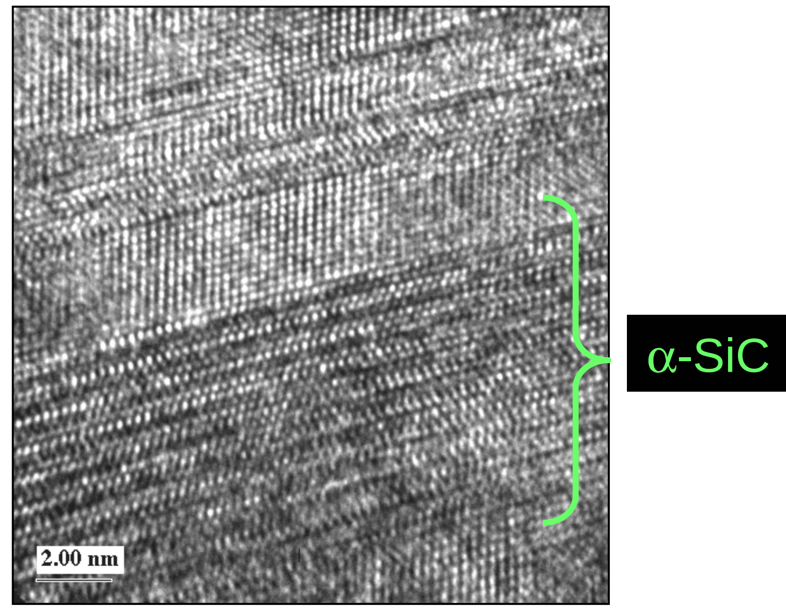
Evidence of crystallographic Stacking Faults (SF) by TEM

Observations along the <110> β-SiC crystal direction

Bright field TEM image

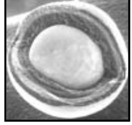


HRTEM image



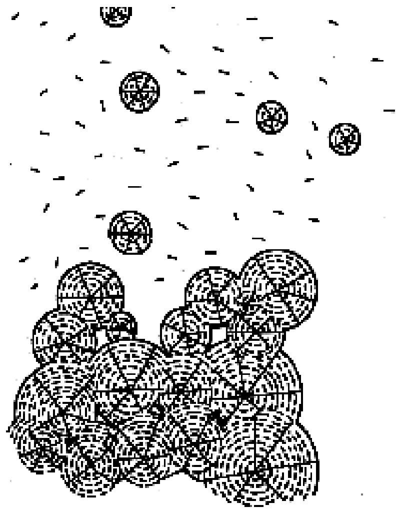
Very few α-SiC

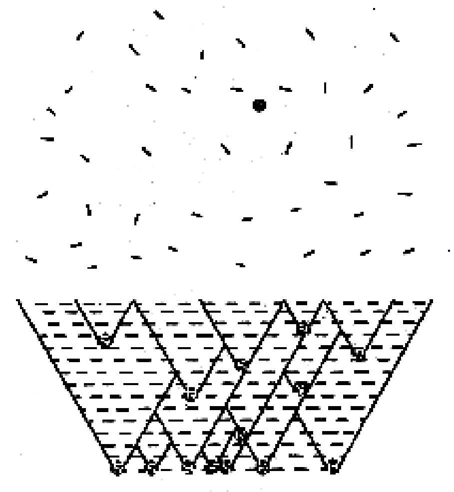
Rather "one-dimensionally-disordered" polytypes



PyC MICROSTRUCTURE

PyC texture : competition of 2 growth mechanisms





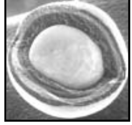
Reactions in the gas-phase :

Isotropic PyC

Direct deposition onto the surface :

Anisotropic PyC

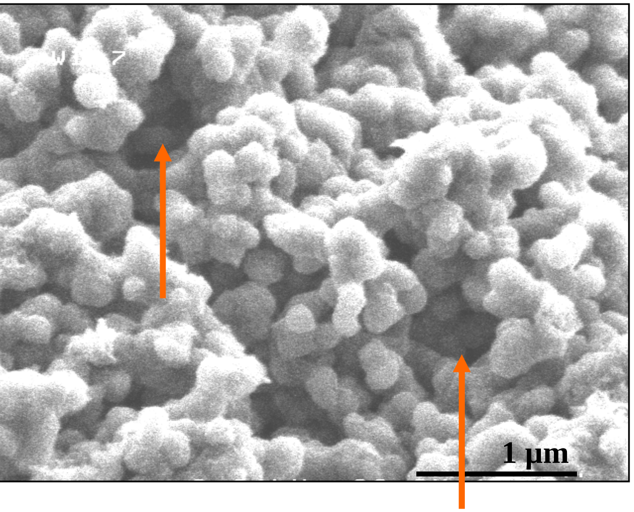
J.L. Kaae, *Carbon*, 23, 6, 665-673, 1985



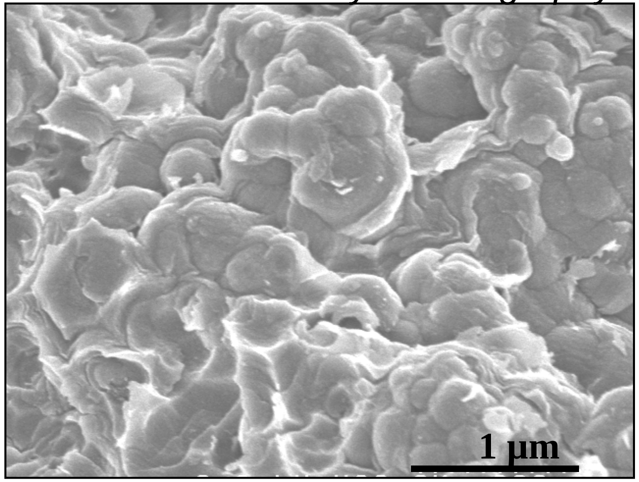
PyC MICROSTRUCTURE

SEM images

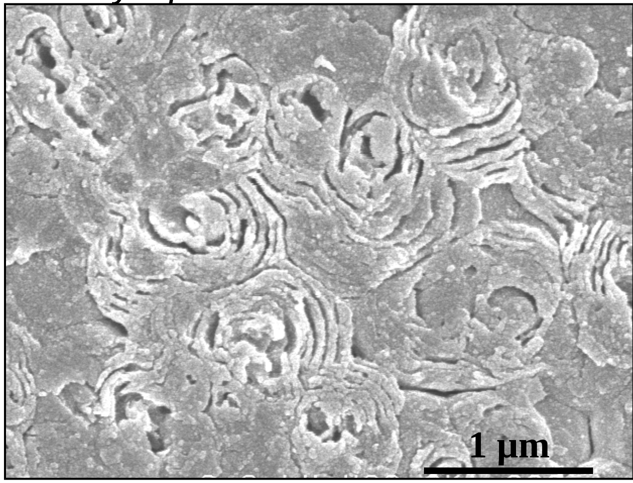
Buffer fractography



I-PyC fractography

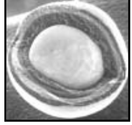


I-PyC polished and etched section



Agglomerated spheroids formed in the gas phase (Diameter = 300-400 nm)

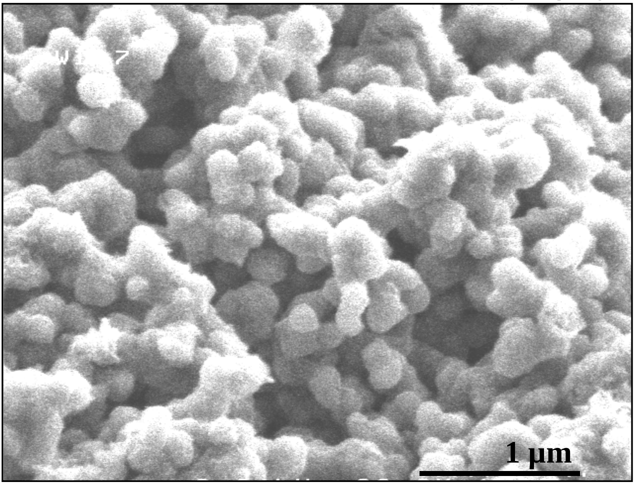
Heterogeneous distribution of opened porosity



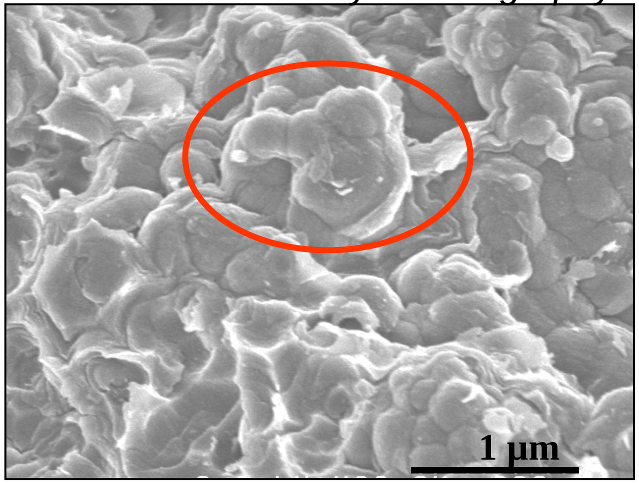
PyC MICROSTRUCTURE

SEM images

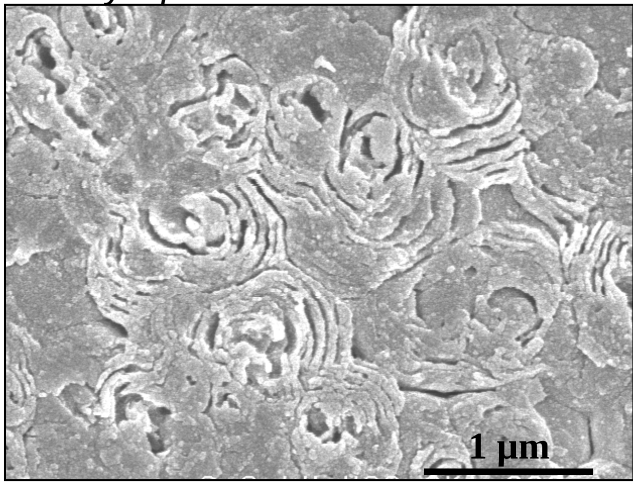
Buffer fractography



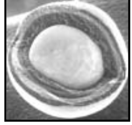
I-PyC fractography



I-PyC polished and etched section

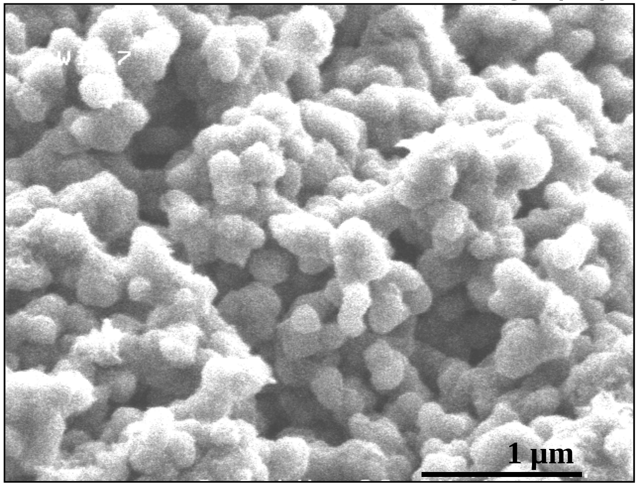


Agglomerated spheroids
(mean diameter=500 nm)
surrounded by PyC deposited
directly on the substrate

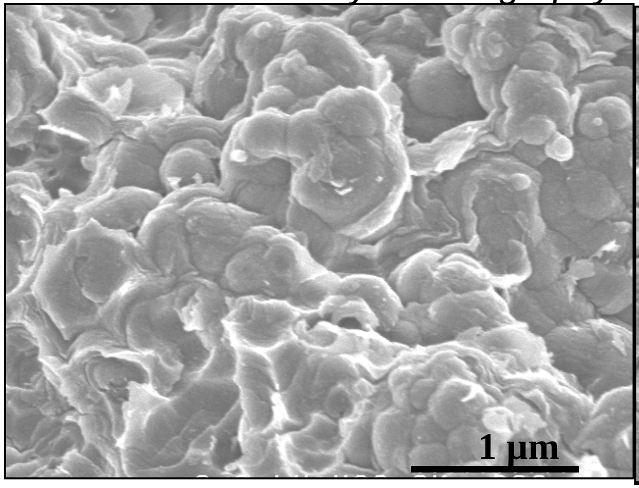


SEM images

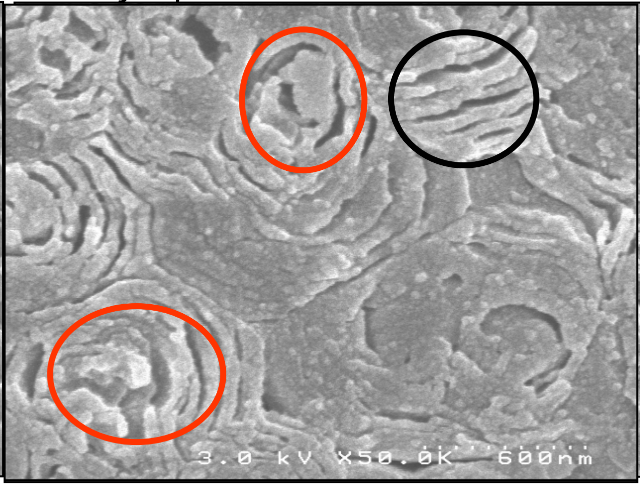
Buffer fractography



I-PyC fractography

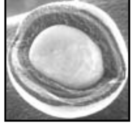


I-PyC polished and etched section



Isotropic PyC fraction

Anisotropic PyC fraction

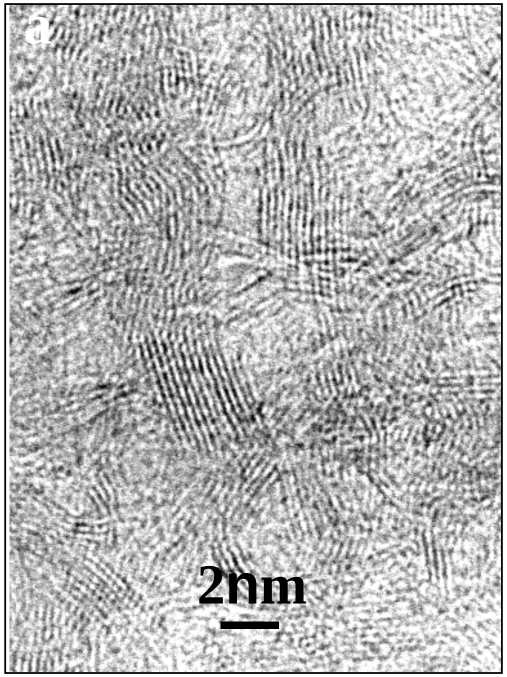


PyC MICROSTRUCTURE

HRTEM images

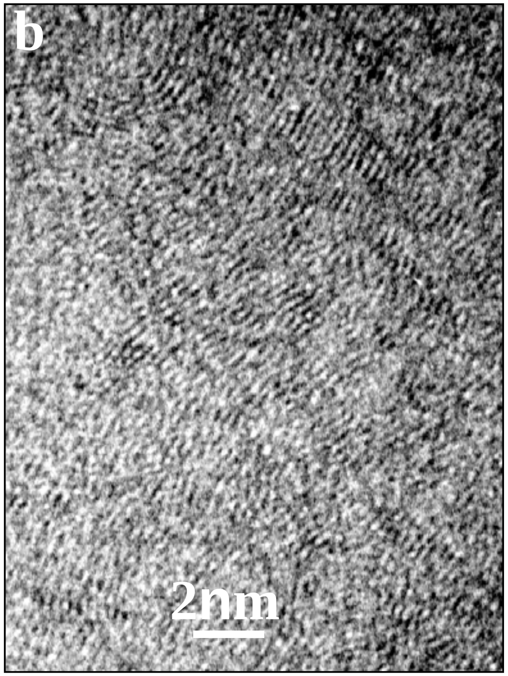
<u>Good agreement with CEA (Pelissier & Lombard) PyC classification (1976)</u>

Buffer



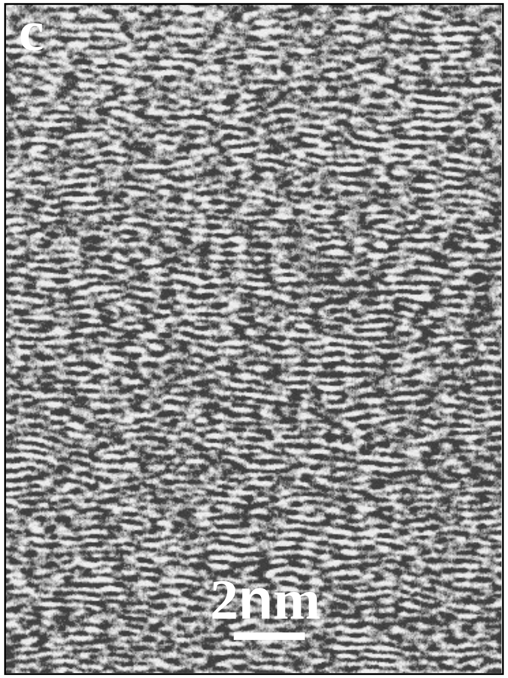
“Tangled fiber”

I-PyC

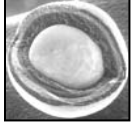


“Layered”

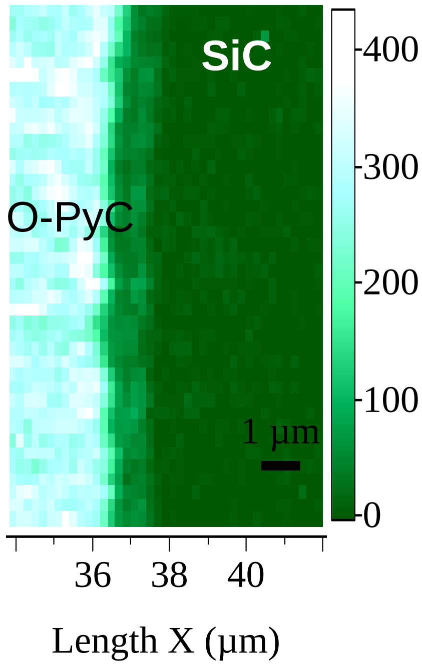
Flat substrate

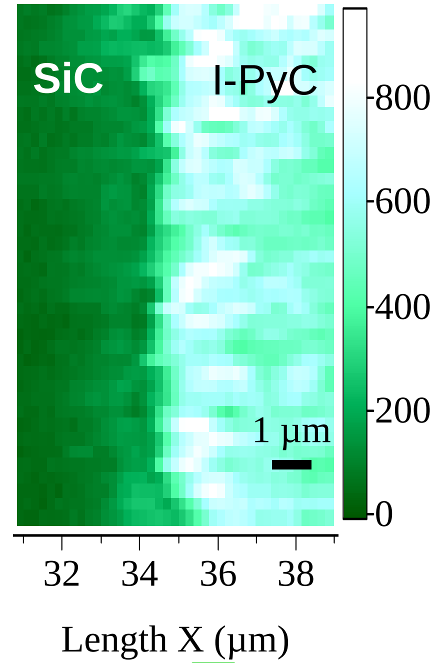


“Mosaic”



Raman mapping on polished cross-sections



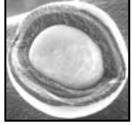


Smooth O-PyC/SiC interface

Weak interface

Rough SiC/I-PyC interface

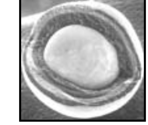
Strong interface



- Re-appropriation of analytical know-how developed in the 1970's

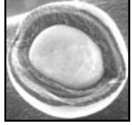
Methods	Specimen preparation	Informations on SiC	Informations on PyC
Fractography	Fracture surfaces	❑ Presence of flaws ❑ Fracture mode (transgranular or intergranular)	❑ Morphology
Etching + SEM	On caps or polished cross-sections	❑ Grains size ❑ Morphology ❑ Stacking faults	❑ Texture ❑ Fraction of anisotropic dense PyC
TEM	Thin slices thinned mechanically and by ion sputtering	❑ Grains size and morphology ❑ Nature of crystallographic defects ❑ Quality of grain boundaries	❑ HR-TEM structure ❑ Texture ❑ Isotropy treshold
XRD	Powders	❑ Presence of hexagonal polytype	❑ Structure ❑ (d_{002} ; L_c)
DAR	Polished cross-sections	_	❑ Isotropy

CONCLUDING REMARKS



• New analytical procedures for qualifying the microstructure of fuel particles

Methods	Specimen preparation	Informations on SiC	Informations on PyC
TEM observations Imaging + diffraction	Thin slices thinned by **Focus Ion Beam (FIB)**	❑ Grains size and morphology ❑ Nature of crystallographic defects ❑ Quality of grain boundaries	❑ HR-TEM structure ❑ Texture ❑ Isotropy treshold
Raman microspectroscopy + mapping	Polished cross-sections	❑ Presence of hexagonal polytypes ❑ Presence of excess Si and C	❑ Crystalline organisation (presence of defects) ❑ Chemical composition near interfaces with the SiC
EBSD	Polished cross-sections	❑ Grains size and morphology ❑ Texture	–
EPMA	Polished cross-sections	❑ Stoichiometry Si/C	–
XPS-ToF-SIMS	Without	❑ Chemical composition of the SiC extreme surface	–



CONCLUDING REMARKS

- Re-appropriation of analytical know-how developed in the 1970’s

- New analytical procedures for qualifying the microstructure of fuel particles

- Next challenge :
  correlation growth mechanisms / microstructure