DE LA RECHERCHE À L'INDUSTRIE

INSPYRE

Investigations Supporting MOX Fuel Licensing in ESNII Prototype Reactors

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Gen IV advanced fuel fabrication routes (Part II)

Fuels for Na-cooled fast reactors

Romain VAUCHY

PHENIX prototypic SFR reactor, Marcoule, France

13 May, 2019 Delft – The Netherlands

Introduction – Gen IV fuels (SFRs)

What is it?

Uranium-Plutonium mixed oxide: $\mathbf{U_{1-y}Pu_yO_{2-x}}$

⚠ Shouldn't be called **MOX**

↓

Only for LWRs

Why?

Use of Pu bearing nuclear fuel: reprocessing strategies

How to burn Pu? Where?

In France : from 1987: Use of MOX fuels in 22 plant units of 900 MWe EdF reactors (LWRs), with about 30 % MOX assemblies

Up to 2007: Management with "hybrid" mode (three-batch reload for MOX fuels whereas four-batch reload for UO_2 fuels)

From 2007: MOX parity program (four-batch reload for MOX and UO_2 fuels, up to 52 GWd/t)

➡ **In the future : more Pu to burn → Pu ex-MOX → GenIV → SFRs**

Introduction – Manufacturing restrictions

- **General radiation protection (radioprotection) control**
- **Criticality problems**
- **Cleanliness of the facilities and protection of the environment**
- **Strict control and accountability of the fissile material**

- ➢ Operations in tight containments up to the stage of the welded rod
- ➢ Atmospheric surveillance with alarm and detection systems
- ➢ Limit workers exposure to γ rays and neutrons
- ➢ Increased protection against the criticality risk: limitation of the unit masses used, suitable equipment geometry and limitation of the moderating materials
- ➢ Suppression or reduction of operator presence near the equipment through state-of-the art mechanization, by limiting the interventions to maintenance and repair operations.

Fuel

Different fuels for SFRs

Fuel without MAs → Fuel for SFRs (PHENIX, SUPERPHENIX, ASTRID, …)

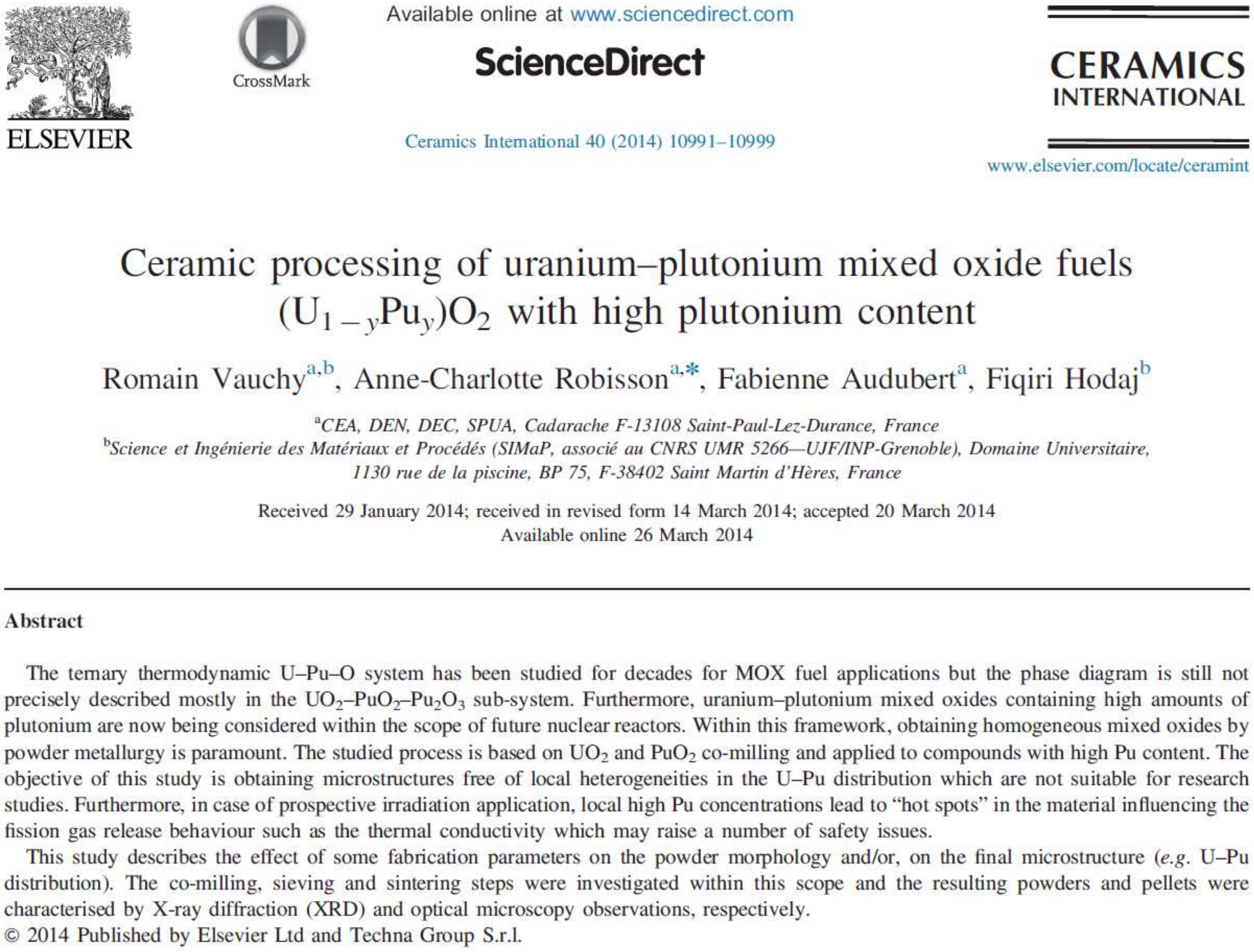
→ **Pu recycling**

Fuel with MAs (Am, Np, Cm) → Fuel for transmutation (GEN IV)

→ **Heterogeneous Recycling: U, Pu and MA in separated way**
→ Solid solution or Composite with high MA contents (from 10 to 20 %)

→ **Homogeneous Recycling: U, Pu, MA recycling**
→ Solid solution with low MA contents (from 2 to 5 %)

Manufacturing of SFR fuels



Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 40 (2014) 10991–10999
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Ceramic processing of uranium–plutonium mixed oxide fuels $(U_{1-y}Pu_y)O_2$ with high plutonium content

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Abstract

The ternary thermodynamic U–Pu–O system has been studied for decades for MOX fuel applications but the phase diagram is still not precisely described mostly in the UO_2–PuO_2–Pu_2O_3 sub-system. Furthermore, uranium–plutonium mixed oxides containing high amounts of plutonium are now being considered within the scope of future nuclear reactors. Within this framework, obtaining homogeneous mixed oxides by powder metallurgy is paramount. The studied process is based on UO_2 and PuO_2 co-milling and applied to compounds with high Pu content. The objective of this study is obtaining microstructures free of local heterogeneities in the U–Pu distribution which are not suitable for research studies. Furthermore, in case of prospective irradiation application, local high Pu concentrations lead to "hot spots" in the material influencing the fission gas release behaviour such as the thermal conductivity which may raise a number of safety issues.

This study describes the effect of some fabrication parameters on the powder morphology and/or, on the final microstructure (*e.g.* U–Pu distribution). The co-milling, sieving and sintering steps were investigated within this scope and the resulting powders and pellets were characterised by X-ray diffraction (XRD) and optical microscopy observations, respectively.

Manufacturing of SFR fuels - specifications

Main specifications

- **Pu content > 20 % → ~30 %**
- **Density > 95% Dth**
- **Homogeneous distribution of cations (U and Pu)**
- **1.94 < Oxygen/Metal ratio < 2.00**

To avoid cladding oxidation

To avoid fuel melting
(as thermal conductivity drops when O/M decreases)

Fabrication process

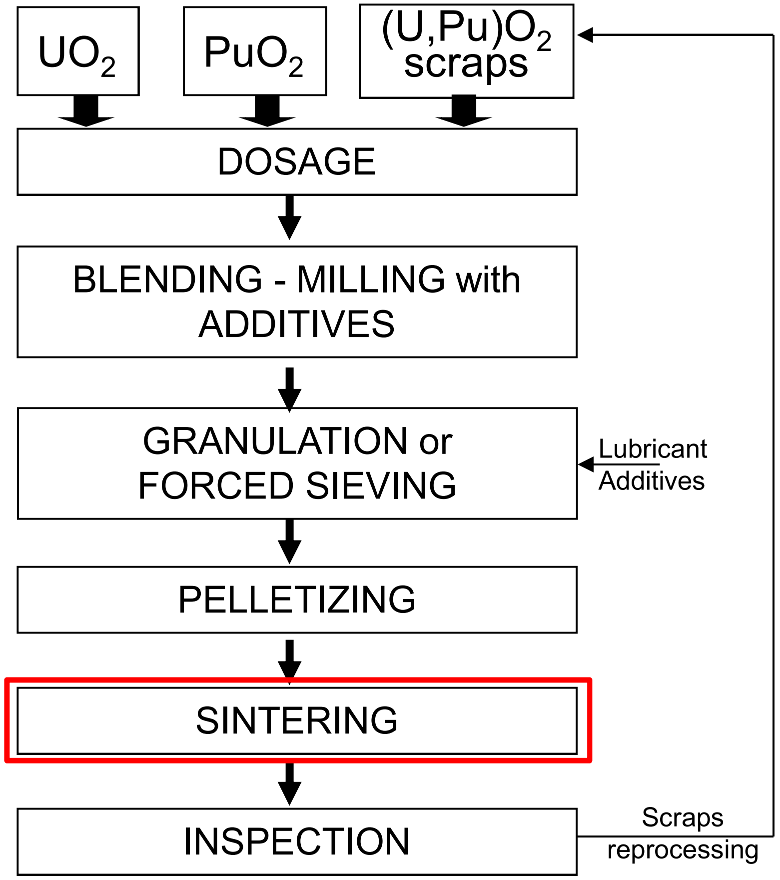
- Manufacturing devices similar to those used for PWR fuels
  - Co-milling with ball mill (uranium-titanium low-alloy balls)
  - Forced sieving → pushing through grids (250 µm)
  - Additives
  - Pelletizing → 500 Mpa
  - Sintering

Manufacturing of SFR fuels – powder metallurgy process

Fabrication process

Developed up to 1995 at CFCa* (30 years) as fast reactors fuels

Direct **co-milling** (co-granulation) of UO_2 and PuO_2 (called **COCA process**)



OBJECTIVES	
Obtention of appropriate U and Pu concentrations	DOSAGE
Micronization → increase in (1) specific surface area and (2) cation distribution homogeneity	BLENDING - MILLING with ADDITIVES
Destruction of « big » agglomerates Improvement of powder flowability	GRANULATION or FORCED SIEVING
Formation of green pellets	PELLETIZING
Densification + formation of solid solution + control of O/M ratio	SINTERING
Control of specifications (to avoid *problems* during irradiation)	INSPECTION

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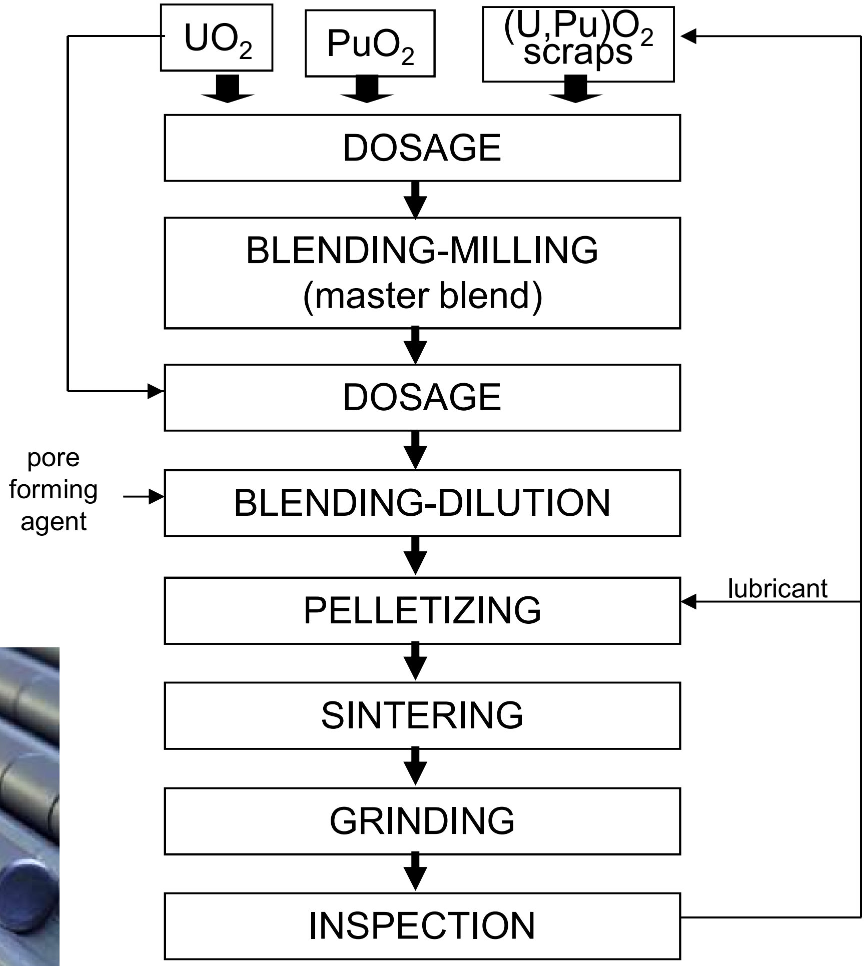
* Complexe de Fabrication de CAdarache (COGEMA)

Manufacturing of SFR fuels – comparison with MIMAS

MIMAS Process (MIcronization of MASter blend)

Industrial process
used at MELOX



For MOX fuel (PWRs)

MOX fuel pellets

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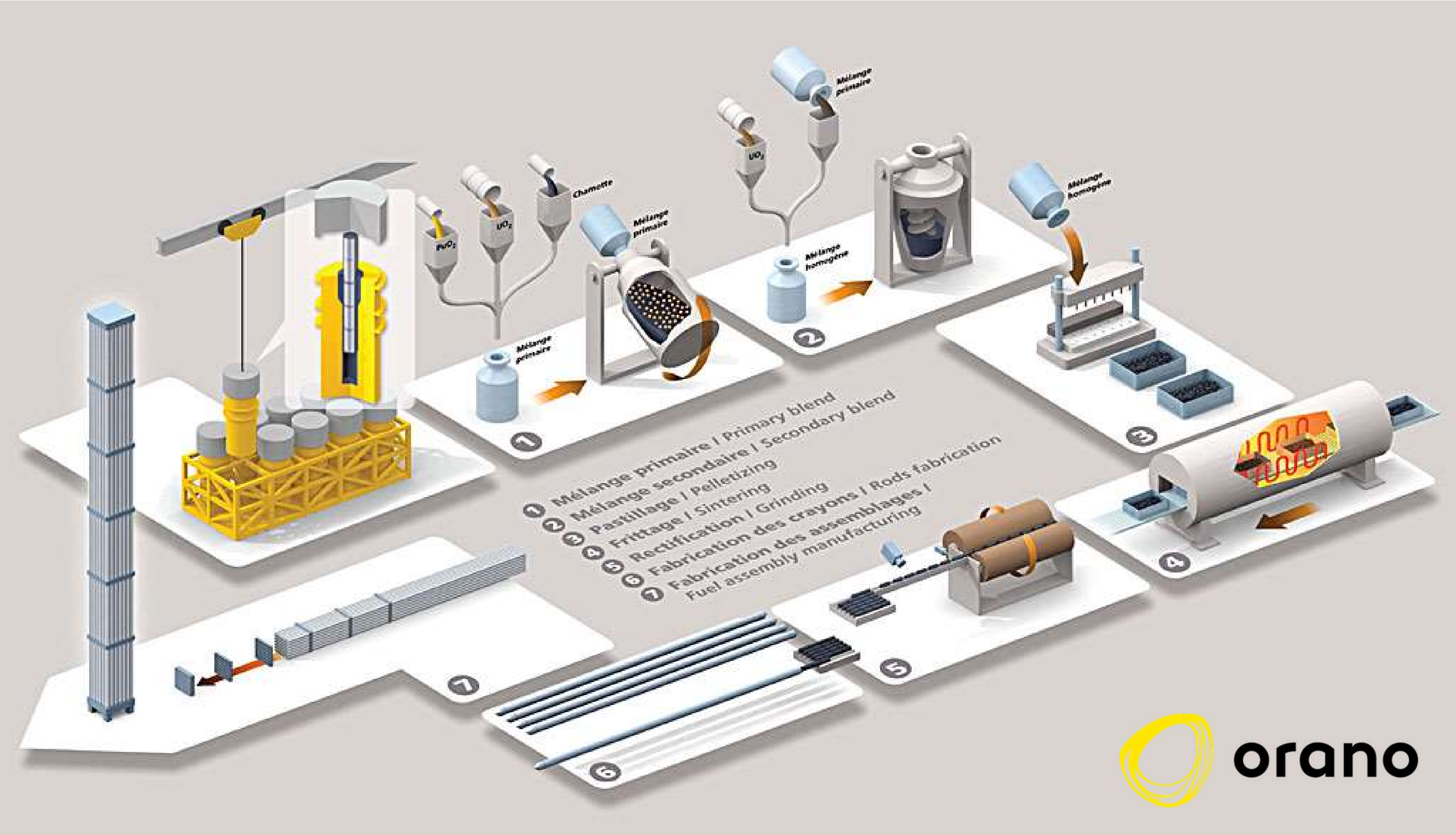
Manufacturing of SFR fuels – comparison with MIMAS

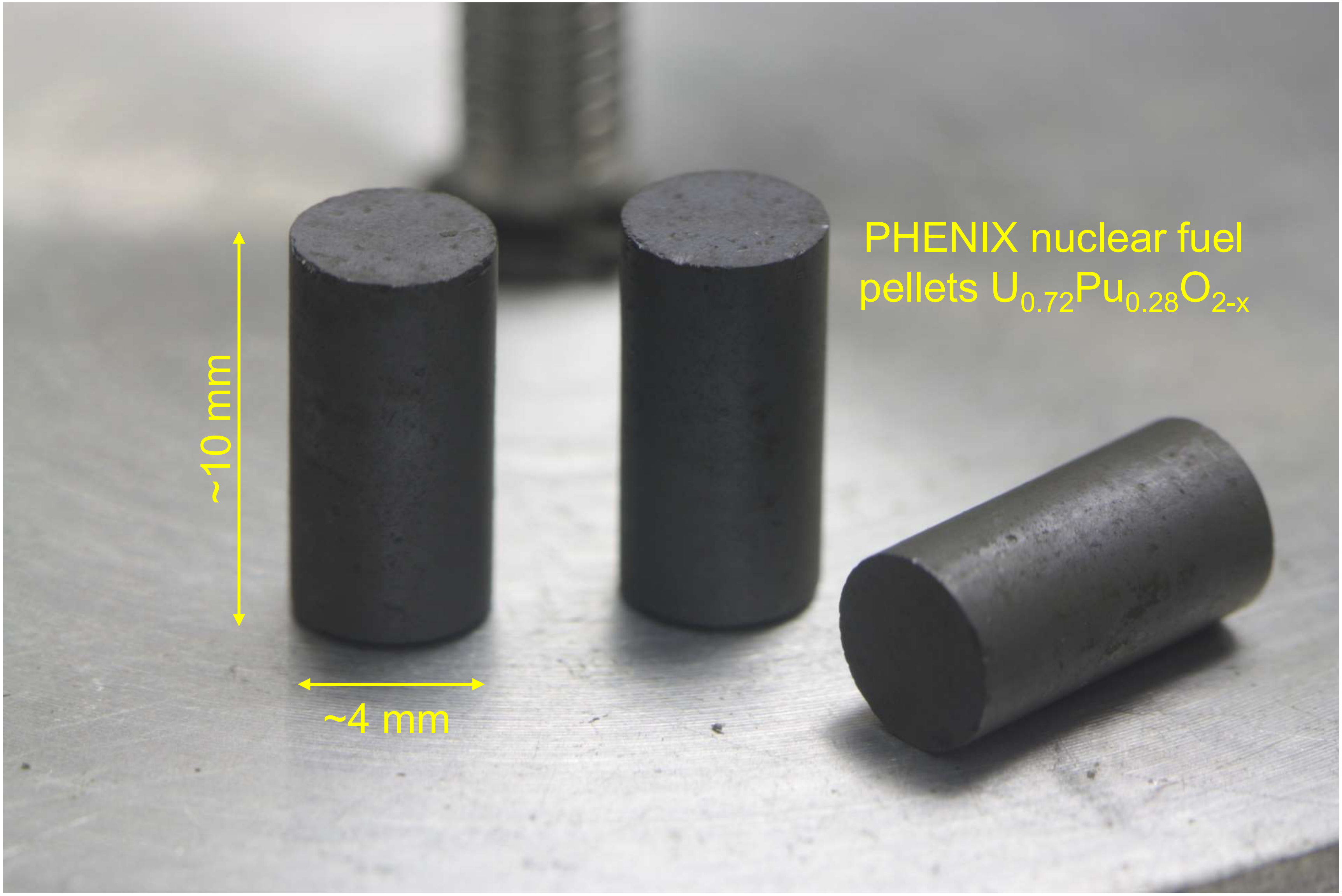


Credit : Orano

What does it look like ?


PHENIX nuclear fuel pellets $U_{0.72}Pu_{0.28}O_{2-x}$

What does it look like ?



PHENIX nuclear fuel pellets $U_{0.72}Pu_{0.28}O_{2-x}$

Manufacturing of SFR fuels – processing tools

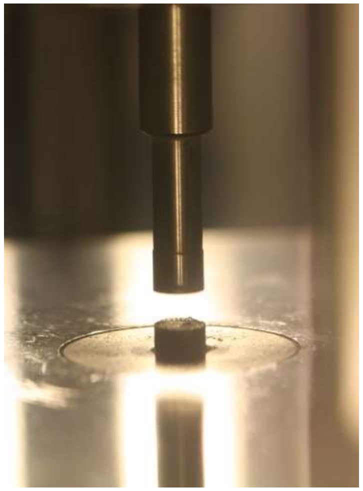
Mixer

- Rotary speed
- Time
- Powder mass
- Tank volume

Ball mill

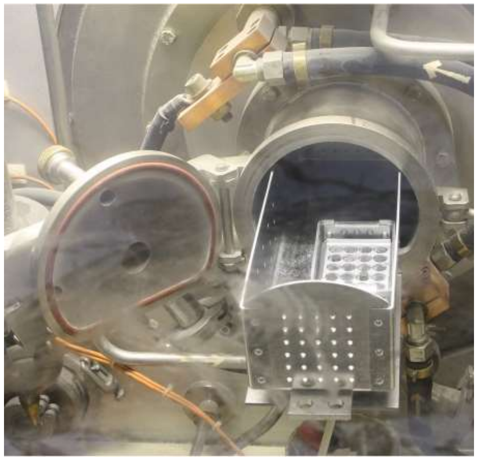
- U, J, K, C parameters
    - Powder mass
    - Powder density
    - Ball size
    - Ball mass
    - Tank volume
- Rotary speed
- Nb tilts
- Duration
- Emptying type

Press



- Powder mass
- Lubrification
- Die size
- Applied pressure
- Transmitted pressure
- Ejection speed

Sintering furnace



- Thermal profil
- Atmosphere
    - pO_2
    - flow

Manufacturing of SFR fuel – characterization techniques

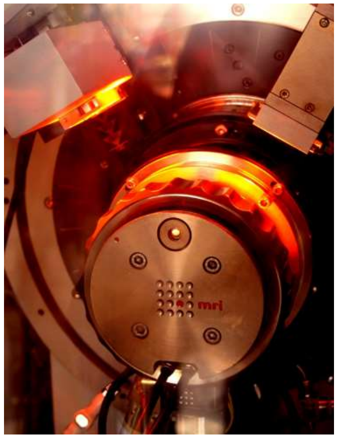

Powder density determination


TGA


C/S and O/N analysis

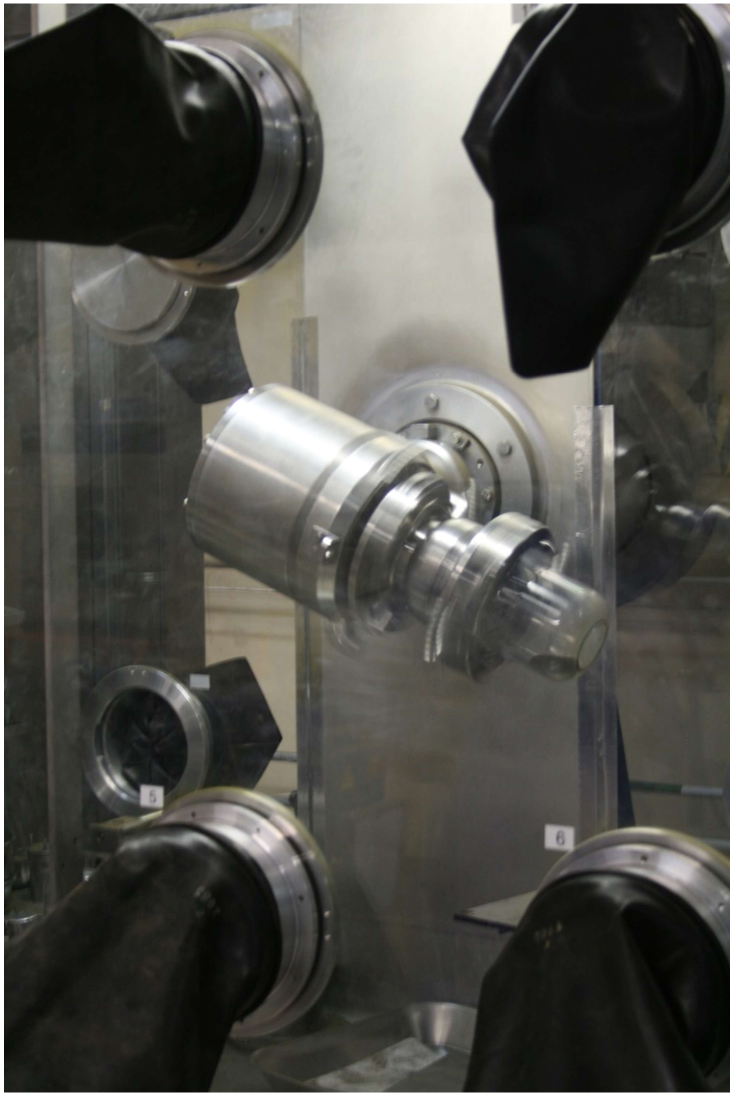

Metrology

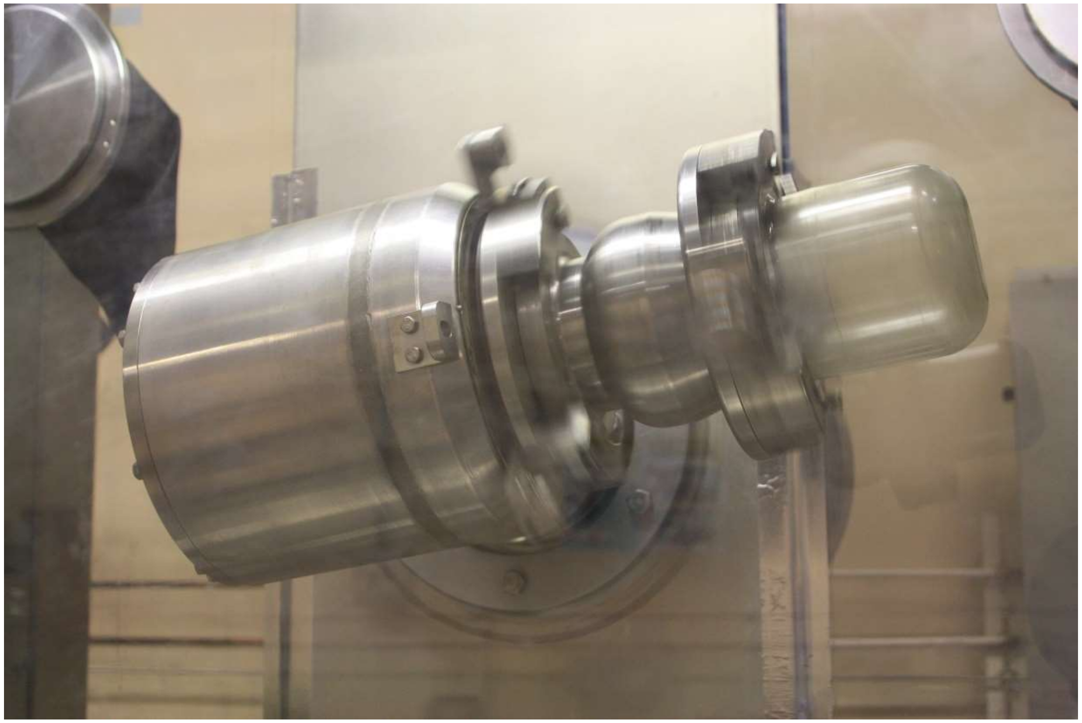

Dilatometer


XRD & HT-XRD


Ceramography

Specific facilities : α-laboratory





LEFCA lab ball mill

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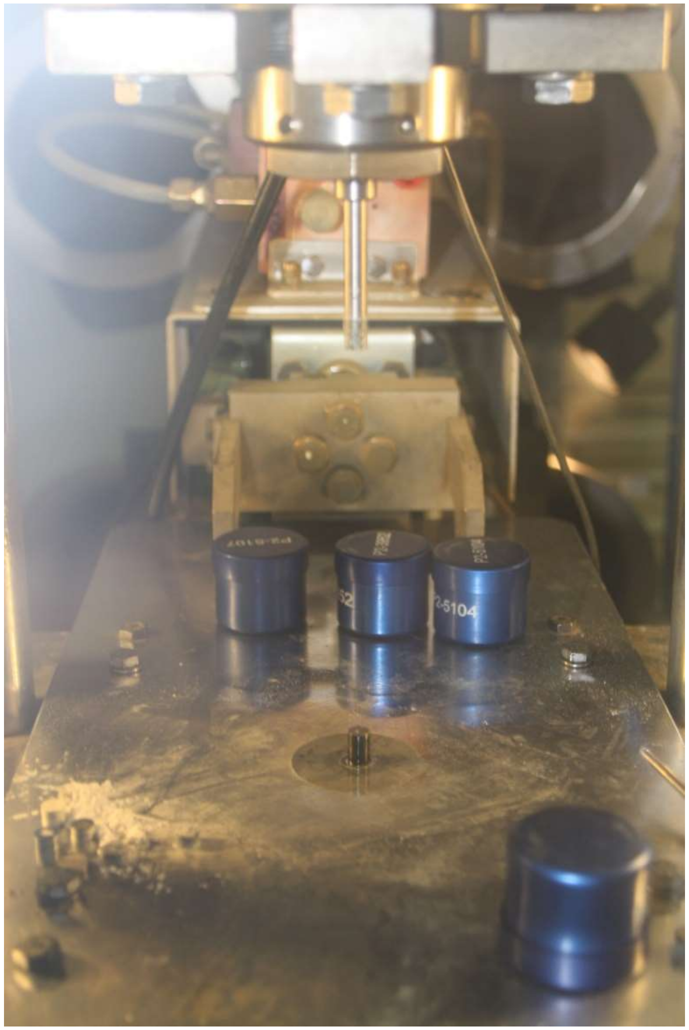
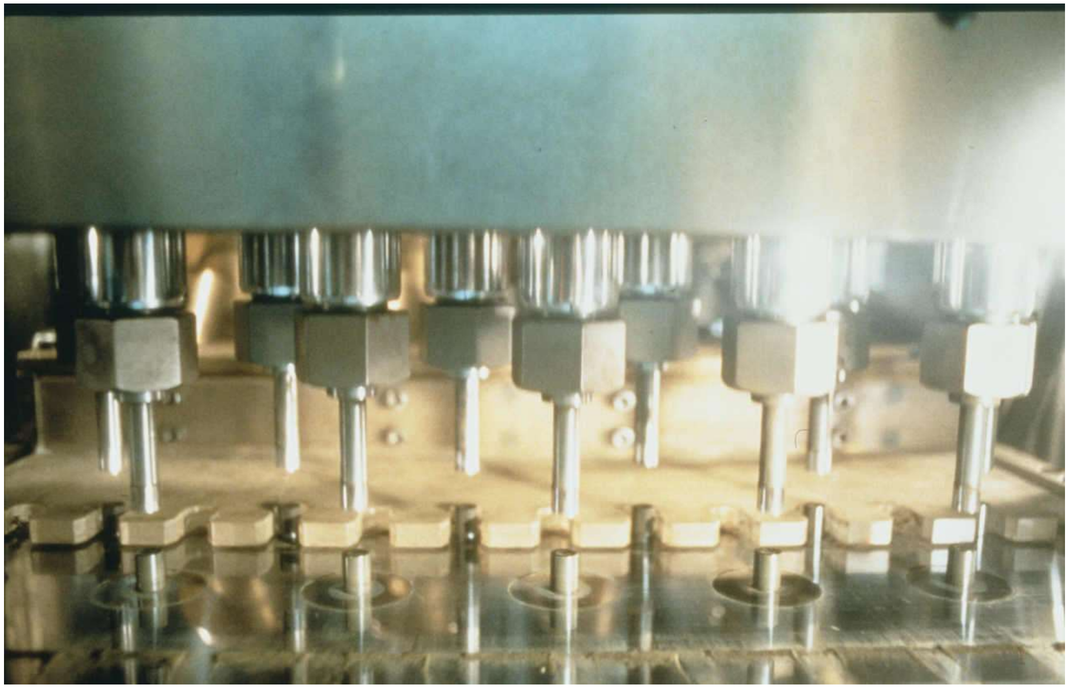
Specific facilities : α-laboratory

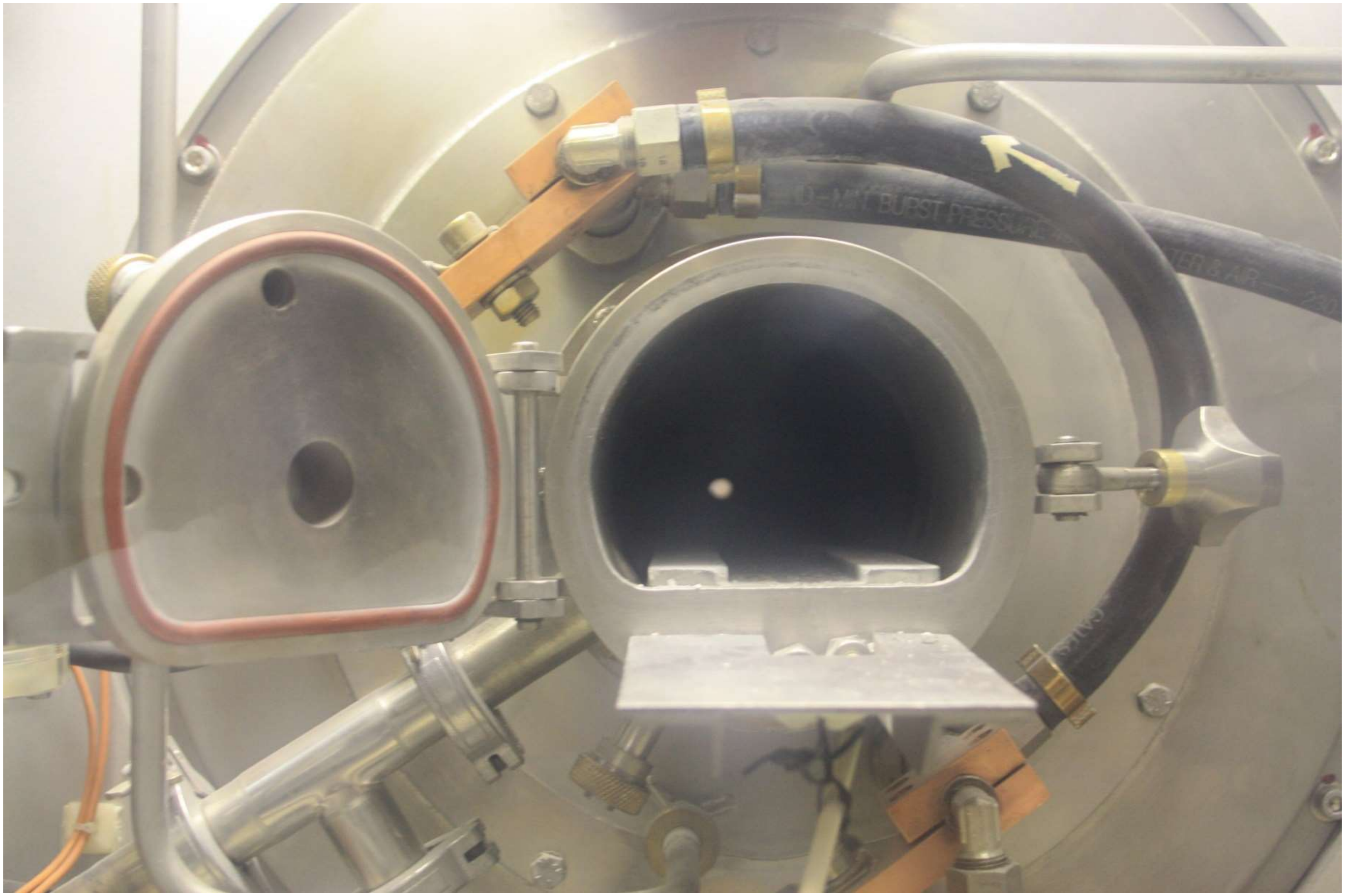


LEFCA lab press



MELOX press (10 punches)

Specific facilities : α-laboratory



LEFCA lab sintering furnace

Specific facilities : α-laboratory

Green pellets

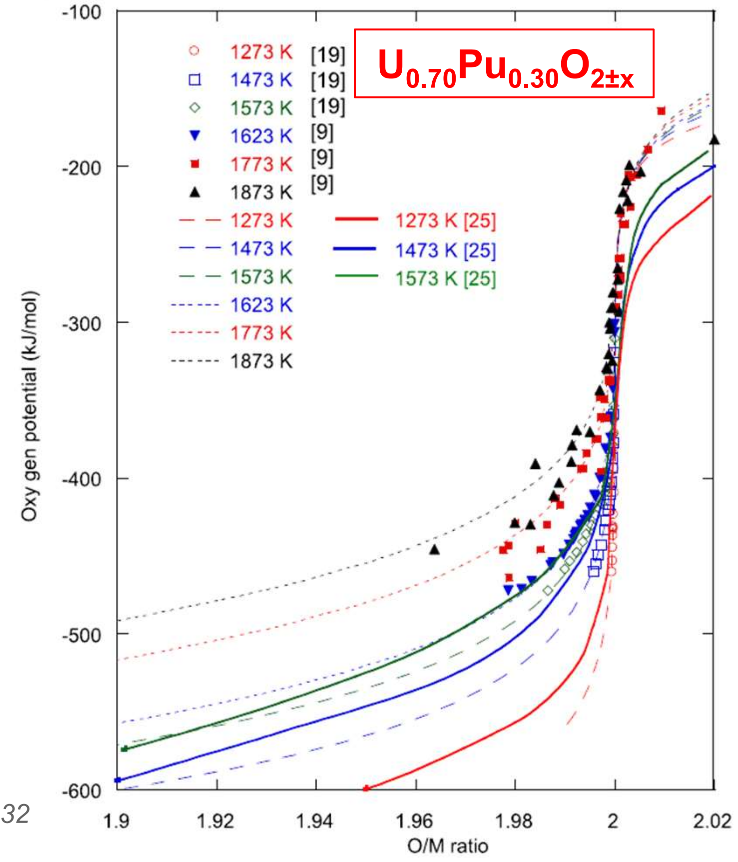
Sintered pellets

Manufacturing of SFR fuels - sintering

Sintering

- 1700°C, 4h, 95% Ar + 5% H_2 + x vpm H_2O
- High Pu content and lower O/M ratio → challenging
- Definition pH_2/pH_2O to control O/M ratio

- ➢ Densification
- ➢ Formation of solid solution
- ➢ Control of O/M ratio



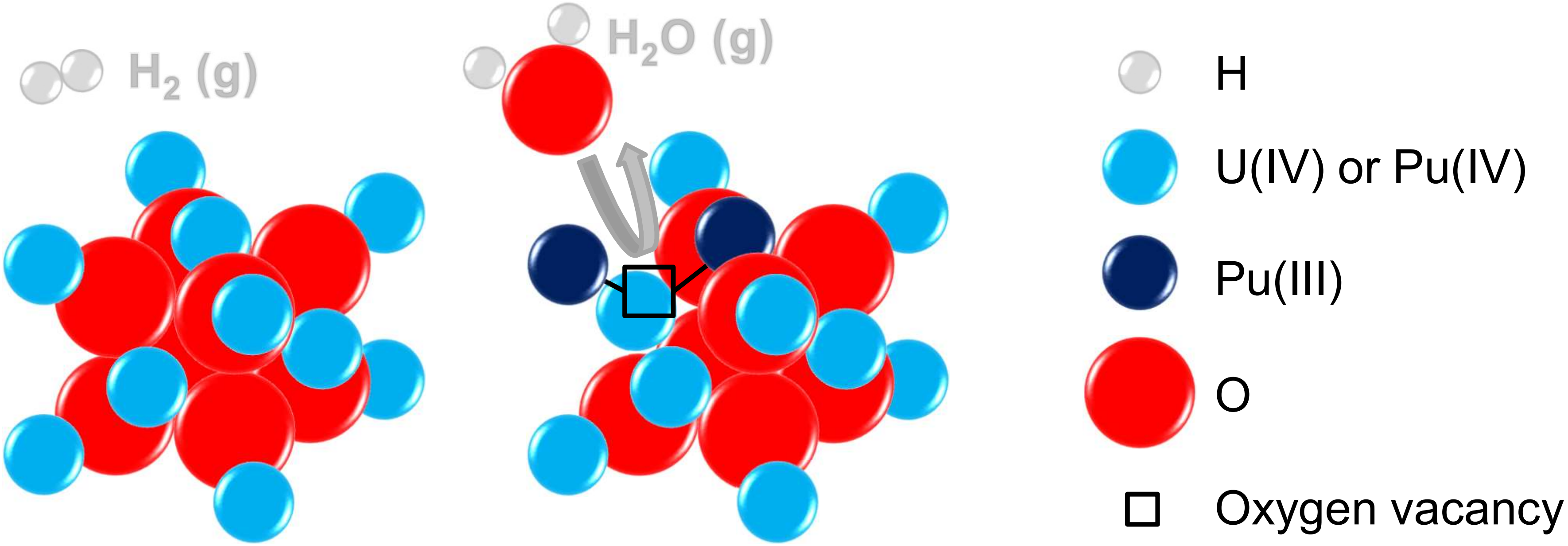
Kato et al., JNM, 487, 2017, 424-432

- Selection of sintering conditions (T, pO_2) ÷ fuel specifications (%Pu, O/M, microstructure)

Manufacturing of SFR fuels - sintering

Sintering

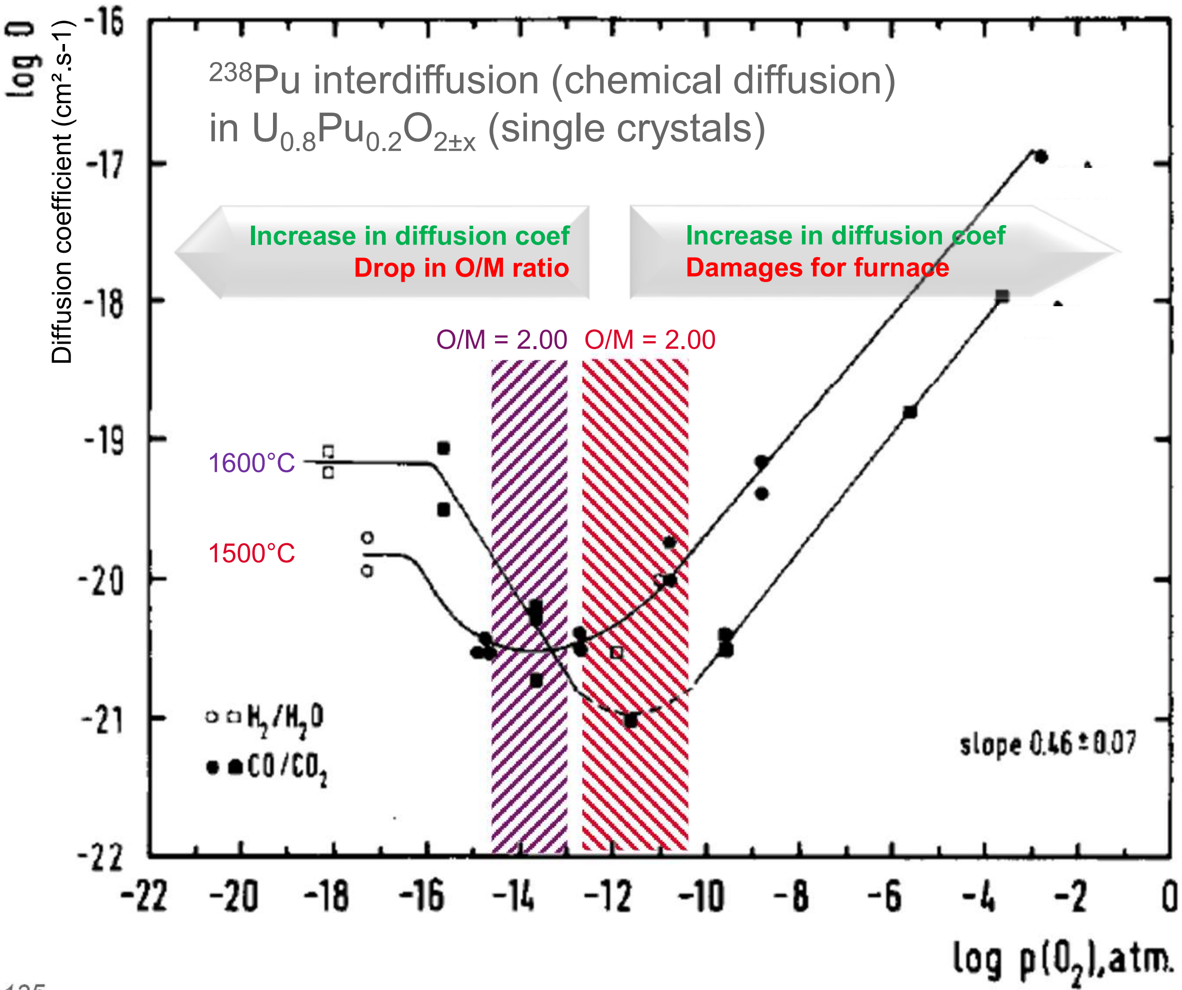
- Physics : increase in temperature → ceram. proc. densification + formation of solid solution
- Chemistry: Red/Ox enhanced process
- Exemple : UO_2, PuO_2 and $U_{1-y}Pu_yO_2$ → *fcc* phase (fluorite, CaF_2 type, $Fm\bar{3}m$, s.g. 225)



Vauchy et al., JNM, 465, 2015, 349-357

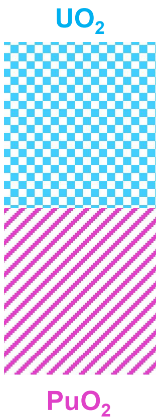
Sintering

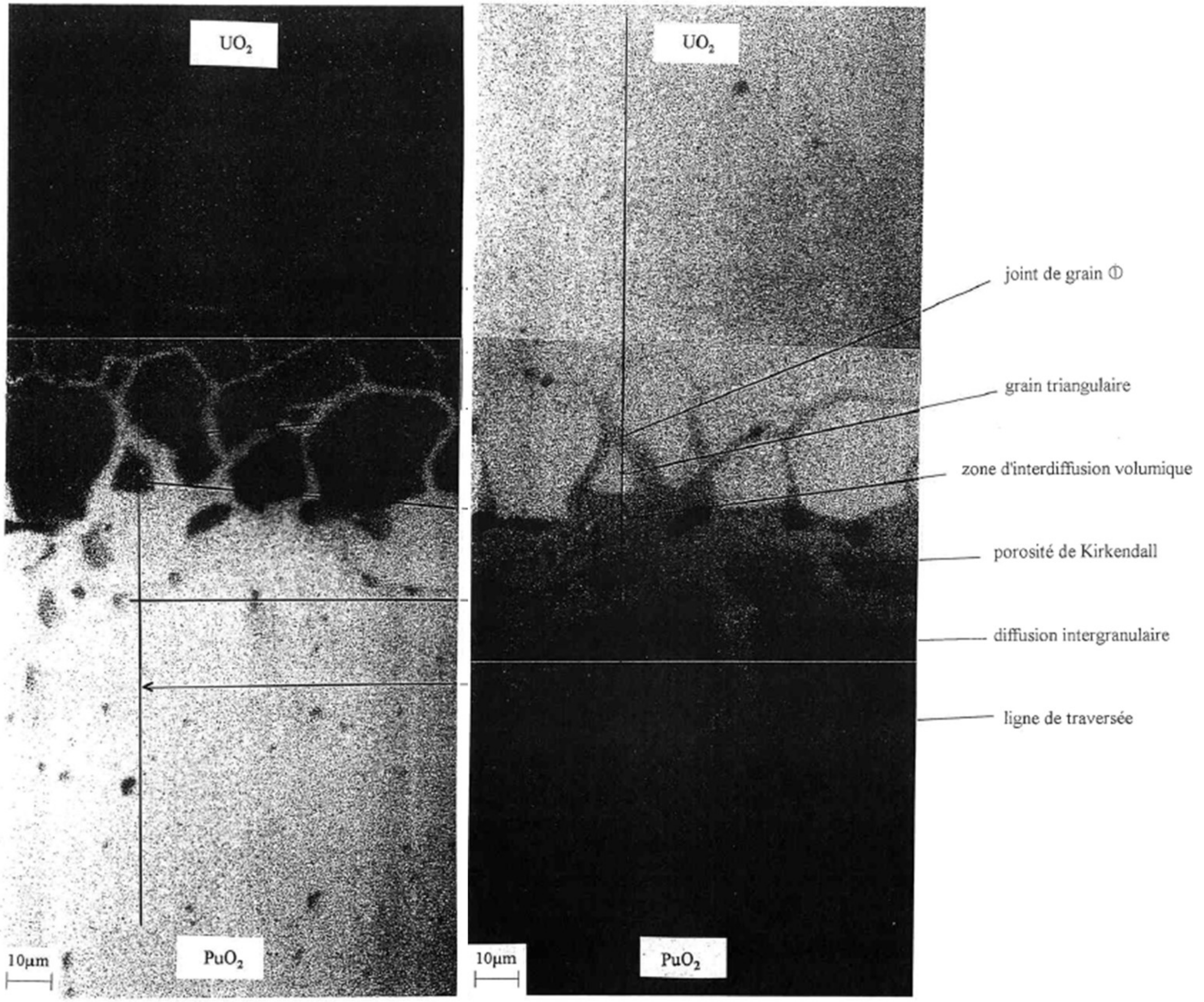
- Red/Ox enhanced process



Matzke, JNM, 114, 1983, 121-135

Manufacturing of SFR fuels – sintering

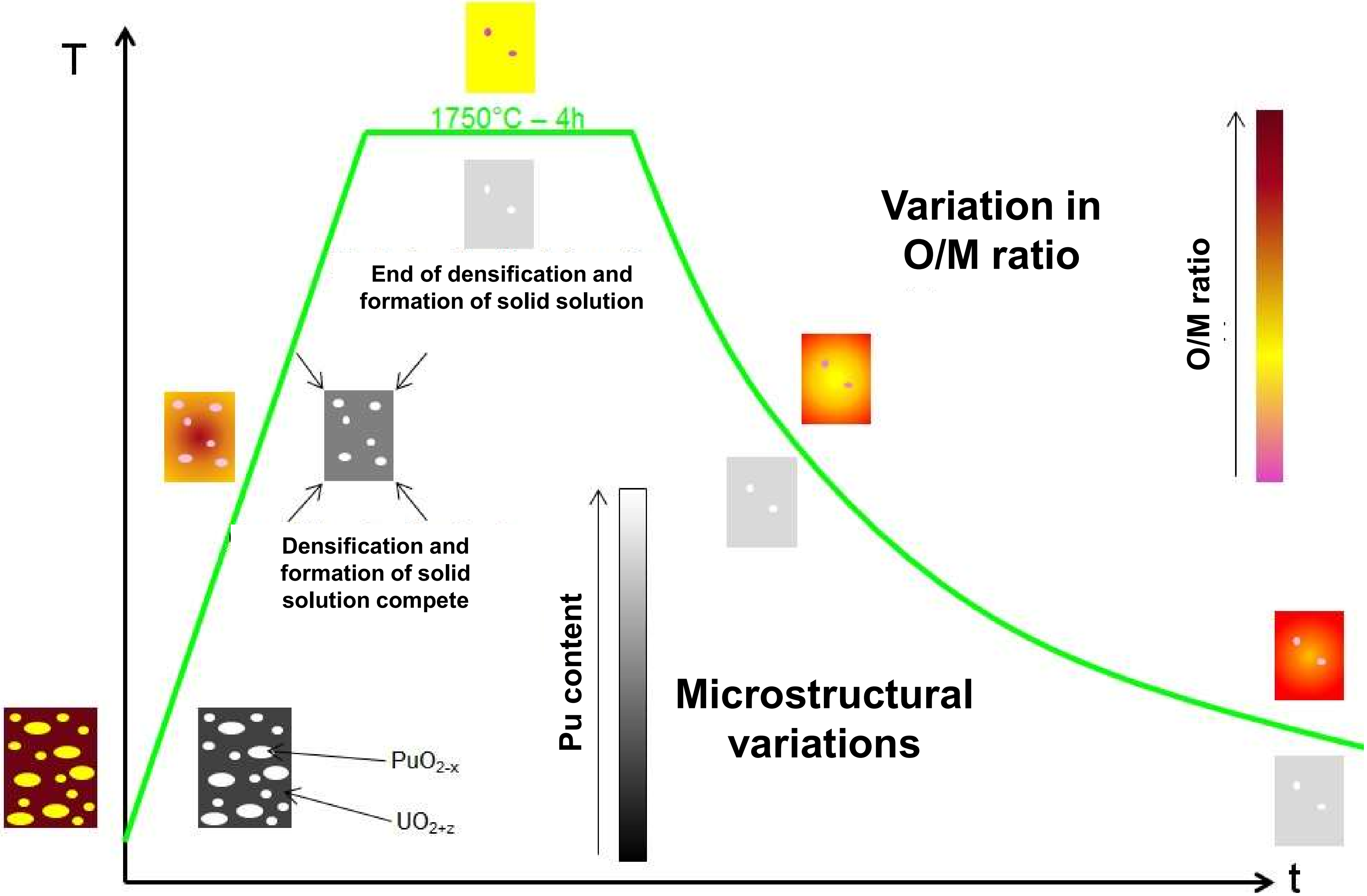




Pu image **U image**

S. Mendez, PhD thesis, 1995

Manufacturing of SFR fuels – sintering



End of densification and formation of solid solution

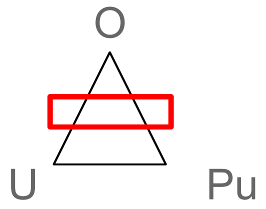
Densification and formation of solid solution compete

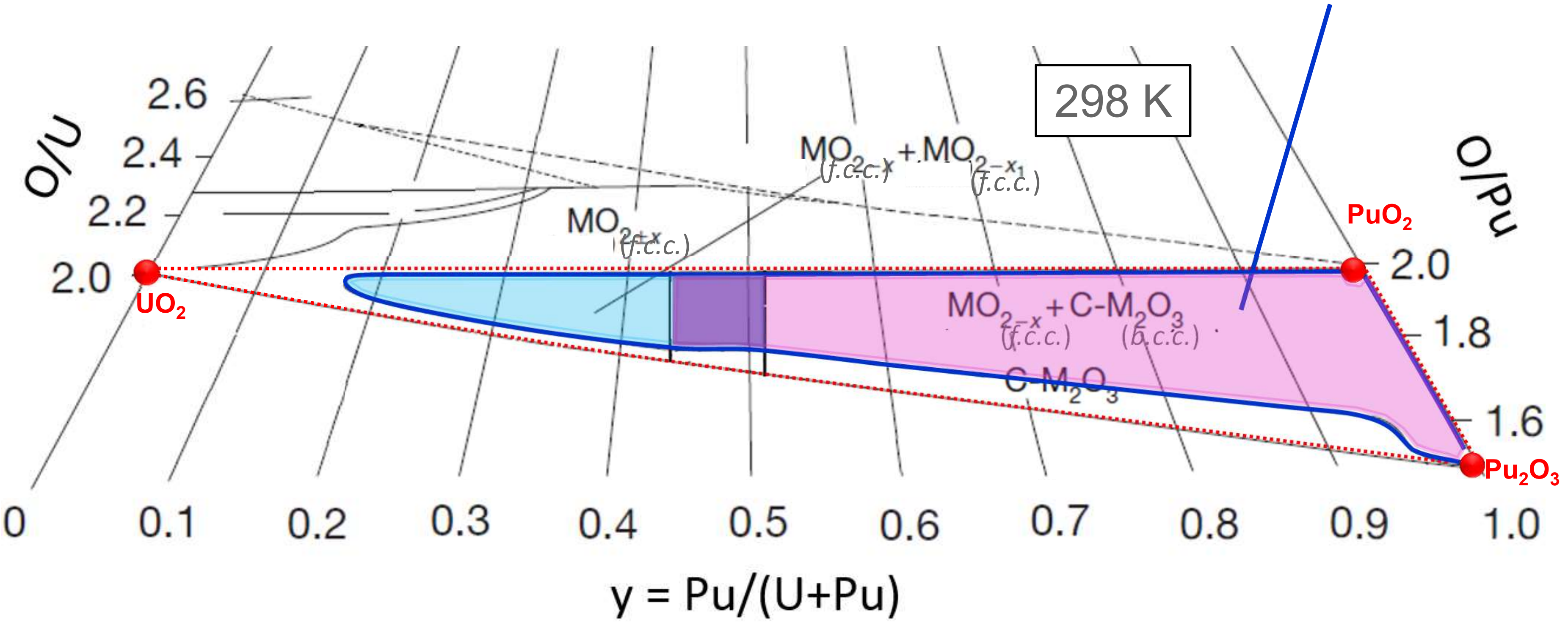
Variation in O/M ratio

Microstructural variations

Thermodynamics

UO_2-PuO_2-Pu_2O_3 at room temperature



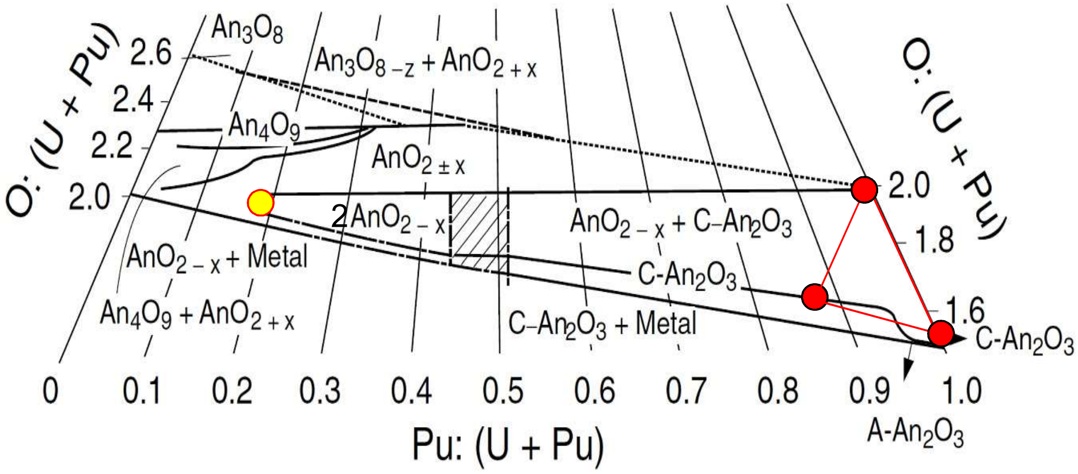


Miscibility gap

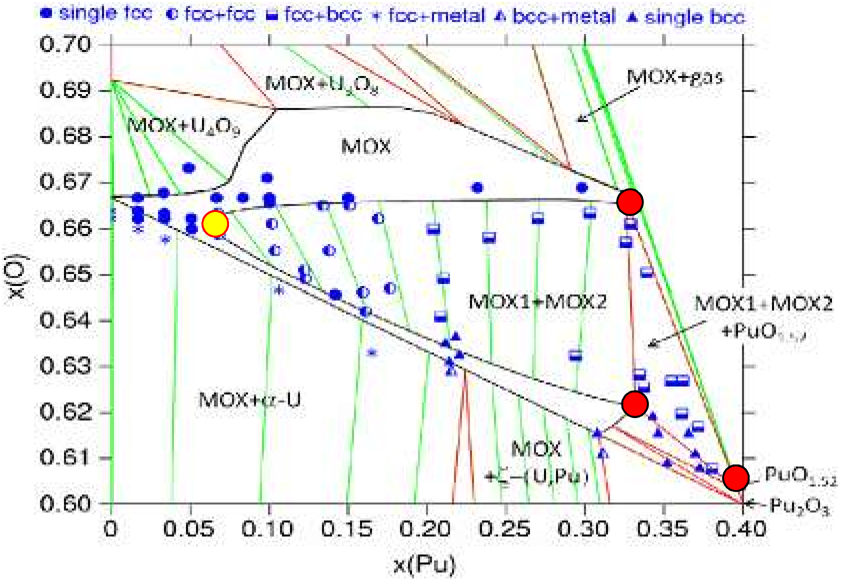
Sari et al., Journal of Nuclear Materials 35 (1970) 267-77

2 x *f.c.c.* phases   2 x *f.c.c.* + *b.c.c.* phases   *f.c.c.* + *b.c.c.* phases

Experiment vs. Modeling



Sari *et al.*, *Journal of Nuclear Materials* 35 (1970) 267-77

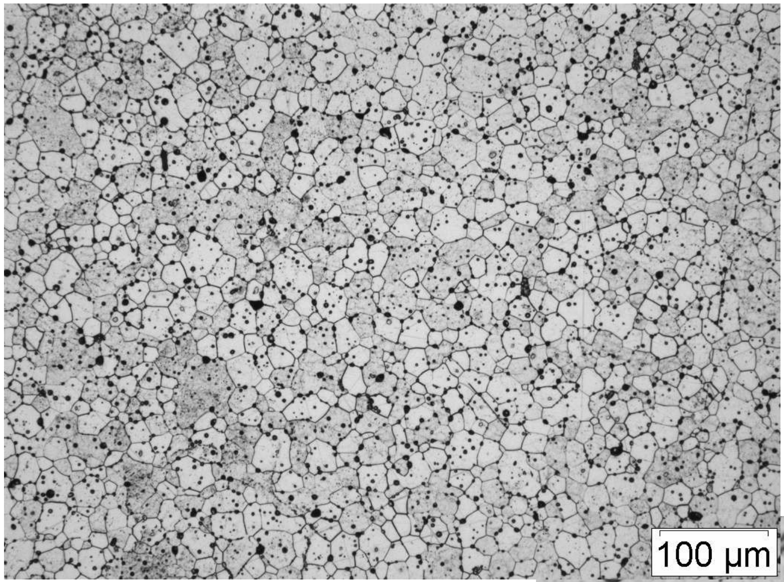


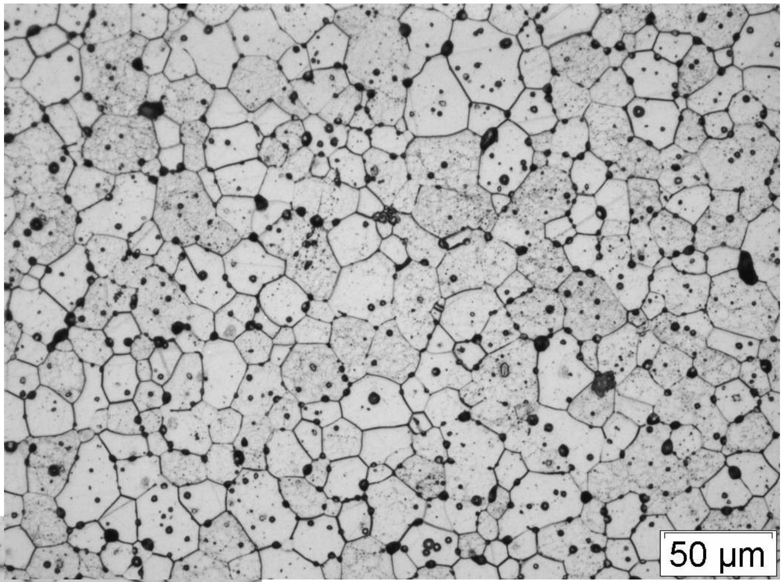
Guéneau *et al.*, *Journal of Nuclear Materials* 419 (2011) 145-167

- Generally : experiment and modeling in good agreement
- Same low Pu content limit for the miscibility gap (~17% Pu)
- Some differences :
  - Biphasic domain $MO_{2-x} + M_2O_3$ not modeled
  - Existence of a three-phases domain $2 \times MO_{2-x} + M_2O_3$

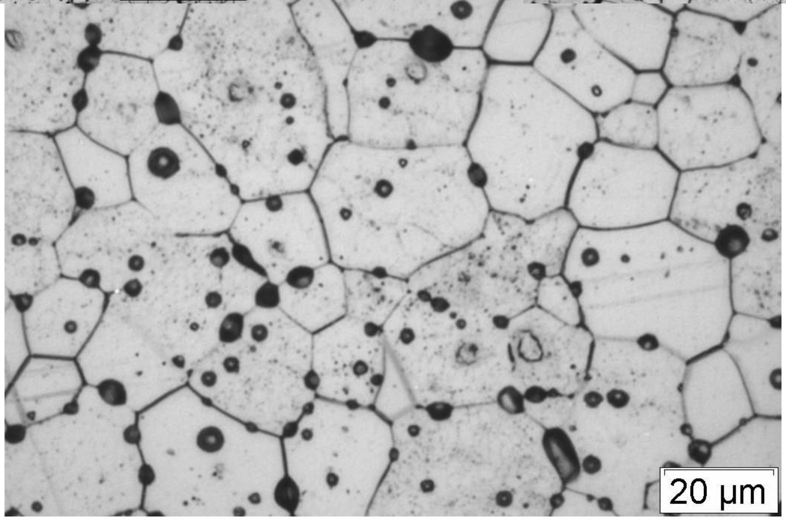
    Calculated composition range far from the hatched area of Sari

High Pu content : microstructures & O/M ratios





$U_{0.55}Pu_{0.45}O_{2.00}$



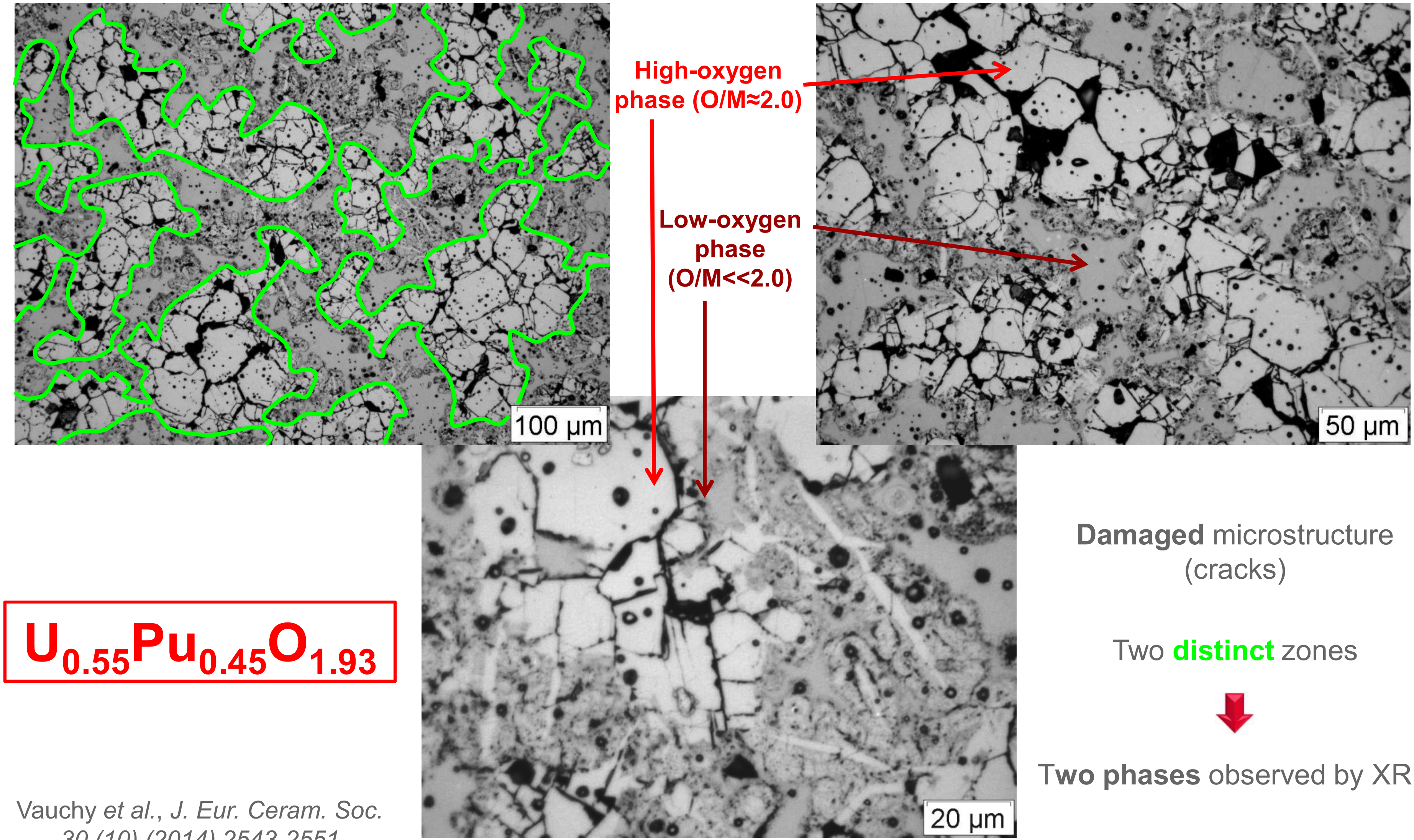
Vauchy *et al.*, *Ceram. Inter.* 40 (7B) (2014) 10991-10999

Monophasic

Damage-free microstructure

Grains visible after chemical etching

High Pu content : microstructures & O/M ratios



High-oxygen phase (O/M≈2.0)

Low-oxygen phase (O/M<<2.0)

$U_{0.55}Pu_{0.45}O_{1.93}$

Vauchy *et al.*, *J. Eur. Ceram. Soc. 30 (10) (2014) 2543-2551*

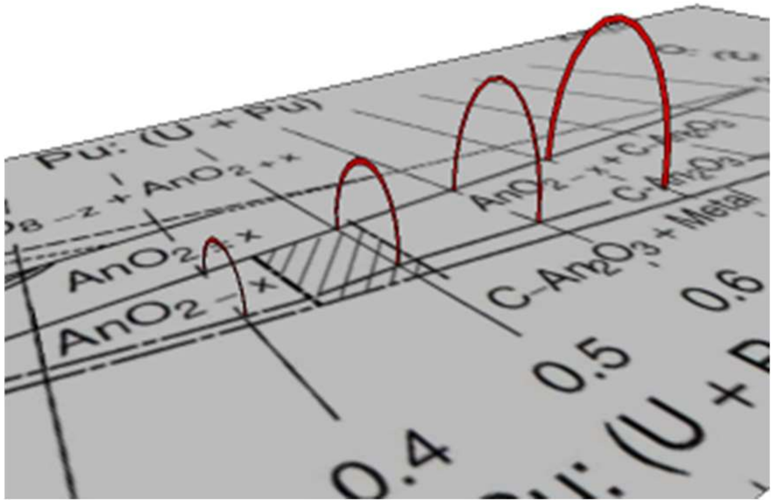
Damaged microstructure (cracks)

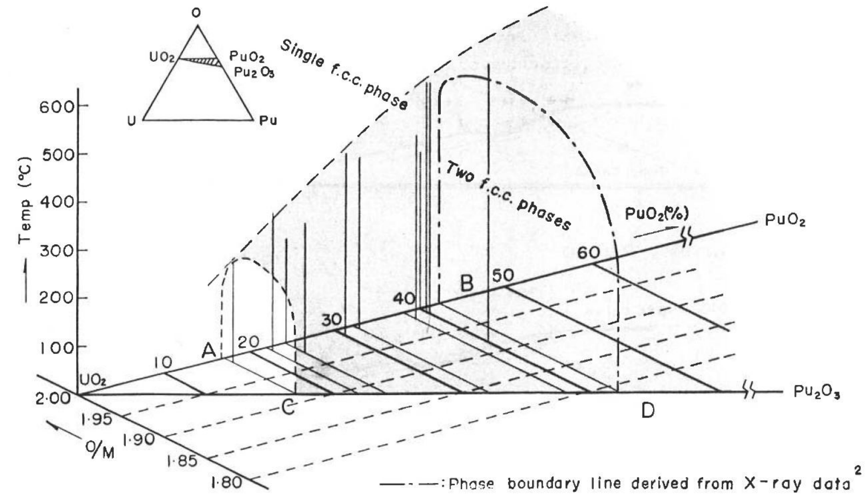
Two **distinct** zones

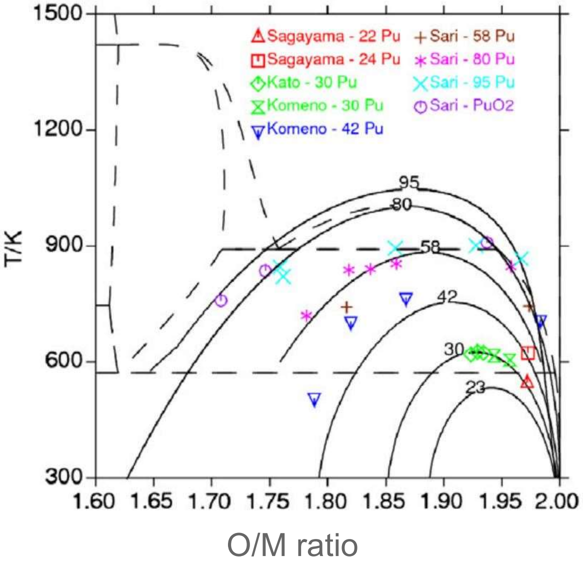
⬇

Two phases observed by XRD

UO_2-PuO_2-Pu_2O_3 at HT

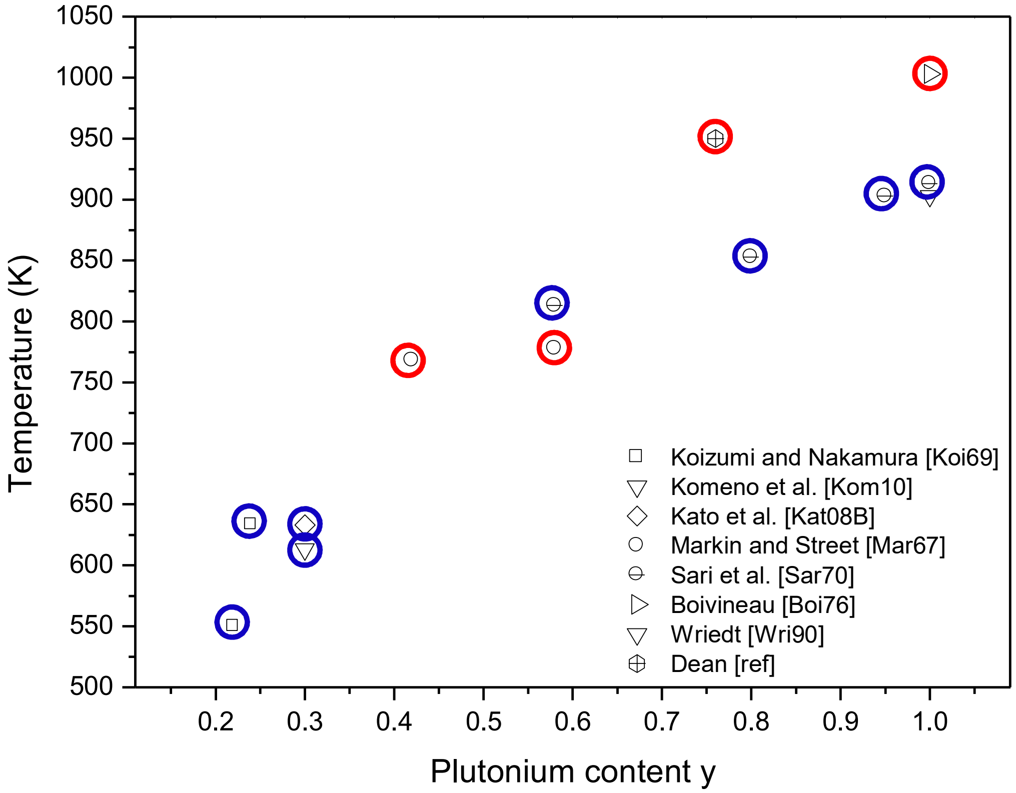






UO_2-PuO_2-Pu_2O_3 at HT

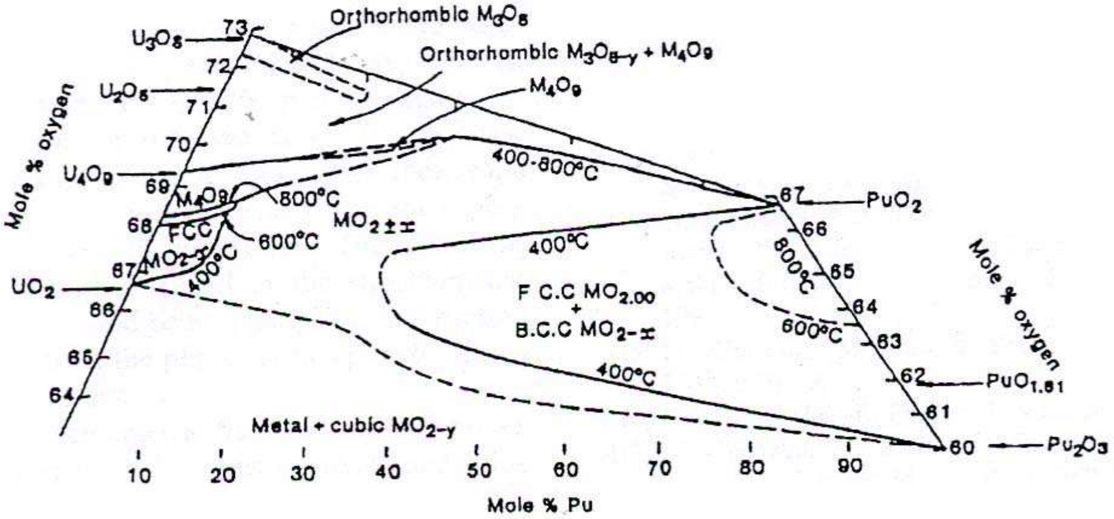
Experimental temperatures of phase separation (DTA, HT-XRD)
→ Entering in the miscibility gap



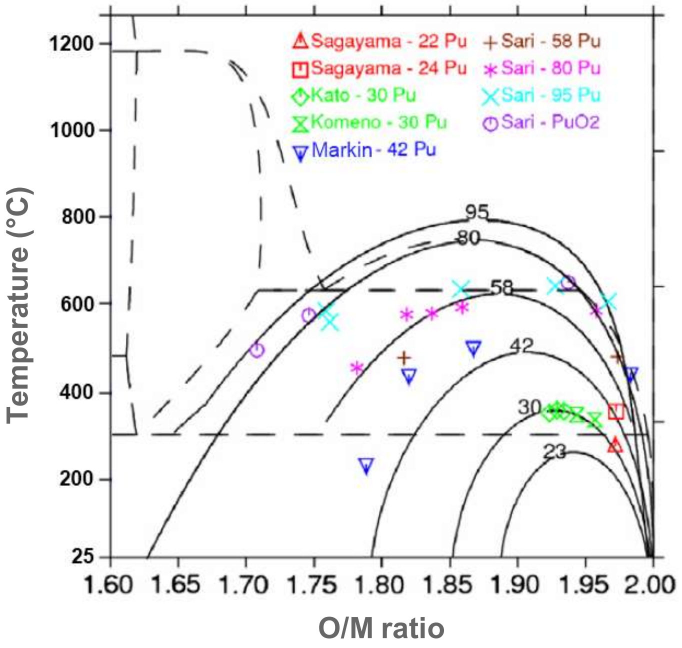
- T increases with Pu content
- Low Pu : only DTA results → scattering confirms the difficulties in measuring at low Pu content
- High Pu : T obtained with DTA lower than with HT-XRD
- PuO_2 : HT-XRD value (1000 K) in agreement with description of Pu-O

Very few experimental results

Experiment vs. Modeling



Markin & Street. *Journal of Inorganical Nuclear Chemistry* 29 (1967) 2265-2280



Guéneau *et al. Journal of Nuclear Materials* 419 (2011) 145-167

- Experiment and calculations agree for y ≤ 0.40
- Difference for y > 0.40 : calculations overestimate $T_{separation}$

New HT studies are required to better describe the phase separation phenomenon

Conclusions

Conclusions

- Main specifications :

  ✓ Pu content > 20 % (about 30%)
  ✓ 1.94 < Oxygen/Metal ratio < 2.00
  ✓ Dense pellets (95% D_{th})

- Fabrication by powder metallurgy :

  ✓ Direct co-milling of $UO_2 + PuO_2$
  ✓ Sintering : key step → densification + formation of solid solution + control of O/M ratio

↳ Challenging because of high Pu content and O/M specifications

↓

At high Pu content : **possible demixtion** (phase separation) during cooling step (sintering)

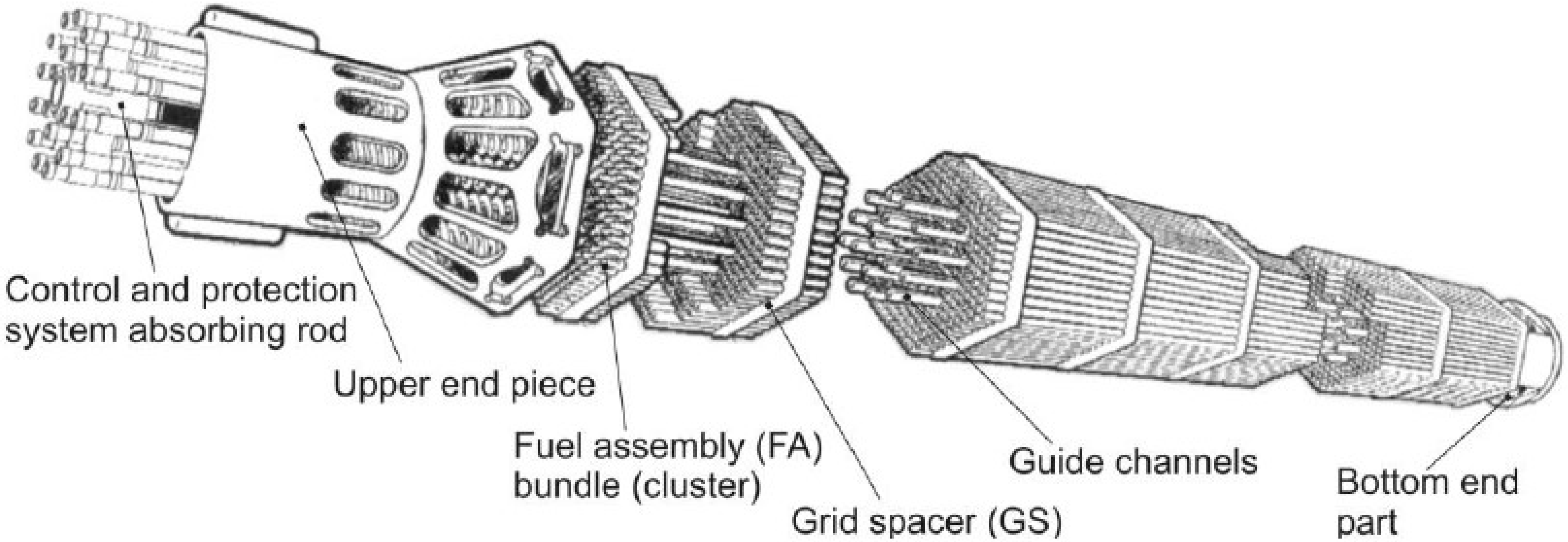
The higher the Pu content, the more difficult the control of O/M ratio

↓

Thursday 16/05 16h00-16h30→ case studies: mixed oxide fuels in fast reactors

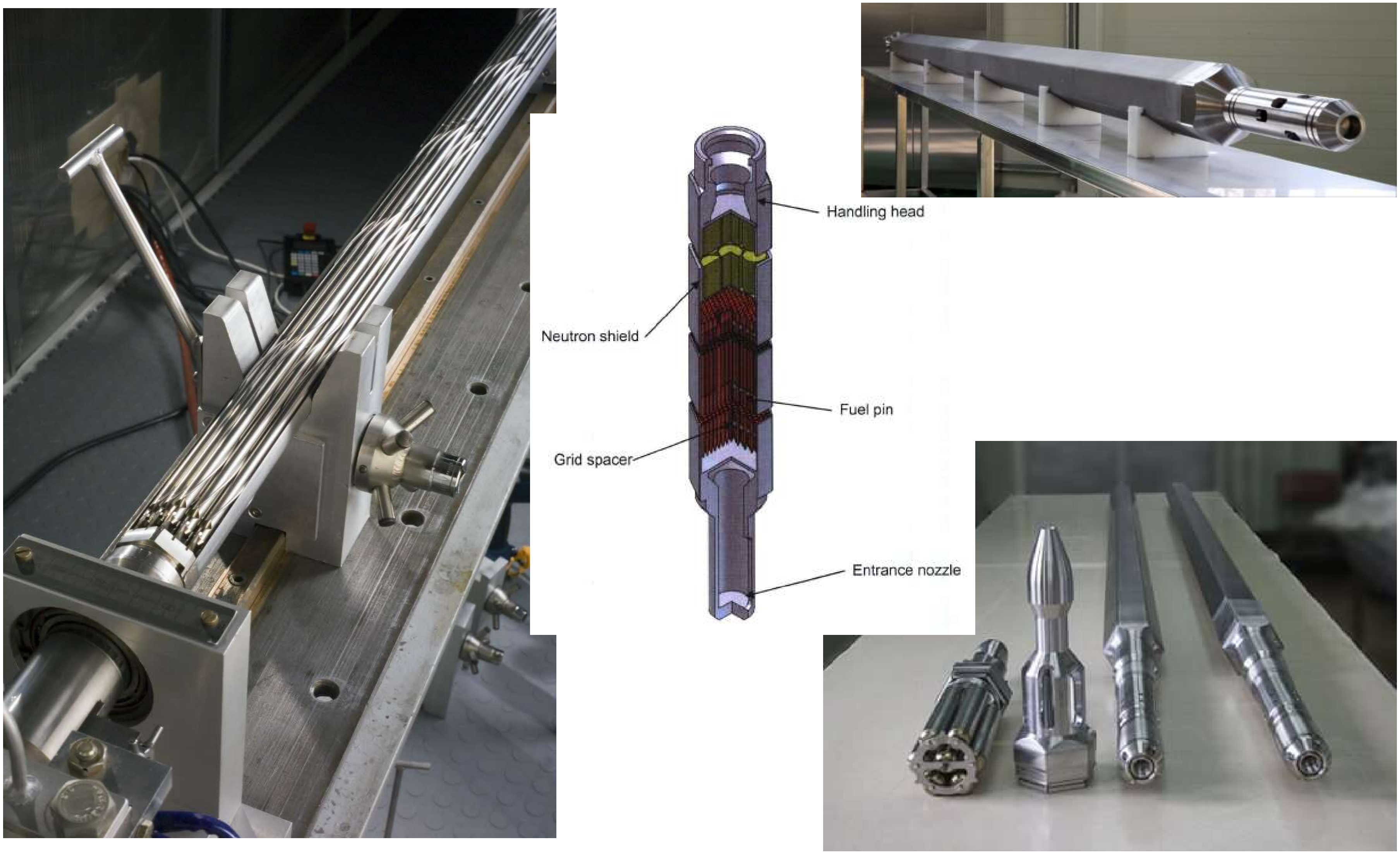
Assemblies and capsules

SFR assemblies



SFR assemblies

SFR capsules



Thank you for your attention

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Nuclear Energy Division
Research Department on Mining and Fuel Recycling Processes
Department of Process Engineering of Actinide Materials Manufacturing

MA-bearing oxide fuel

Objectives

- Reducing quantity and radiotoxicity of long life MA (Am, Np, Cm)
- Demonstrating transmutation feasibility into FR

Reactors

- HFR – Netherlands (analytical tests)
- BOR 60 – Russia } (innovative options and validation tests)
- *Phenix – France* }

Selected concepts

- Homogeneous recycling:
  → **Solid solution with low MA contents (from 2 to 5 %)**
- Heterogeneous recycling:
  → **Solid solution or Composite with high MA contents (from 10 to 20 %)**

- European programs since 1991: transmutation of Am in uranium-free targets
- In-pile and out-pile studies on a lot of matrices
- Focus on two materials: MgO and $(Zr,Y)O_2$ as inert matrices (composite materials)

Impact of MA on the fabrication process

Neutron and gamma activity Appropriate radioprotections

1g $^{241}AmO_2$ powder → 10 rad/h (gamma)
1g $^{244}CmO_2$ powder → 300 rad/h (gamma)

- Heavily shielded cells, thick concrete;
- Water shields (neutron Cm);
- Remote handling for all operations.

Contamination and dispersion Precursor handling/batch preparation

- Powder metallurgy using separated oxide powder;
- Generation of fine and dust dispersion;
- High contamination level.

→ Direct synthesis particles containing the MA’s
(co-conversion, solution infiltration)

Thermal behaviour of the batch and pellet

- Curium heat released (2.8 W/g);
- Significant increase of batch and pellets temperature;
- Lubrication properties lost of pressing additives.

Impact of MA on the fabrication process

Powder pressing

- Use of organic lubricants difficult;
- MA fuels loose of lubrication properties rather quickly (radiolysis);
- Mechanical instability and swelling of green pellets during storage

Development of press dies
➡ *ATALANTE example: ejection free matrix device (three parts dies)*

Cladding and storage

- Forced cooling necessary during all operation and for storage;
- Transport of pin at a reasonable T.

Objective : simple and reliable process limiting scraps and machining

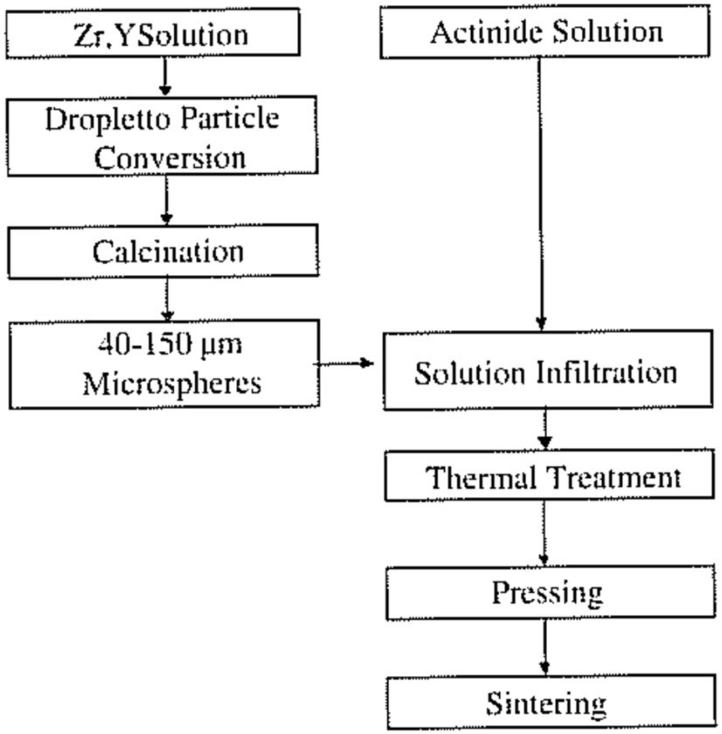
MA-bearing oxide fuel – Solid solution

Solid solution

- Fabrication of Am-bearing ceramics oxides
- Handling of highly radioactive americium → development of new technologies

Example: $Am_{0.06}Zr_{0.78}Y_{0.16}O_{1.89}$

Infiltration technique



From Croixmarie et al. (2003)

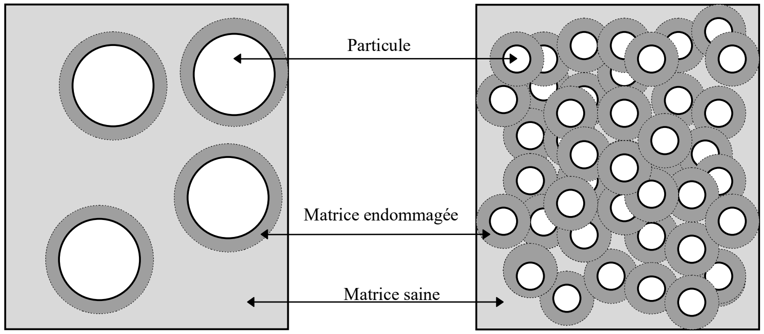
MA-bearing oxide fuel - Composite

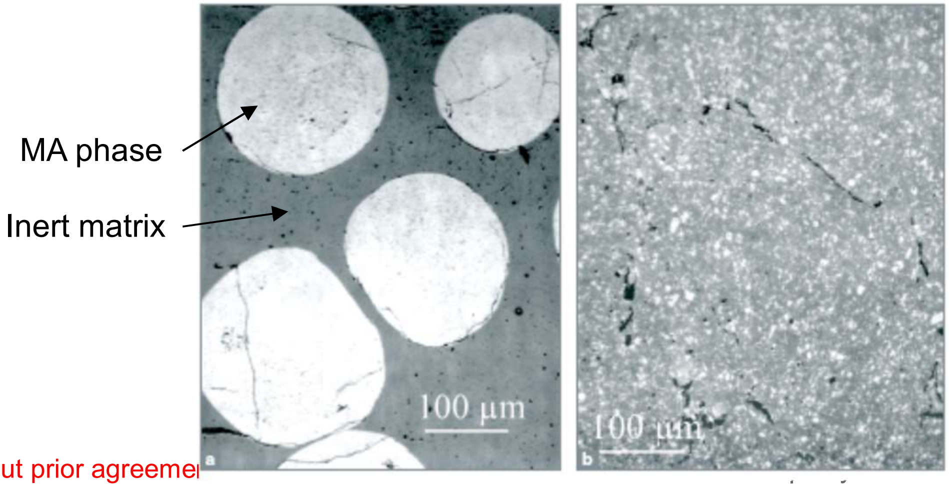
Composite materials

Inert matrix	Actinide phase
MgO, $MgAl_2O_4$, ZrO_2, $Ln_2Zr_2O_7$	AmO_x, $(Am,Zr)O_x$, $Am_2Zr_2O_7$
CeO_2, Y_2O_3, $Y_3Al_5O_{12}$	$(Am,Zr,Y)O_x$
TiN, ZrN, CeN	$(Pu,Am,Zr)N$
W, V, Cr, Nb	

Two model microstructures (to evaluate matrix damage by recoil of FP and alpha particles)

- **macro dispersion → Grain size = 50-200 µm**
- **micro dispersion → Grain size < 50 µm**



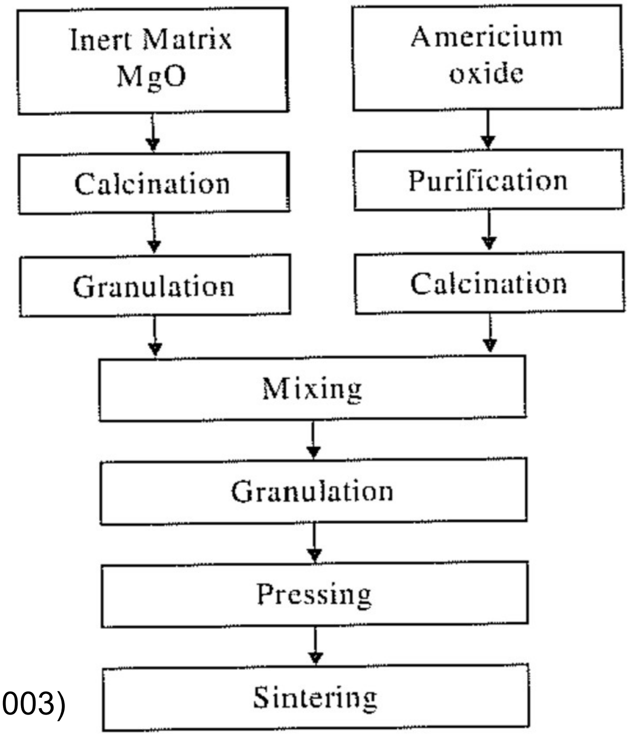


MA-bearing oxide fuel - Composite

Example: microdispersed heterogeneous target

MgO (microdispersed) + AmO_2 (grain size between 1 and 50 µm)

Classical powder metallurgy process



From Croixmarie et al. (2003)

MA-bearing oxide fuel - Composite

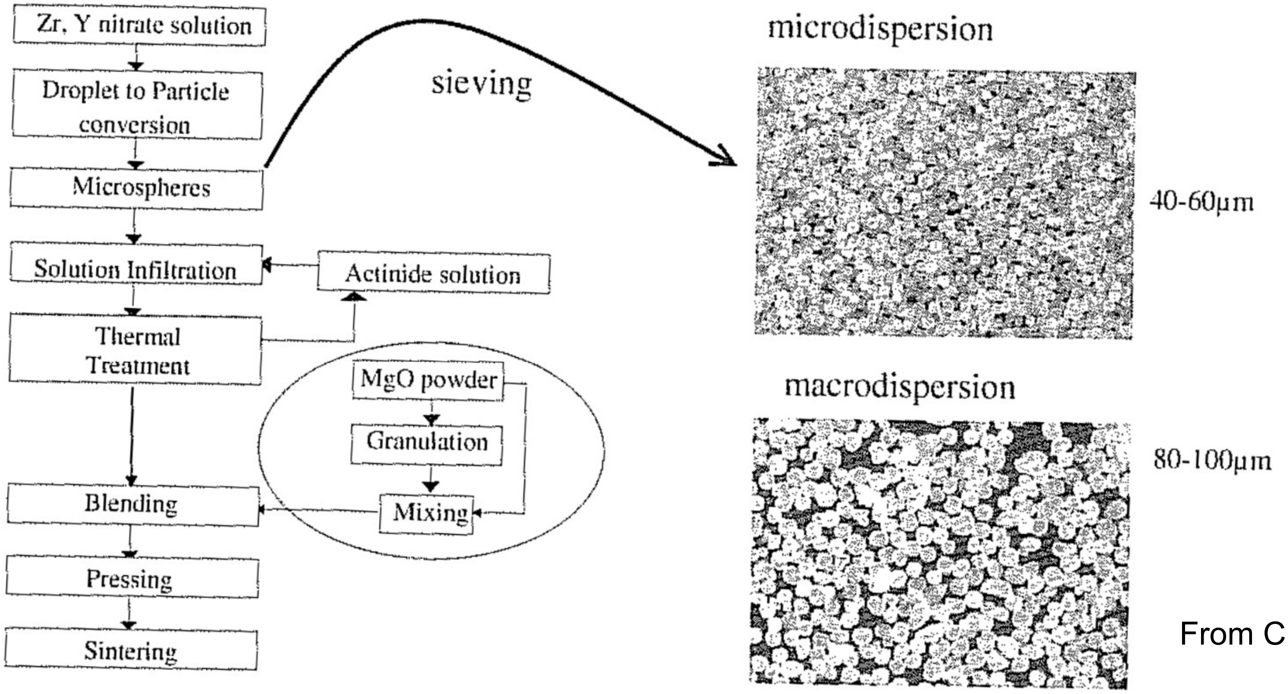
Example: micro and macrodispersed heterogeneous target

MgO + $(Am,Y,Zr)O_{2-x}$

→ Microdispersion in MgO: $(Am,Y,Zr)O_{2-x}$ grain size between 30 and 50 µm

→ Macrodispersion in MgO: $(Am,Y,Zr)O_{2-x}$ grain size between 90 and 130 µm

Infiltration technique



From Croixmarie et al. (2003)

MA-bearing oxide fuel

In progress

- **Favour He release during irradiation**

  by creating FG release paths: interconnected and stable under irradiation porosity
  = new microstructure with high open porosity content

  by increasing operating temperature by Pu introduction: $(Pu,Am)O_2$ + Inert Matrix

- Increase transmutation capacity: **increase Am content**

- **Introduce Cm**: technological stake

- Progress on composite materials: new irradiation tests in progress to study and qualify the MABB concept: **10-20% MA on UO_2**

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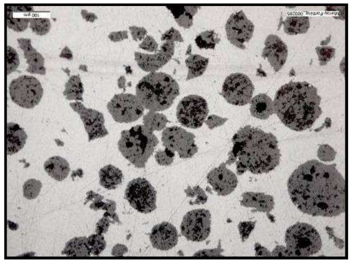
Fuel candidate selection

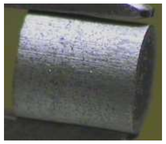
Potential fuel compositions, forms and packing:

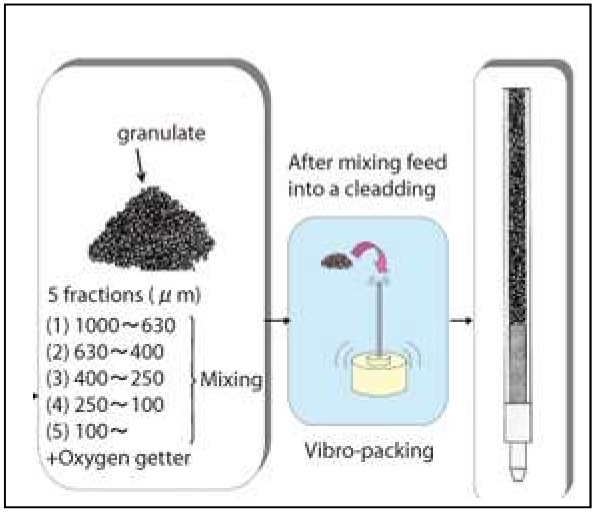
- Composition : oxide, metal, nitride, carbide, …

- Form: solid solution, composite



- Packing : Pellet, particles





(T. Ishii, 2004, JNST, vol.41, 1204-1210)

Carbide fuel

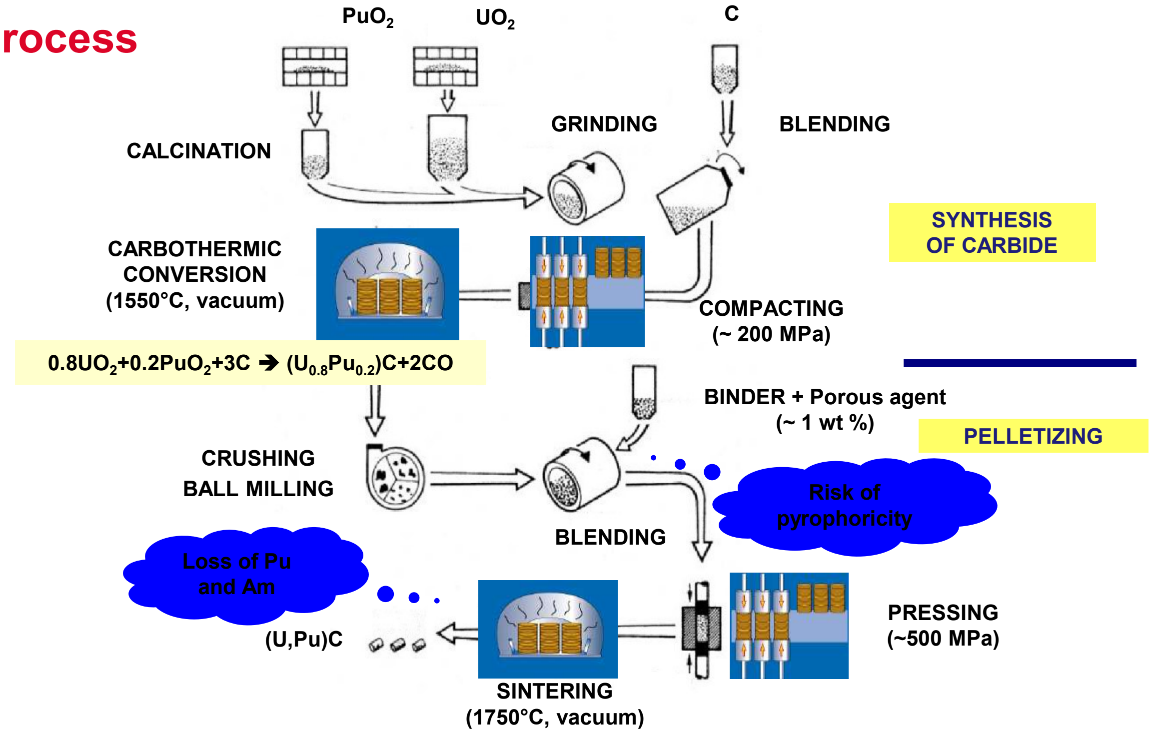
History

Large experience achieved in the past in many countries

France, UK, USA, Japan, Russia, …

New studies in France since 2005

Fabrication process



PuO_2

UO_2

C

CALCINATION

GRINDING

BLENDING

SYNTHESIS OF CARBIDE

CARBOTHERMIC CONVERSION (1550°C, vacuum)

COMPACTING (~ 200 MPa)

$0.8UO_2+0.2PuO_2+3C \rightarrow (U_{0.8}Pu_{0.2})C+2CO$

BINDER + Porous agent (~ 1 wt %)

PELLETIZING

CRUSHING BALL MILLING

Risk of pyrophoricity

BLENDING

Loss of Pu and Am

PRESSING (~500 MPa)

(U,Pu)C

SINTERING (1750°C, vacuum)

Carbide fuel

Synthesis by carbothermic reduction

- Milling of oxide powders and graphite carbon
- Pelletizing
- Reaction under vacuum

$$(1-x)UO_2 + xPuO_2 + 3C \rightarrow U_{1-x}Pu_xC + 2CO$$

Mechanisms study (A. Handschuh, Thesis, Université de Lille (2010))

- Step 1: Reduction of UO_{2+x} (700-1200°C)

$$(1-x)UO_{2,03} + xPuO_2 + C \rightarrow (1-x)UO_2 + xPuO_{2-y} + CO_2$$

- Step 2: Carbothermic reaction (>1200°C)

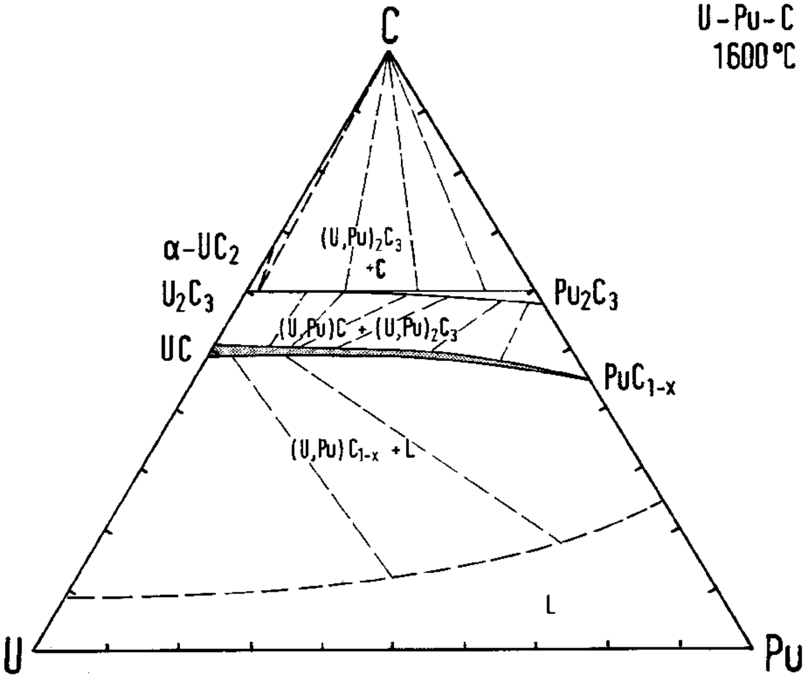
$$(1-x)UO_2 + xPuO_{2-y} + C \rightarrow U_{1-z}Pu_zC + U_{1-a}Pu_aC_{1.5} + CO + Pu(g)$$

➢ **Formation of (U,Pu)C and $(U,Pu)_2C_3$**

Carbide fuel

Thermodynamic considerations / Specifications

Equilibrium between (U,Pu)C and $(U,Pu)_2C_3$ → from 5 to 10 % $(U,Pu)_2C_3$



Oxygen solubility → (U,Pu) oxycarbide → oxygen content < 1000 – 3000 ppm

Carbide fuel

Sintering under controlled atmosphere or under vacuum

Occurrence of (U,Pu)$_2$C$_3$ → inhibit grain growth, favour sintering

Occurrence of (U,Pu)(C,O) → inhibit grain growth and densification

Use of Ni as sintering additive: liquid sintering at 1650 – 1850°C
→ Increase of densification rate
→ Decrease of oxygen content

Density of sintered carbide depends on:

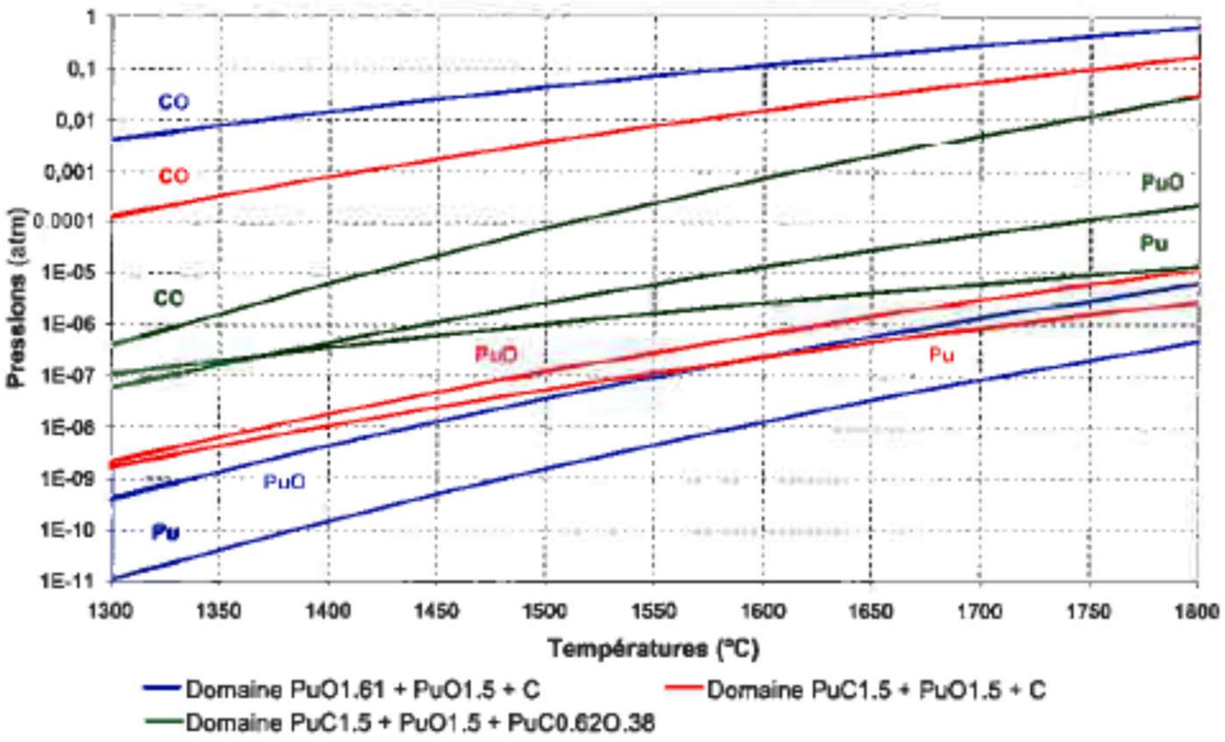
- Sintering T and t
- Specific surface area of carbide powder
- Binding agents
- Sintering agents (like Ni)
- **Oxygen content of the carbide powder**

Carbide fuel

Pu volatilisation

Vapour pressure of Pu(g) >> Vapour pressure of uranium and of carbon

Mixed carbide incongruent sublimation → formation of Pu(g), PuO(g) and CO(g)



Carbide fuel

Specifications for optimized carbide pellets (GFR)

Low density (80 - 85 % TD) ⇔ swelling management
Open porosity ⇔ reduce fission gas release
Stable porosity ⇔ avoid high densification at BOL
Low oxygen content (< 1000 ppm) and M_2C_3: 5 – 10 %⇔ reduce swelling rate
Ability to incorporate MA
→ Loss during sintering ⇔ issue with carbide
Pyrophoricity to be taken into account

Main stakes

- Stringent management of oxygen pollution (pO_2 and moisture)
- Improve powder homogeneity
- Control and reduce Pu (and Am) volatilisation
- Reduce the number of steps

Nitride fuel

Context

French CEA program started in 1985 (Bernard, 1989)

Many similarities with carbide

Two main drawbacks of nitride

- ➢ Neutron capture on ^{14}N
  - ➔ Deleterious effect on the neutron balance
  - ➔ production of ^{14}C → Need for enrichment of N
- ➢ Instability at high temperature

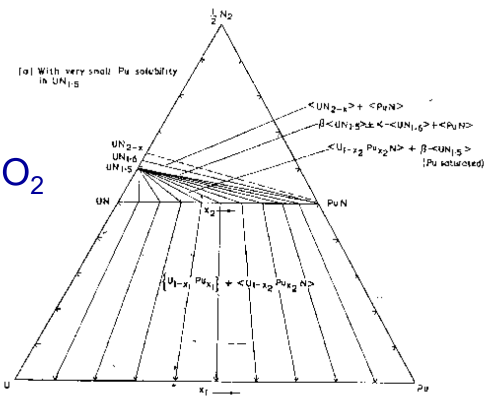
Thermodynamic considerations (Agarwal et al., 1999)

In presence of carbon and oxygen impurities,

(U,Pu)N in equilibrium with $(U,Pu)_2N_3$ and in equilibrium with $(U,Pu)O_2$

Calculated thermodynamic properties:

(U,Pu)N ⇔ $(U,Pu)O_2$ will be superior to the one with $(U,Pu)_2N_3$



Nitride fuel

Fabrication process (Bernard, 1989)

in an industrial and conventional oxide line
= Carbothermic reduction and consolidation by cold pressing

① Ball-milling of the oxides

② Blending carbon powder

③ Pressing into coarse briquettes

④ Carbothermic reduction in N_2 then in N_2-6%H_2 at 1550°C:

$$(1-x)UO_2 + xPuO_2 + (2+y)C \xrightarrow{N_2} (U_{1-x}Pu_x)_N + 2CO + yC$$

⑤ Crushing and grinding the clinkers

⑥ Pelletizing with pore former

⑦ Sintering at 1725°C under reducing atmosphere (at 1650°C in vacuum)

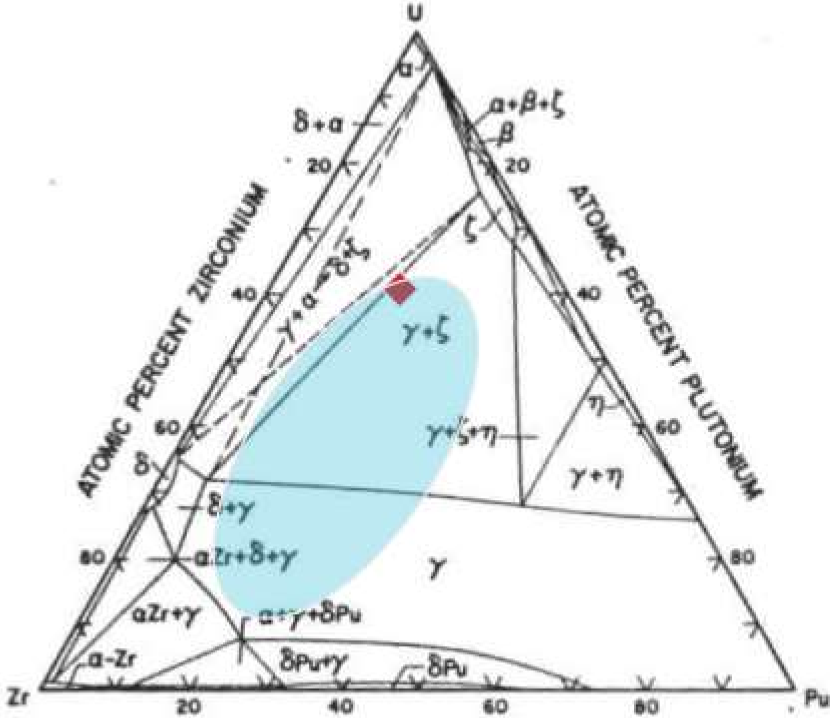
→ Sintered density: 80 – 90 % theoretical density
→ Low and controlled level of residual oxygen and carbon contents

Metal fuels

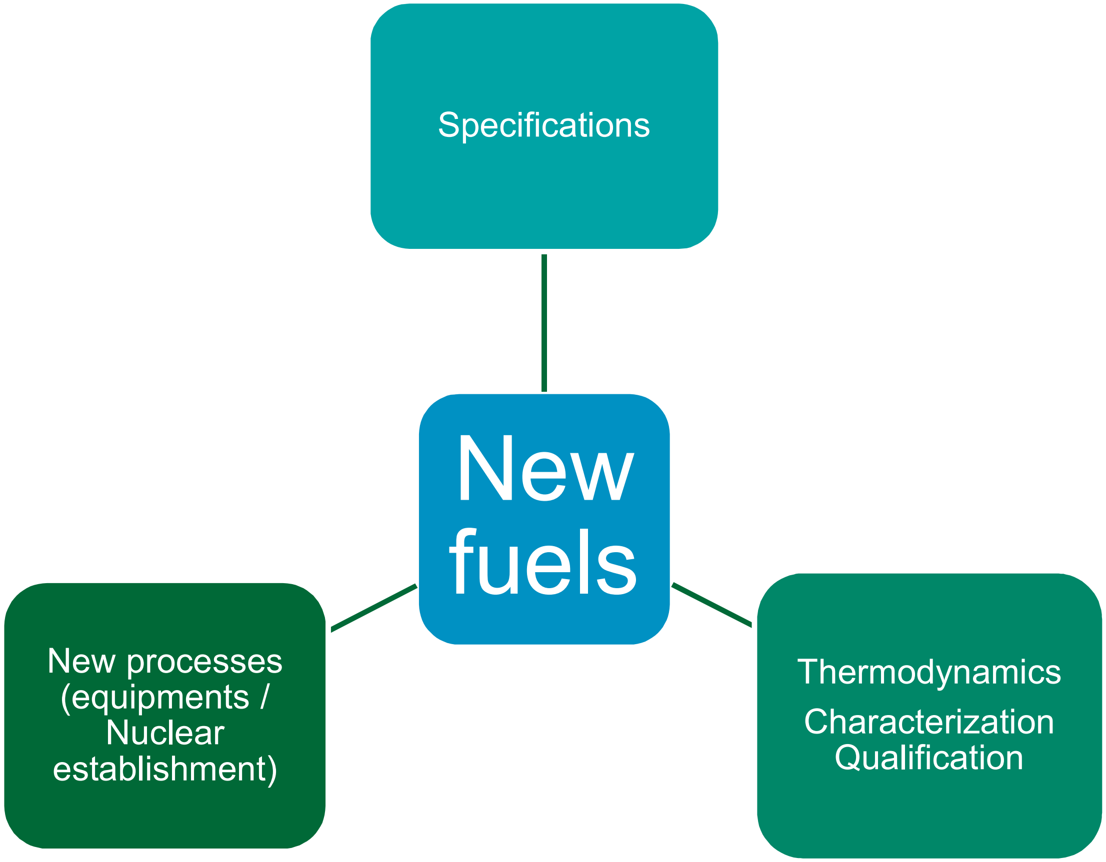
Metallic fuel UPuZr

- Considered is the main alternative to oxide in many countries (USA, Japan, Korea, India)
- Large experience mainly in USA (irradiation into EBR II, Idaho falls)
- Experience under progress of metallic fuel with MA: (U,Pu,Zr) + Np, Am and Cm

- Fabrication in the form of metallic rods:
  - → melting in a crucible
  - → casting in quartz tubes by injection



R&D on new fuels - Summary



Specifications

New fuels

New processes (equipments / Nuclear establishment)

Thermodynamics

Characterization
Qualification