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Elaboration of $(U,Pu)O_{2-x}$ mixed oxides with high plutonium contents (≥ 60 mol.% Pu)

DE LA RECHERCHE À L'INDUSTRIE

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CONTEXT 1/3 - THERMAL GRADIENT

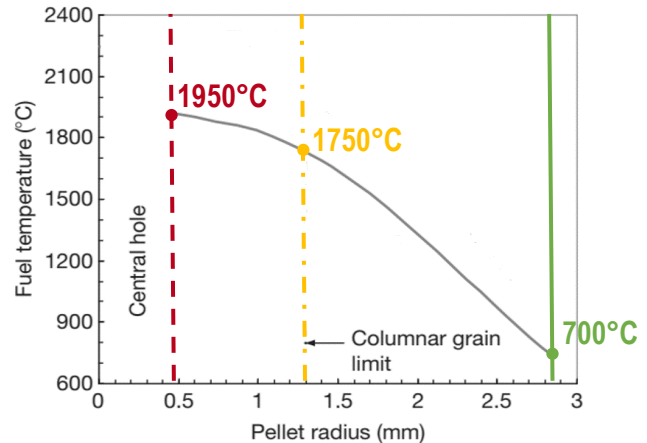
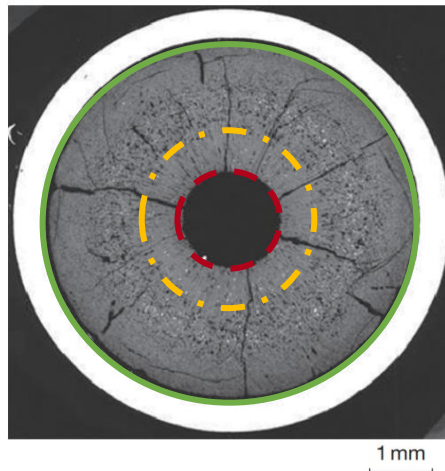
MOX



Currently studied as part of the fast reactors development.

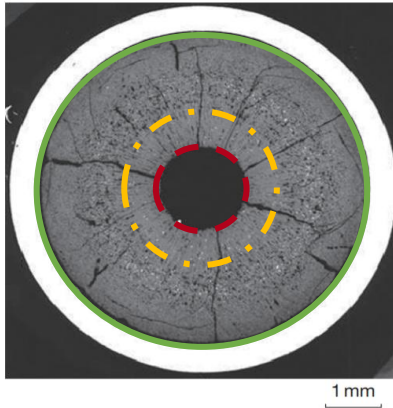
Under irradiation : Linear power 400-500 $W \cdot cm^{-1}$

Thermal Gradient from 500 °C to over 2000 °C

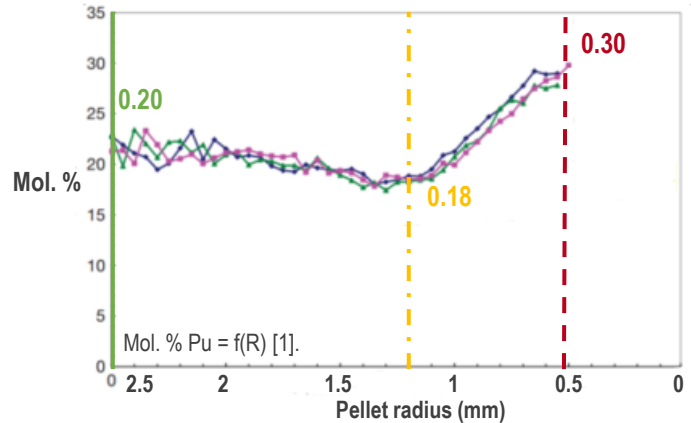


The maximum temperature reached along the fuel pellet radius remains below the melting temperature.

CONTEXT 2/3 – REDISTRIBUTION OF PU AND O ATOMS



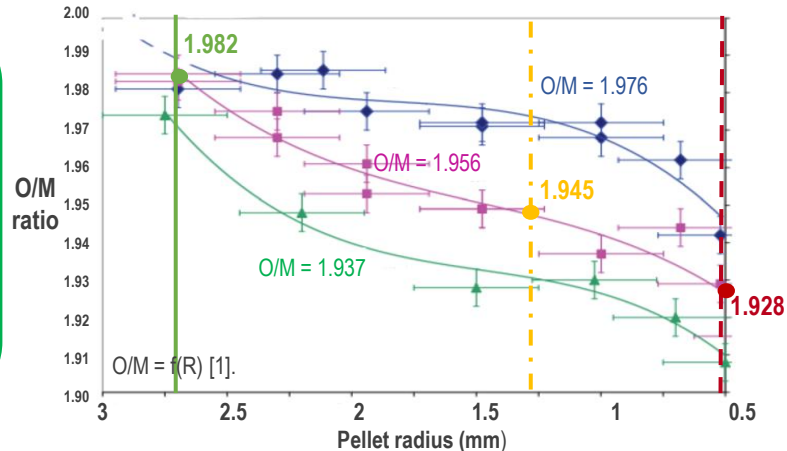
Metallography
Pu content 20 mol. %
Irradiated: 13 % at. [1].
Central hole
Columnar grain limit
Border



Central hole: enriched in Pu 30 – 70 mol. % range and O/M <~ 1.945

Border: depleted in Pu 20 mol. % and O/M ~ 2.00

Depending on the pellet position inside the reactor core, the O/M ratio and Pu content initials

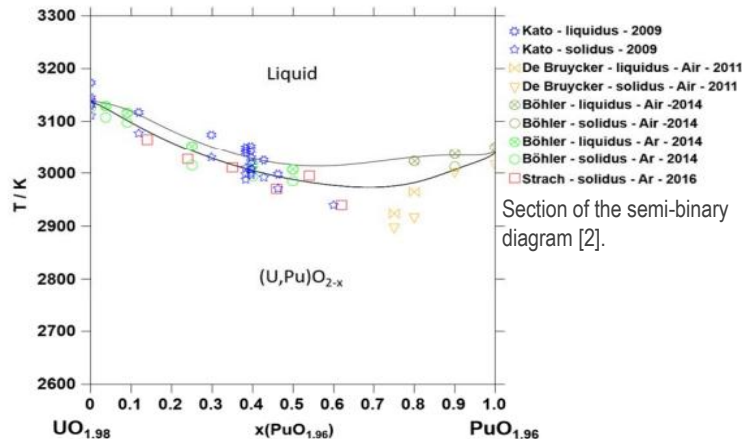


Significant heterogeneities in the MOX properties along the pellet radius

The local melting point depends upon both the O/M ratio and the Pu content.



The melting temperature decrease as Pu content increase = a diminution of the security margin of the reactor.



Goals

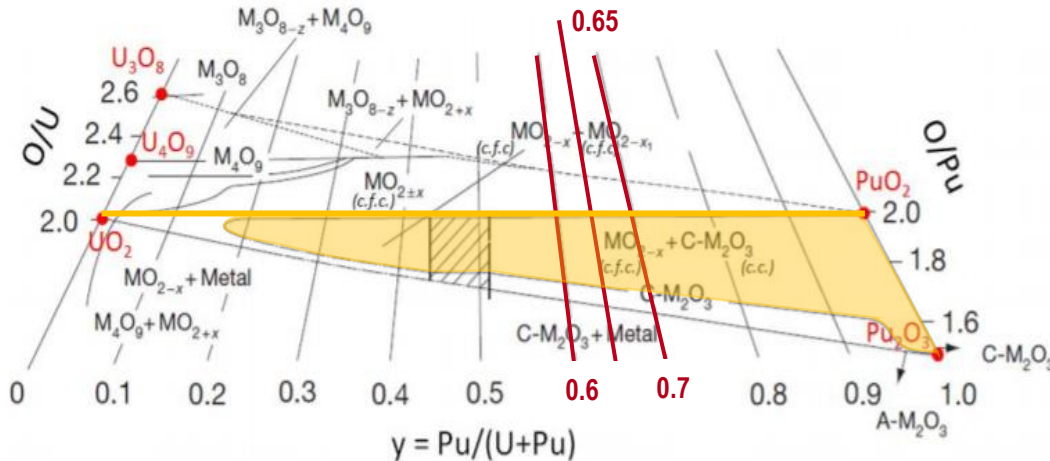
Fill the lack of data (structural, microstructural, thermal and thermodynamic) for MOX with Pu content greater than 45 mol. % and more specifically for Pu > 60 mol. %.



Feed the database for the GERMINAL performance calculation code and enhance the modelling of the U-Pu-O phase diagram by the CALPHAD method.

Needed properties

- Density after sintering > 94% of d_{theo}
- Microstructure without crack and macroporosity
- Homogeneous chemical distribution of cations and oxygen (O/M ratio)
- Monophasic (solid solution) and stoichiometric (O/M = 2.00) material

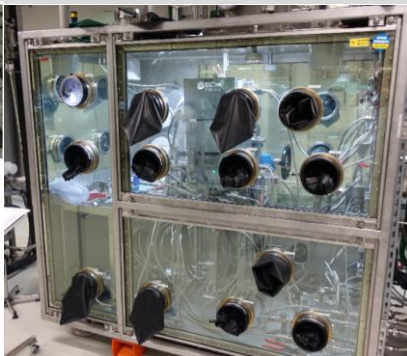
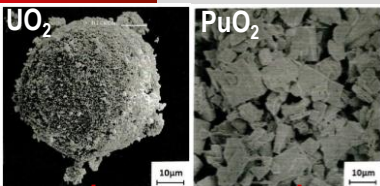


60, 65, 70 mol. %

O/M=2.00
O/M<2.00

Ternary phase diagram U-Pu-O at room temperature for an O/M ratio between 1.5 and 2.7 [3]

ELABORATION 2/2 - CO-MILLING PROCESS (ATALANTE)



After sintering: height of 5 mm, diameter of 5 mm and weight of 1 g

Best compromise for needed samples for the thermodynamic characterizations

Dosage
20 pellets -> 31g

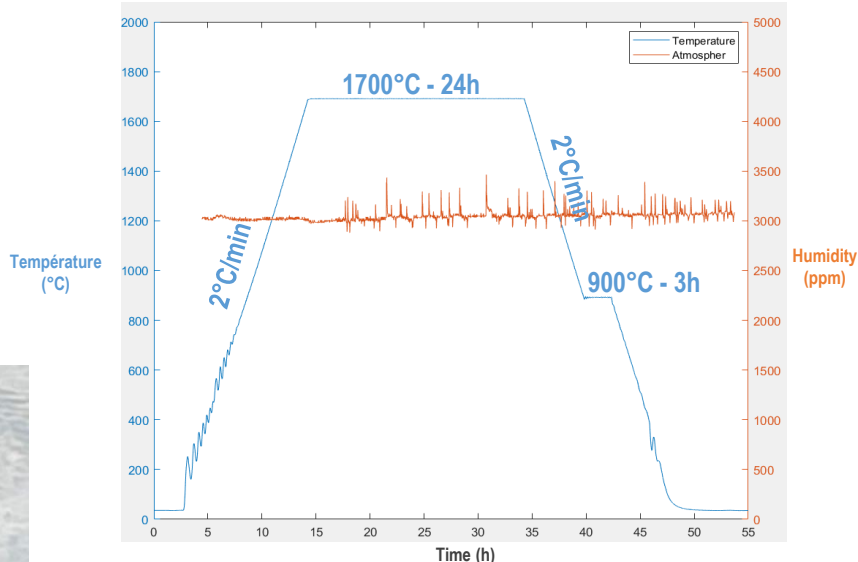
Blending
30min

Milling
4h, U-Ti, U=1

Granulation
200 µm

Pelletizing
450 MPa, 6 mm

Sintering
Ar + 4.3% H₂

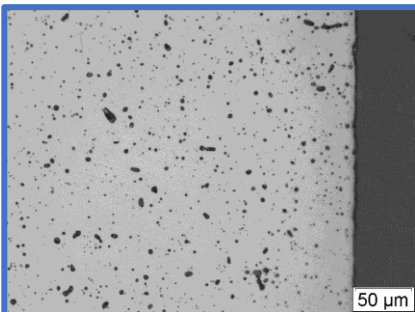
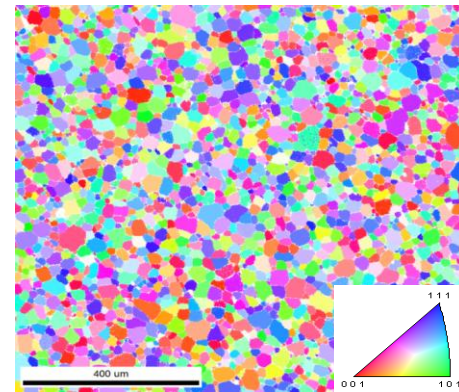
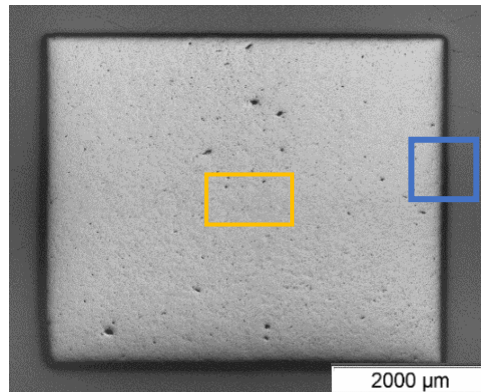
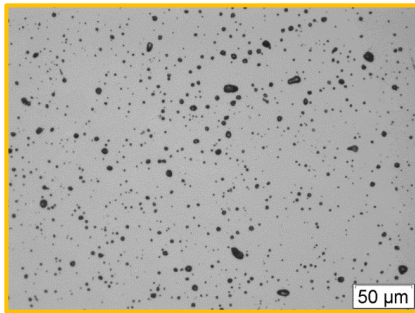


Density measurement* : Apparent density = 96.01 ± 0.07 % d_{theo} - Open pores = 0.54 ± 0.1 vol. %
 - Closed pores = 3.45 ± 0.1 vol. %

Dissolution:

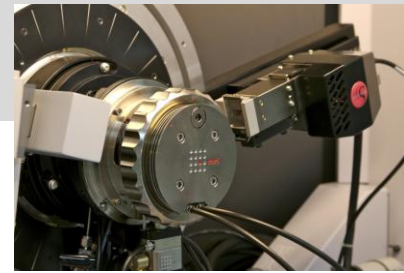
Optical microscopy: None crack and few macropores (maximum 60 μ m)

SEM/EBSD: Mean grain size 15.7 ± 0.5 μ m



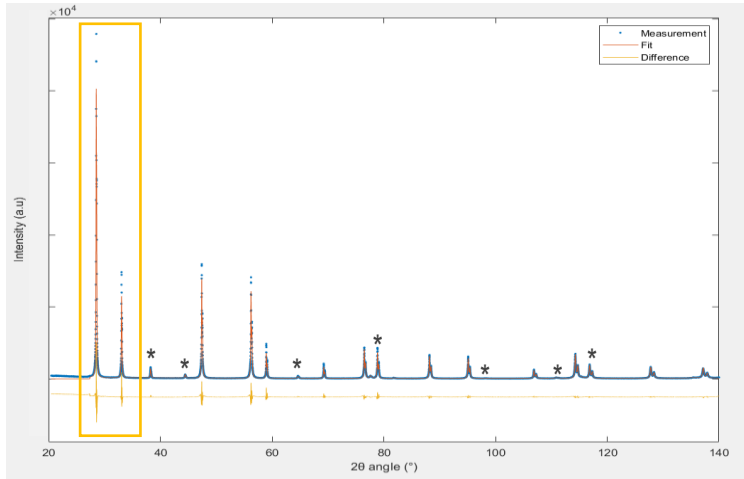
Dense pellet without crack and macropore

* Hydrostatic density by immersion in bromobenzene solution

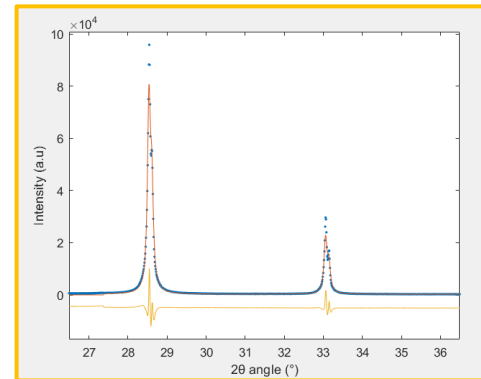


D8 Brucker

Setting: angle step 0.1 ° each 5s – acquisition between 20 and 140°



* : Au reference



Identification of the phases: Monophasic - FCC structure - $U_{1-y}Pu_yO_{2-x}$

Determination of the lattice parameter : $a = 5.426 \pm 1.10^{-3} \text{ \AA}$

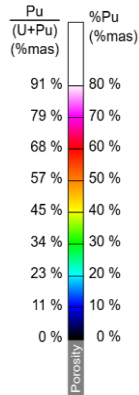
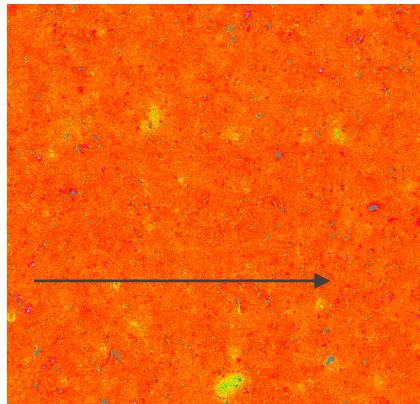
Estimation of the O/M ratio:

2.0 ± 4.10^{-3} (Duriez et al. law [5])

Monophasic material $U_{0.4}Pu_{0.6}O_2$

CHARACTERIZATION - ELECTRON PROBE MICRO-ANALYSIS

Setting: Map of 1024x1024 pixels = 1 μm^2
 - 20kV electron accelerating voltage - 20 ms. pixel^{-1}

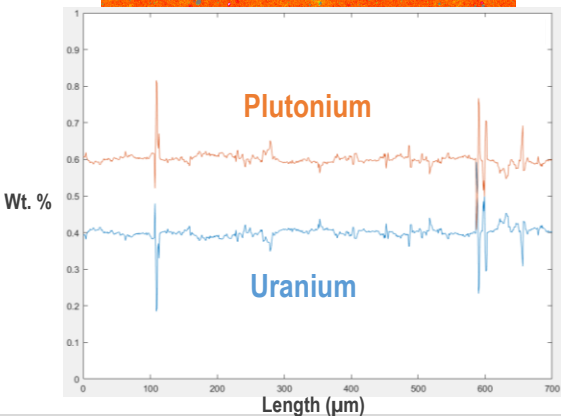


Electron Probe Micro-Analysis
CAMECA SX100

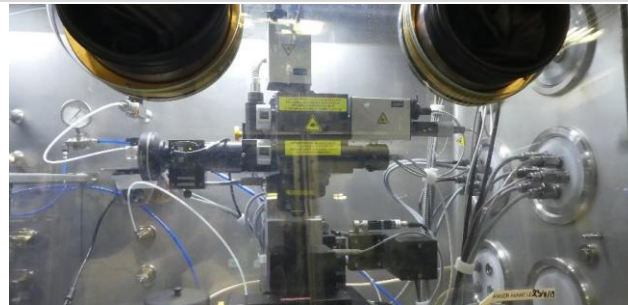
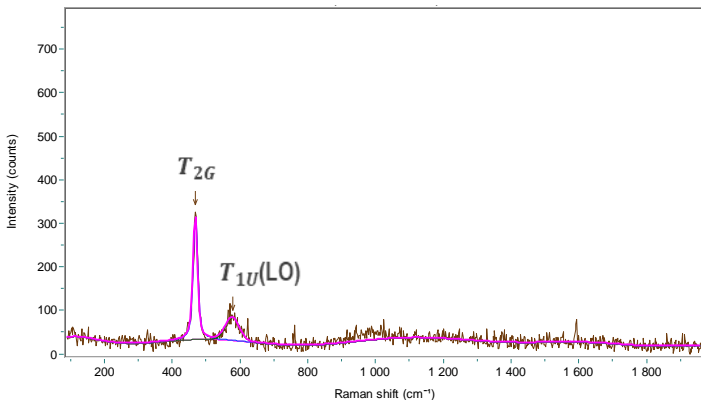
Estimation of the Pu content :

$$y = 0.595 \pm 6.10^{-3}$$

Homogeneous distribution of cations with acceptable uranium agglomerate.

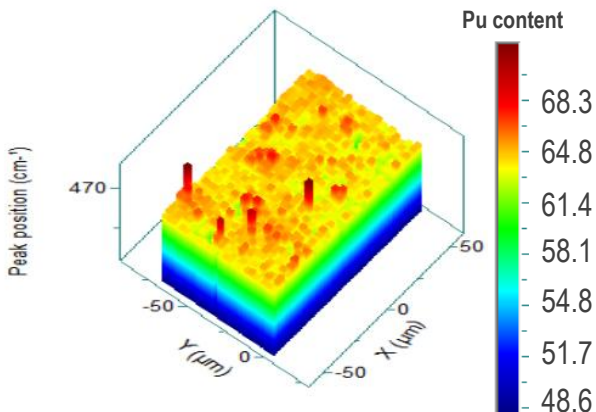


Setting: Green laser (10%) 11mW - Magnification x100



Raman Micro-Spectroscopy

Line (3000 μm): 30 s/point each 1.5 μm
 Map (120x70 μm): 30 s/point each 1.5 μm



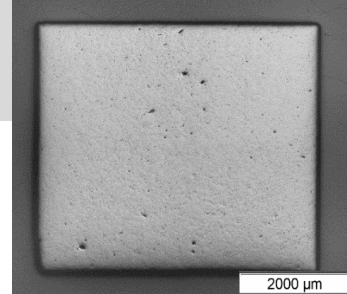
Estimation of the Pu content with the T2G band position:

$$467.5 \text{ cm}^{-1} \rightarrow y = 0.597 \pm 3.10^{-2} [4]$$

Monophasic solid solution and homogeneous repartition

Conclusions:

- Dense pellet (96% of d_{theo})
- Microstructure without crack and macroporosity
- Homogeneous cationic distribution (EPMA)
- Monophasic and stoichiometric $U_{0.40}Pu_{0.60}O_{2.00}$ mixed oxide



Next steps:

- Elaboration of pellets with 65 and 70 mol.% of Pu (End of 2021).
- Thermodynamic properties measurements at JRC-Karlsruhe (melting temperature, enthalpy, heat capacity, conductivity, ...) and at Marcoule (thermal expansion and oxygen potential).



Thank you for your attention

DE LA RECHERCHE À L'INDUSTRIE

References

- [1] Y. Guerin. 2012. « 2.21 - Fuel Performance of Fast Spectrum Oxide Fuel ». In *Comprehensive Nuclear Materials*, édité par Rudy J.M. Konings, 547-78. Oxford: Elsevier.
- [2] C. Guéneau et al., 2019, « D1.1 - Thermodynamic modelling of the (U-Pu-Am-O) system », CEA pour Inspyre, www.eera-jpnm.eu/inspyre.
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- [4] L. Medyk et al., 2020, Determination of the plutonium content and O/M ratio of (U,Pu)O_{2-x} using Raman spectroscopy, *Journal of Nuclear Materials*. 541 152439.
- [5] C. Duriez et al., 2000, Thermal conductivity of hypostoichiometric low Pu content (U,Pu)O_{2-x} mixed oxide, *Journal of Nuclear Materials*. 277 (2000) 143–158.