GEN IV : Evaluation of Oxygen Stoichiometry during the Sintering of (U, Pu)O_2 Fuel

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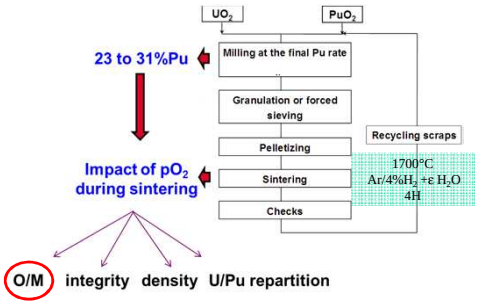
Introduction

In the frame of the development of 4th generation Sodium Fast Reactors (SFR), various fuel-manufacturing processes are under consideration. For ceramics such as (U, Pu)O_2, diffusion phenomena occurring during sintering are affected by the oxygen content of the atmosphere. The latter imposes the nature and the concentration of structural defects which govern diffusion mechanisms inside the material. The oxygen partial pressure, pO_2, of the sintering gas in equilibrium with MOX pellets needs to be precisely controlled; otherwise a large dispersion in critical parameters for fuel manufacturing could be induced [1]. Among them, the oxygen over metal ratio (O/M) after sintering defines many properties of the fuel in operation (thermal conductivity, mechanical properties,…). SFR fuels have to be hypostoichiometric with a O/M ratio close to 1,98. To achieve this, it is crucial to understand the relation between the sintering atmosphere and the fuel along the thermal cycle. In this study, oxygen potential monitoring of the sintering gas was carried out by measuring oxygen partial pressure (pO_2) at the outlet of a dilatometer by means of a zirconia probe.

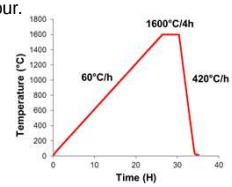


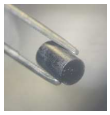
↳ Dilatometer controlled in pO_2

Description of the actual work

Dilatometry Experiments

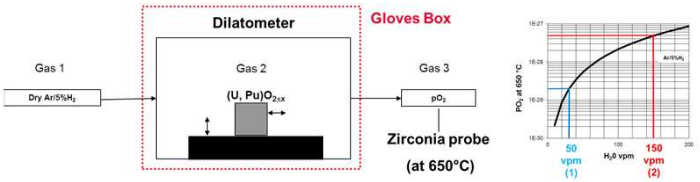
The UO_2/PuO_2 mixtures are fabricated in a glove box in the LEFCA facility, Three compositions of 0, 30 and 100wt%Pu are studied. These mixtures were pressed into green cylinders of 6 mm in diameter and height.
Dilatometric measurements are carried out under dry Ar/4%H_2. The dilatometer used is a SETARAM® TMA 92. The sample holder and the probe are made of alumina. The input gas flow renews the atmosphere of the furnace 10 times per hour.



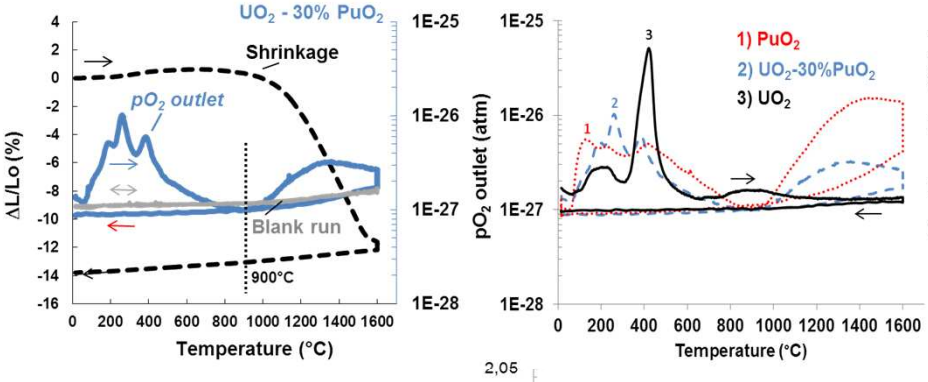


Atmosphere

Oxygen partial pressure measurements of the dilatometer gas outlet by means of a SETNAG® zirconia probe give information about O_2 exchanges between the solid sample and the atmosphere. The amount of released O_2 depends on the composition of the gas which can be deduced from the inlet H_2 partial pressure and the outlet measured pO_2.



Results



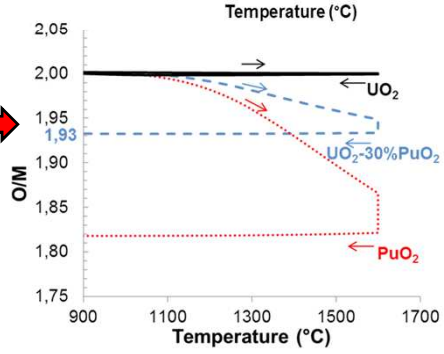
The comparison of measurements coming from the sintering of respectively PuO_2, UO_2 and UO_2-30%PuO_2 pellets with thermodynamic data [2] allows to draw some conclusions.

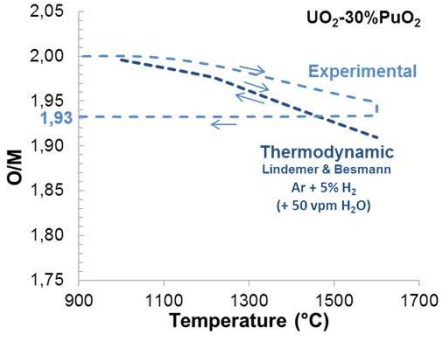
- **20-900°C** : elimination of adsorbed moisture and organic species from the powder fabrication route,
- **300°C-900°C** : reduction of UO_{2+x} into $UO_{2,00}$,
- **900-1600°C** : reduction of PuO_2 into PuO_{2-x} or reduced compounds [2] ($PuO_{1,61}$, $PuO_{1,52}$, Pu_2O_3).

By integrating the overall oxygen loss measured throughout the experiment we can calculate the corresponding weight loss. Considering that each material O/M ratio is equal to 2.00 at 900°C, it is possible to derive the evolution of the O/M ratio.

These final O/M values are in good agreement with results from thermogravimetry experiments.

	UO_2	UO_2-30%Pu	PuO_2
O/M after sintering	2,000(3)	1,931(3)	Not done





- **Kinetic of reduction of Plutonium during a sintering cycle up to 1600°C**
- **Important gap between thermodynamic calculation and experimental measurement especially during the cooling down**
- **Necessity to increase the pO_2 of the sintering gas to obtain a O/M close to 1,98**

Conclusion / Recommendations

Coupling thermal cycle with an outlet gas pO_2 measurement permits to identify different redox phenomena. The evolution of oxygen stoichiometry can be determined during the sintering of (U, Pu)O_2 as well as its final O/M. Based on our results, It is possible to make recommendations on the choice of the sintering atmosphere and the sintering thermal cycle in order to obtain a O/M ratio closer to the target value. Moreover coupling the evolution of the O/M ratio with the shrinkage and microstructure observations, density and U-Pu homogenization can be enhanced for the generation 4 of SFR fuels.

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