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

S. Vaudez, J. Léchelle, S. Berzati

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

S. Vaudez, J. Léchelle and S. Berzati

CEA, DEN, DEC, SPUA F-13108 Saint Paul lez Durance, France, stephane.vaudez@cea.fr

INTRODUCTION

In the frame of the development of 4th generation Sodium Fast Reactors (SFR), various fuel-manufacturing processes are under consideration. The standard powder metallurgy route for future SFR oxide fuels involves co-milled UO_2 and PuO_2 with a plutonium content around 30wt%. Sintering cycles for mixed uranium-plutonium oxide fuels are characterized by a plateau of a few hours long at 1700°C under an Ar/4%H_2 atmosphere containing trace amounts of moisture.

For ceramics such as (U, Pu)O_2, diffusion phenomena occurring during sintering are affected by 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.

DESCRIPTION OF THE ACTUAL WORK

Raw Materials and Sample Preparation

The UO_2/PuO_2 mixtures are fabricated in a glove box in the LEFCA facility at Cadarache center by a powder metallurgy process optimized for small amounts of powder (40 g). Three compositions of 0, 30 and 100wt%Pu are studied.

These mixtures were pressed into green cylinders of 6 mm in diameter and height.

Dilatometry Experiments

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, allowing measurements up to 1600°C. The thermal cycle consiste in heating at 1°C / min, soaking during 4 hours at 1600°C and cooling at 7 °C/min. The input gas flow is around 10 renewals of the furnace atmosphere per hour in order to eliminate efficiently the released O_2.

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. These data provide a quantitative value of the quantity of O_2 absorbed or released by the sample between two times t and t+δt. 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 measured O_2 partial pressure. A reference measurement of pO_2 is taken prior to any experiment.

RESULTS

In figure 1, three main oxygen release peaks are observed during the heating stage.

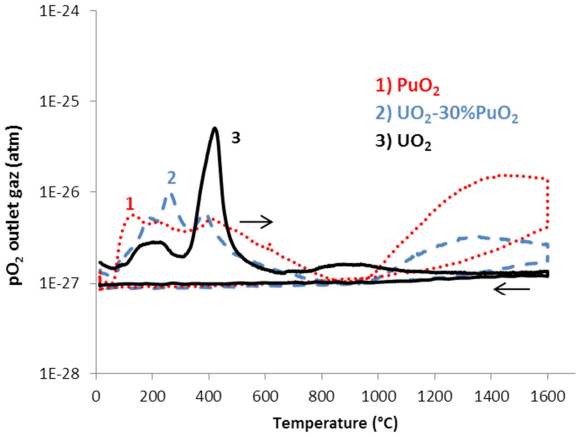

Fig.1: O_2 exhausting gas during the sintering of PuO_2, UO_2 and UO_2-30%Pu.

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 $UO_{2,0}$,
- 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 as presented in figure 2 as well as the final O/M.

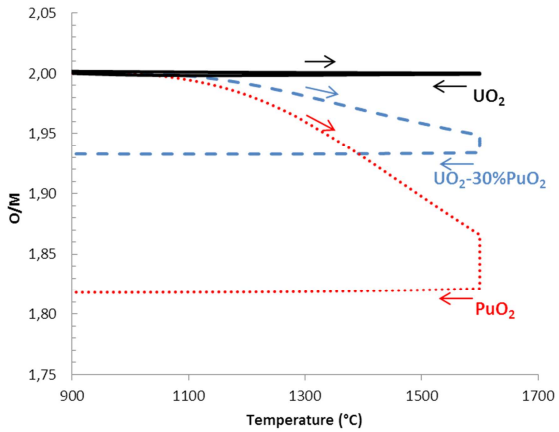

Fig.2 : evolution of the O/M ratio during the sintering of PuO_2, UO_2 and UO_2-30%Pu.

These final O/M values are in good agreement with results from thermogravimetry experiments. As can be observed in figure 2, the final O/M of the 30% Pu sample (1.93) was found to be significantly lower than the recommended value of 1.98.
Thus, the same analysis was performed under three different atmospheres with increasing pO_2. Coupling the evolution of the O/M ratio with the shrinkage and microstructure observations has then been realized for the three materials.

Based on our results, it is possible to make recommendations on the choice of the sintering atmosphere in order to obtain a O/M ratio closer to the target value. Moreover microstructure properties such as U-Pu homogenization and density can be enhanced for the generation 4 SFR fuel.

ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to the AFCOE program which provided the funding needed to carry out the experiments.

REFERENCE

1. S. BERZATI, S. VAUDEZ, R. C. BELIN, J. LECHELLE, Y. MARC, JC. RICHAUD, JM. HEINTZ
"Controlling the Oxygen Potential to improve the Densification and the Solid Solution Formation of Uranium–Plutonium Mixed Oxides" *Journal of Nuclear Materials*, **447**, 115–124 (2014).

2. C. GUENEAU, N. DUPIN, BO SUNDMAN, C MARTIAL, JC DUMAS, S. GOSSE, S. CHATAIN, F. DE BRUYCKER, D. MANARA, R. J. M.KONINGS
"Thermodynamic modelling of advanced oxide and carbide nuclear fuels: Description of the U–Pu–O–C systems" *Journal of Nuclear Materials*, **419**, 145-167 (2011).