SPS synthesis of UO_2 samples containing Cs, Mo, Ba and Zr bearing phases

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Highlights

- Synthesis of dense UO_2 containing different FP bearing phases.
- Incorporation of Cs into UO_2 ceramic.
- Sintering behavior impacted by the presence and the nature of the additives.

1. Introduction

Within the frame of nuclear reactor development, some studies are led on the behavior of nuclear fuel in case of severe accident. In such conditions, the three containment barriers can fail leading to Fission Products (FP) release in the environment. The behavior of these elements during the accidental sequence depends on their properties and notably on their volatility. Moreover, FP can interact with each other and with the fuel, leading to modifications of the source term (nature and quantity of radioactive materials released during an accident).

The development of realistic models for FP behavior during a severe accident requires experimental data on FP speciation into the fuel. Due to the limitations in terms of experiments and characterization techniques available to study FP speciation in irradiated nuclear fuels, simulant materials called SIMFUEL are often used [1]. These materials are composed of UO_2 with different species representative of the major types of FP produced in the fuel during irradiation cycles in a light water reactor. They are usually prepared by sintering at 1700°C under H_2 [2]. This synthesis process does not allow the study of volatile FP (such as Cs) because they are totally released during the high temperature sintering stage. Recently, Spark Plasma Sintering (SPS) was shown to enable the synthesis of dense UO_2 samples containing cesium iodine [3].

In this work, the SPS synthesis of SIMFUEL samples containing Cs, Mo, Ba and Zr bearing phases have been investigated in collaboration with the JRC-Karlsruhe, Germany. The samples are composed of UO_2 with one or two chemical phases containing FP surrogates. The thermal behavior of the different phases has been previously studied by TGA.

2. Methods

All sample preparation was performed in a glovebox under an argon atmosphere. The additive powders were first manually ground in an agate mortar and mixed with a commercial UO_2 powder. The concentrations in FP surrogates varied from 0.5 wt% to 4 wt%. The UO_2 batch chosen to perform the syntheses was highly hyperstoichiometric, with an oxygen to uranium ratio (O/U) of 2.16. It was thus reduced before mixing during 4h at 800°C under Ar/6.5% H_2 to obtain a final O/U of 2.01.

ThermoGravimetricAnalysis of the mixtures was performed with a Netzsch STA 449C Jupiter.

About 0.5 to 1 g of the {FP compounds-UO_2} mixture was loaded into a 6 mm graphite die containing a graphite foil. The die was loaded into an SPS equipment (FCT Systeme GmbH, Rauenstein, Germany), specifically adapted for operations into a glovebox [4]. The powder was pre-pressed at 500 N (17.7 MPa) then pressed up to 2.5 kN (88 MPa). The chamber was evacuated to <10 Pa and refilled with Ar. The die was heated at 200°C/min to 1200°C, held there for 5 min. The cooling rate was 200°C/min to 400°C, followed by free cooling to room temperature. Then the pressure was decreased in 10 s.

The density of the sintered samples was measured geometrically and confirmed using the Archimedes method in water. The apparent density was determined by He pycnometry. The relative density during sintering was calculated from the displacement of the SPS piston, taking into account the final density and after correcting for thermal expansion as determined in a blank run. Scanning electron microscopy was performed with a Tescan Vega LSH device equipped with an EDX detector. The chemical composition of the samples after sintering was determined by IDMS, ICP-AES (AGILENT Technologies 5100) and ICP/MS (VARIAN 820 MS and PERKIN-ELMER Elan DRC).

3. Results and discussion

The sintering behavior depends on the nature of the additives. The sintering of UO_2 + $BaZrO_3$ is not complete whereas the sintering of UO_2 + $BaMoO_4$ is appropriate. As for example, Figure 1 reports the comparison between UO_2 and UO_2 + $Cs_2U_xO_y$ + MoO_3 SPS curves. The effect of the additives on the shrinkage and the sintering temperature is clearly highlighted.
The presence of Cs was confirmed by chemical analysis and SEM observation (Figure 2, Cs containing particle in the red circle).

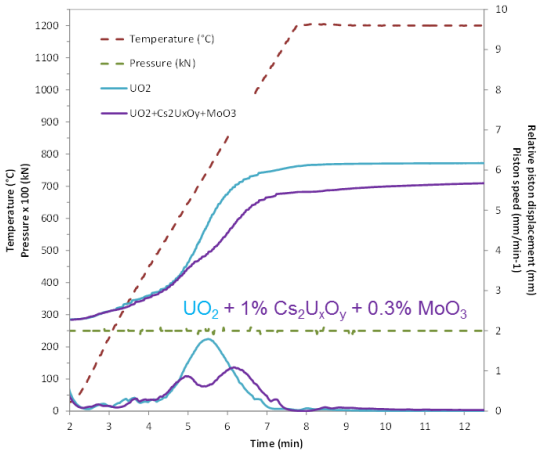

Figure 1. SPS curves of UO_2 and UO_2 + $Cs_2U_xO_y$ + MoO_3.

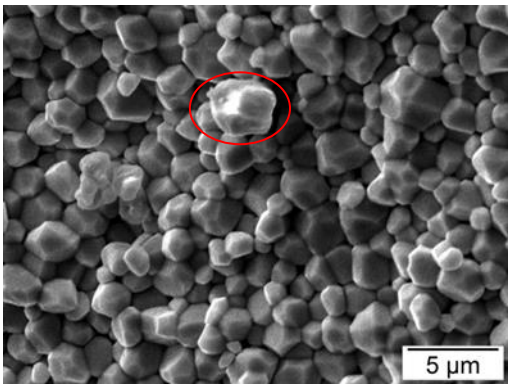

Figure 2. SEM image of fractured surface of UO_2 + Cs_2MoO_4

The relative density of the pellets as a function of the Cs phases added is given in Table 1. Differences between geometric and hydrostatic and apparent densities can be explained by the shape of the pellets and the presence of residual graphite layer on the surface.

Table 1. Densities and porosities of the final pellets

Batch	Geometric density (%d_{th})	Hydrostatic density (%d_{th})	Apparent density (%d_{th})	Closed porosity (%)	Open porosity (%)
UO_2 + Cs_2MoO_4	84	92	93	7	3
UO_2 + $Cs_2U_xO_y$	88	97	97	2	1
UO_2 + $Cs_2U_xO_y$ + MoO_3	60	96	97	3	1

4. Conclusions

Uranium dioxide pellets containing several FP bearing phases were synthesized. The sintering behavior as well as the final density of the different samples were strongly impacted by the presence and the nature of the additives. Additional studies are necessary to improve the incorporation of some phases and the homogeneity of the samples.

References

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