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Fission products behaviour in UO_2 submitted to nuclear severe accident conditions

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Abstract. The objective of this work was to study the molybdenum chemistry in UO_2 based materials, known as SIMFUELS. These materials could be used as an alternative to irradiated nuclear fuels in the study of fission products behaviour during a nuclear severe accident. UO_2 samples doped with 12 stable isotopes of fission products were submitted to annealing tests in conditions representative to intermediate steps of severe accidents. Samples were characterized by SEM-EDS and XAS. It was found that Mo chemistry seems to be more complex than what is normally estimated by thermodynamic calculations: XAS spectra indicate the presence of Mo species such as metallic Mo, MoO_2 , MoO_3 and Cs_2MoO_4 .

1. Introduction

Severe Accidents in nuclear power plants may involve the release of radioactive elements such as Fission Products (FP) into the biosphere. Many integral and analytical international research programs, such as PHEBUS FP, HI/VI, VEGA, VERCORS, etc. [1], have been carried out aiming at understanding the behaviour of FP during a Nuclear Severe Accident, like that of Fukushima in 2011. Most of them used irradiated nuclear fuel from Pressurized Water Reactors or Boiling Water Reactors. Another possibility would be to use model materials, known as SIMFUEL, consisting in UO_2 samples doped during fabrication with stable FP (Ba, Ce, Cs, La, Mo, Nd, Pd, Rh, Ru, Y and Zr) in concentrations representative of a given burn-up. Despite the limitations of SIMFUELS, such as the difficulty to reproduce some phenomena directly linked to irradiation, these materials could be used to study FP behaviour such as precipitation, release and species formation in severe accident conditions. These conditions can be recreated in dedicated annealing test under controlled atmosphere. Besides, one of the main advantages of SIMFUELS is that they lack of radioactivity, other than that of natural uranium, reducing radioprotection constraints and enabling to use powerful characterisation techniques such as XAS. Among the many FP, molybdenum presents a particular interest. The Mo/ MoO_2 redox couple is believed to act as a oxygen potential buffer, affecting the chemical state of other FP and their release [2]. In order to study Mo chemistry in oxidizing conditions, three SIMFUELS samples doped with 12 stable FP in concentration representative of a 76 GWd.t^{-1} irradiated fuel were submitted to annealing tests under flowing argon + 1% O_2 . Mo behaviour has been characterized by SEM-EDS and XAS.



2. Methods and materials

2.1. Samples characteristics

SIMFUEL samples were acquired from the Chalk River Laboratories, Canada. Samples fabrication process is described in [3] and were latter implanted with Cs. The concentration of each FP, presented in **Table 1**, matches that of a 76 GWd.t⁻¹ Burn-up UO₂ irradiated fuel. Samples are 500 μm thick, polished quarter discs made from 10 mm diameter discs.

Samples composition (at. %)											
Ba	Ce	Cs	La	Mo	Sr	Y	Zr	Rh	Pd	Ru	Nd
0.26	0.61	0.35	0.20	0.61	0.13	0.06	0.60	0.03	0.42	0.64	0.91

Table 1: FP concentration in SIMFUEL samples

2.2. Experimental loop and test conditions

The annealing tests were performed in the DURANCE experimental loop, very similar to the MERARG one [4], located at the *Bernard François laboratory* (CEA Cadarache, France). The PO₂ in the inlet gas was monitored thanks to a MicroPoas probe (GENAIR), allowing to calculate the oxygen potential for each test (μO₂). Three annealing sequences were performed under flowing argon containing 1% O₂. Sample A was annealed at 300°C for 2 h, Sample B at 300°C for 2 h and then at 1200 °C for 30 min, and finally Sample C at 1700°C for 10 min.

2.3. Characterization methods

2.3.1. Scanning Electron Microscopy. Scanning Electron Microscopy (SEM) was performed using a Philips XL30 FEG instrument, equipped with an EDAX-EDS system allowing us to determine the distribution and content of Mo using Energy Dispersive X-ray Spectroscopy (EDS). Acceleration tension was set to 15 kV. Mo La1 X-ray lines were used to analyse samples.

2.3.2. X-ray Absorption Spectroscopy. Measurements were carried out at the MARS beam-line, SOLEIL synchrotron radiation facility (France) [5], under top-up 430 mA ring mode, in the (17.6 - 22.4) keV energy range. A Si(220) double-crystal monochromator (DCM) was used. The monochromatic beam was focused to 350 x 350 μm². XAS spectra were collected in fluorescence mode, with a Vortex-90-EX silicon drift detector. The acquired spectra were processed using the ATHENA software [6]. Pre-edge removal and normalization was achieved using linear functions. The post-edge line for XANES spectra was taken using the position 30 eV and 150 eV relatively to edge position E₀. The E₀ and white line positions were taken as the first inflection point and the first zero-crossing of its first derivative, respectively. Linear combination fits were performed in the (-10, +50) eV range relative to the absorption edge.

3. Results

3.1. SEM-EDS

SEM-EDS images and Mo X-ray maps of samples A, B and C are presented in **Figure 1**. Two main precipitates are observed in sample A: Mo precipitates which contain Ru, Rh and Pd, with a Mo/Ru ratio equal to 0.87 and the second type containing Ba, Sr, Zr, Ce, Y, U and O. Three different precipitates were observed in sample B, two of them containing Mo and Ba along with Sr, Ce and Zr, with Mo/Ba ratios equal to 1.2 and 7.0, respectively. The third type contains also Pd, Rh and Ru, with a Mo/Ru ratio equal to 0.1. Three types of precipitates containing Mo were observed in Sample C: the first ones contain also Ba, with a Mo/Ba ratio equal to 8.4 while the other two were constituted by Mo, Ru, Rh and Pd, with different Mo/Ru ratios: 4.5 and 1.0, respectively. No Cs precipitates were observed in the three samples. A predominance diagram, calculated using the FactSage software/SGPS database, is presented in **Figure 2**. The calculated oxygen potentials were: -350, -210 and -230 kJ.mol⁻¹ for samples A, B and C, respectively. According to **Figure 2**, the stable species in

samples A and B would be BaMoO_4 , MoO_2 and Cs_2MoO_4 (zone 3), while for sample C they would be BaZrO_3 , MoO_2 and Cs_2MoO_4 (zone 2).

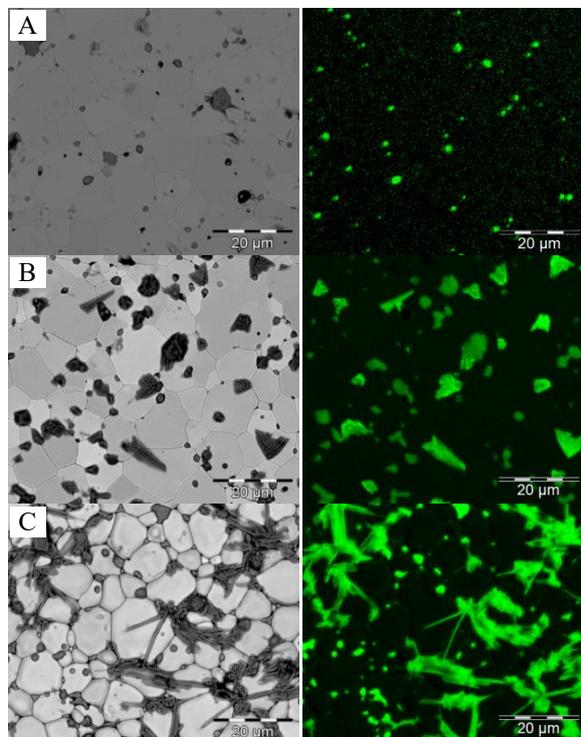


Figure 1: SEM images (left) of samples A, B and C, along with the respective Mo X-ray maps (right)

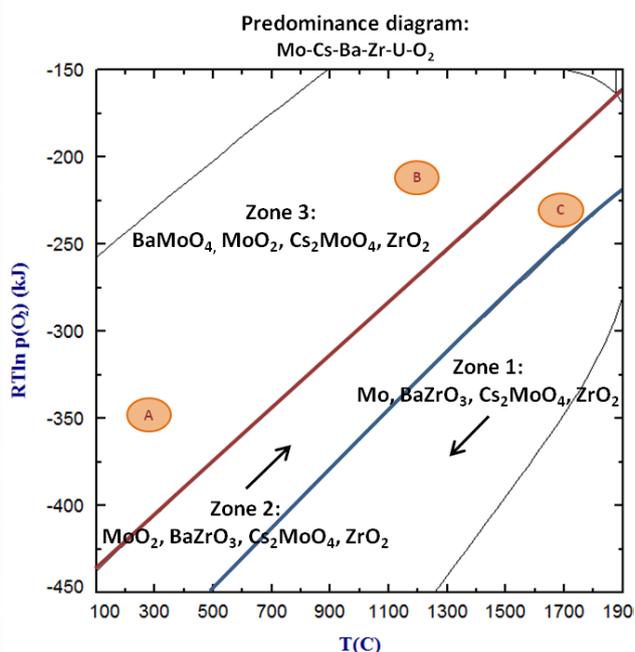


Figure 2: Mo-Cs-Ba-Zr-U-O₂ predominance diagram

3.2. XANES

Mo XANES spectra obtained for the three samples and four reference compounds spectra: metallic Mo, MoO_2 , MoO_3 and Cs_2MoO_4 , are presented in **Figure 3**. The E_0 and white line energies for each acquired spectra are presented in **Table 2**. As observed, these values were modified as consequence of the annealing tests: sample B presents an E_0 energy shift of 2.9 eV regarding to sample A, while the E_0 position of sample C presents an energy shift of -0.2 and -3.1 compared to Samples A and B, respectively. Linear combination fits results are presented in **Table 3**.

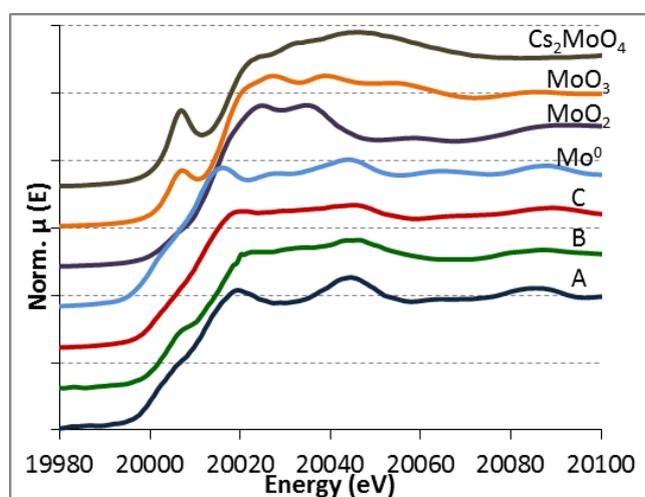


Figure 3: Samples and reference compounds Mo K-edge XANES spectra

Sample	E_0 (eV)	White line (eV)
A	20001.4	20019.3
B	20004.3	20023.0
C	20001.2	20019.1
Mo	20000.0	20016.6
MoO_2	20005.0	20025.0
MoO_3	20004.6	20026.8
Cs_2MoO_4	20003.8	20045.5

Table 2: Samples and references compounds spectra E_0 and white line position

Sample	Reference weight				R factor
	Mo	MoO ₂	MoO ₃	Cs ₂ MoO ₄	
A	0.729	0.093	-	0.158	0.002367
B	0.317	0.099	0.427	0.144	0.000833
C	0.592	0.251	0.136	0	0.000720

Table 3: Mo spectra fit results

4. Discussion

SEM-EDS and XANES results highlight the evolution of the chemical phases as consequence of the annealing tests under oxidizing atmosphere. Regarding to sample A, SEM-EDS results show that Mo is found only in precipitates containing Pd, Rh and Ru. These precipitates have already been observed in irradiated nuclear fuels and are referred to as white inclusions [2]. Though these precipitates are supposed to be metallic, XANES results indicate that Mo oxidized species such as Mo⁴⁺ and Mo⁶⁺ are present as well. Based in thermodynamic estimations (**Figure 2**), the existing species would be MoO₂ and BaMoO₄. Regarding to sample B, SEM-EDS results indicate the presence of three different Mo precipitates: the first ones containing Mo, Pd, Rh and Ru, the two others containing Ba, Ce, Mo, Sr, Y and Zr, with an important difference in their Mo/Ba ratio. As described in bibliography, Ba is normally found in an oxide phase with perovskite structure, described as (Ba, Cs, Sr)(Mo, Zr, U, RE)O₃ (RE = Rare Earths) [2]. XANES results confirm the presence of Mo oxidized species. The presence of two different types of Mo/Ba precipitates would imply the existence of Mo species other than BaMoO₃ or BaMoO₄, not predicted by thermodynamic estimations. Regarding to sample C, SEM-EDS results show the presence of big sized precipitates, with an equivalent circle diameter superior to 40 μm, containing Ba, Sr and Ce, but no Zr. Sample C Mo XANES spectrum presents an energy shift to lower energy compared to that of sample B, which would imply an important presence of metallic Mo. SEM-EDS results confirm this, since more precipitates containing Mo, Pd, Rh and Ru are observed in this sample. The presence of Mo⁰ in the three samples would indicate that chemical equilibrium was not attained during tests.

5. Conclusion

Molybdenum chemistry in oxidizing conditions was studied in model materials representative of high burn-up irradiated nuclear fuels. Three samples were studied, which were annealed up to 300, 1200 and 1700°C. Samples were characterized by SEM-EDS and XAS. It was found that Mo, initially present in metallic precipitates, was oxidized and interacted with other FP such as Ba, Sr, Ce and Cs. Though there is a rather good agreement between experimental observations and thermodynamic estimations, an unidentified species other than BaMoO₃ or BaMoO₄ seems to be created at 1200°C.

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