

## The role of Eu on microstructure and behaviour of UO<sub>2</sub> during interim storage.

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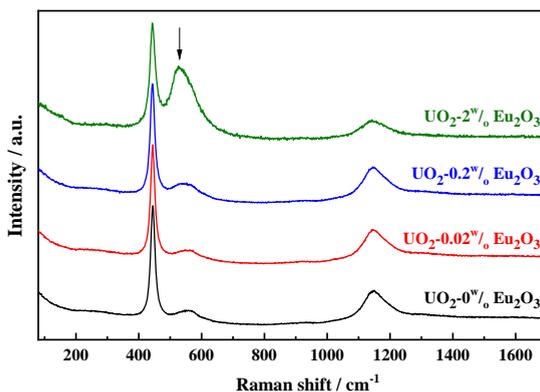
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Fission products formed during nuclear fuel operation for electricity production are found within its matrix as oxide precipitates and solid solutions, and as metallic inclusions ( $\epsilon$ -particles), among others. Additionally, the physico-chemical properties of the irradiated fuel get considerably modified [1-3] as a function of time and radial position. Among the fission products, the rare earth elements (REE) form a substantial fraction; and particularly, around 4-20 wt% of light REE corresponds to europium and gadolinium [4]. REE are typically present as solid solution within the uranium oxide fuel matrix, due to their capacity to substitute U atoms in the lattice [5-7]. The solid solubility of Eu<sub>2</sub>O<sub>3</sub> in UO<sub>2</sub> and defect chemistry have been studied and reported in the literature [6-8]. The knowledge of the influence of fission products on spent nuclear fuel (SNF) integrity is relevant for the physicochemical processes involved in the pre-disposal stages. After discharge from the reactor, the spent fuel is stored in pools at the reactor site to allow for the residual heat removal and decay of the very short-lived nuclides. Subsequently the fuel is transferred to wet or dry interim storage. Interim storage solutions for SNF are needed regardless of the fuel cycle strategy. The long-term integrity of SNF is almost ensured; however, the likely lifetime extension programs of such storage facilities should include ageing and degradation studies to demonstrate the safe long-term performance, including that of undetected damaged fuel. To our knowledge, no studies have been carried out investigating the impact of Eu in the UO<sub>2</sub> matrix alteration.

In the present work, the matrix corrosion under environment conditions representative of interim storage are presented by means of uranium–europium mixed oxides, the results of which may have an impact on final disposal. To gain knowledge on separate and synergic effects and to develop/conduct fundamental research, the use of non-irradiated alternatives is the simplest system to be addressed. In addition, the complexity for a full understanding and radiological constraints of irradiated fuel are added reasons for research with surrogate materials. Here, a series of Eu-doped and undoped UO<sub>2</sub> pellets (UO<sub>2</sub>, UO<sub>2</sub>-0.02 % Eu<sub>2</sub>O<sub>3</sub>, UO<sub>2</sub>-0.2 % Eu<sub>2</sub>O<sub>3</sub> and UO<sub>2</sub>-2 % Eu<sub>2</sub>O<sub>3</sub>) were firstly prepared and characterised. Samples were obtained by pressing the powder mixtures of precursor oxide powders in weighted amounts, and then sintering under reducing atmosphere. A detailed characterisation of the pellets was carried out previous to be used in dry oxidation experiments and dissolution tests. The X-ray diffraction characterisation of the samples shows that an increase in Eu dopant content yields a lattice contraction of the fluorite structure probably due to joint effects not well studied of smaller cation size of Eu(III) and shorter U/Eu-O bonds; possible hypo-stoichiometry; or partial oxidation of U(IV) to U(V) and oxygen vacancies annihilation [9, 10]. The latter hypothesis is ruled out from the analysis by Raman spectroscopy that confirms the presence of oxygen vacancies in the structure as a consequence of Eu doping, demonstrated by the increasing intensity of the so-called “defects band” (marked with an arrow in Figure 1) with Eu concentration [11]. The specific surface area (SSA) was measured by N<sub>2</sub> BET method, giving very low values of 0.2 to 0.5 m<sup>2</sup>·g<sup>-1</sup>.

Some of the pellets were crushed and milled for dry oxidation experiments, while others remained unaltered for dissolution experiments. On the one hand, we investigated the effects of Eu doping on the thermal stability of UO<sub>2</sub>. For this purpose, powdered samples were subjected to a thermal treatment consisting of a heating ramp up to 900 °C at two oxygen concentrations (1% and 21% O<sub>2</sub>). These studies showed that adding Eu to UO<sub>2</sub> slightly retards oxidation to orthorhombic U<sub>3</sub>O<sub>8</sub>. Kinetic data confirm this trend, and likewise verify that lowering the oxygen concentration available delays the oxidation. On the other hand, we studied the chemical durability of the pellets under two boric acid concentrations (1600 and 3500 ppm), mimicking some relevant wet storage conditions (spent fuel pools). The trend and values of both U concentrations and normalised dissolution rates (to BET-SSA) for U are similar for both leaching media, *i.e.* a decrease of dissolution rate is observed with increasing Eu content in the solid solution. The presence of Eu has an important impact on the rate of oxidation from U(IV) to U(VI). It can be hypothesised that this reduction in the dissolution rate with increasing Eu is due to the presence of trivalent elements, which promotes and stabilises the formation of oxygen vacancy clusters (in order to maintain charge neutrality) [6], as in the case

of gadolinium-doped  $\text{UO}_2$  [6, 12-14] or cerium-doped  $\text{UO}_2$  [11]. This effect is particularly well emphasised in the final values of normalised dissolution rates. Values corresponding to the sample of  $\text{UO}_2$  doped with 2 %  $\text{Eu}_2\text{O}_3$  are clearly the lowest, thus indicating that the presence of such quantity of Eu makes  $\text{UO}_2$  significantly less susceptible to oxidative-dissolution than those undoped or with lower Eu content under both considered  $\text{H}_3\text{BO}_3$  concentrations.



**Figure 1 Raman spectra of the as-prepared samples:  $\text{UO}_2$  and  $\text{Eu}_2\text{O}_3$  doped  $\text{UO}_2$ .**

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