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DISCO

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DELIVERABLE D2.1

Initial state report: sample characterisation and experimental set-up

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CO	Confidential, only for partners of the Disco project	

1 Introduction

This initial state report concerns progress in the preparation and characterization of materials that will be used in the dissolution experiments. The materials are both synthesized model materials and real spent fuel. The use of model materials, handled outside of Hot Cell facilities, permits access to various methods that might be difficult for highly radioactive spent nuclear fuel. The rationale is that advanced micro-analytical tools can be deployed more readily on model (unirradiated, depleted or natural uranium material) that could not be deployed at all on spent nuclear fuel itself and to align model studies with higher activity experiments. One set of model materials are doped with alpha-emitting nuclides, and the synthesis of these samples is more challenging than the U and Th oxide materials. The package is split into three sections for experiments involving Hot Cells *(*WP 2.1), Alpha Glove Boxes (WP 2.2) and U/Th Laboratories (WP 2.3). NB some spent fuel samples for hot cell work in WP3 were already prepared and characterized by Studsvik and CTM and have been made available for dissolution studies, but are not included in this report. These are described in the DisCo Deliverable D1.10 "1st Annual Meeting Proceedings", available on the DisCo web page (https://www.disco-h2020.eu/Home/ProjectOutcomes) and in the FIRST-Nuclides Deliverable No: 1.1 "Characterisation of spent nuclear fuel samples to be used in FIRST-Nuclides – relevance of samples for the Safety Case" , available on the FIRST-Nuclides web page (http://www.firstnuclides.eu/deliverables.aspx).

In this first version of the deliverable, the synthesis and characterization of some samples are still to be finalized. Therefore, this report will be updated when all samples are available.

2 Spent fuel samples used in WP2.1: Hot Cells

2.1 WP 2.1(a): Hot cell work at KIT-INE

Fuel	Burn-up	Forms
MOx	38 MWd/kg_{HM}	Three samples: two de-cladded fragments, one cladded segment.

The details of the irradiated MOx sample are as follows:

The samples come from the Obrigheim PWR (Germany) and was a 3.2% plutonium MOx fuel fabricated with the optimised co-milling method. The fuel was in the reactor for 1157 days with an average linear power of 200 W cm^{-1} and an average burn-up of 38 MWd/kg_U. It has cooled for 32 years and the fission gas release was 6%.

Four samples with zircaloy cladding have been cut from this material with a low speed saw and are being kept in a closed steel container, flushed with argon to prevent oxidation. One 4mm segment is to be used for inventory determination and the second, 6mm segment, for ceramography. One 10 mm cladded segment and fragments of a decladded segment will be used for dissolution experiments.

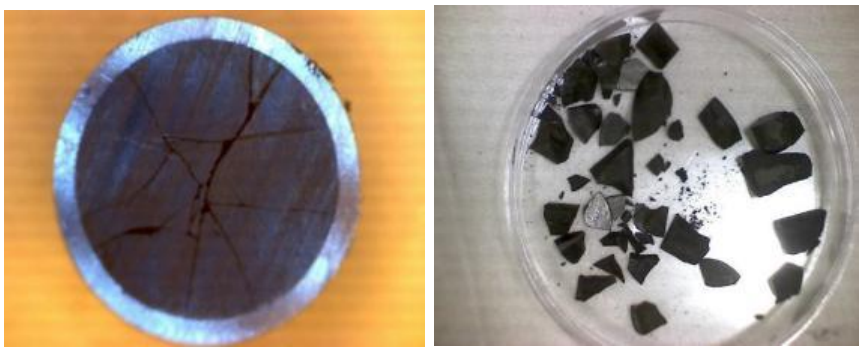


Figure 2.1.1 (a) cut pellet with zircaloy cladding (b) fragments for leaching experiments

2.2 Spent fuel samples in WP 2.1(b): Hot cell work at JRC

Fuel	Burn-up	Forms
MOx	40-60 MWd/kg_{HM}	Cladded segments.
Cr-UOx	40-60 MWd/kg_{HM}	De-cladded fragments

Details of the samples are as follows:

The MOx spent fuel (M502) was fabricated by the short binderless route (SBR) and had five power cycles in the Beznau PWR to give an average burn-up of 54 GWd/T_{HM} with an average linear power rating of 18 kWm^{-1}. Two samples have been cut, MOx-H and MOx-L with local burn-ups estimated from gamma scans of 56 and 48 GWd/T_{HM}, respectively. Both yielded a 2.5 % fission gas release. Three cladded segments have been prepared for leaching, microscopic characterisation and chemical inventory & burn-up measurements.

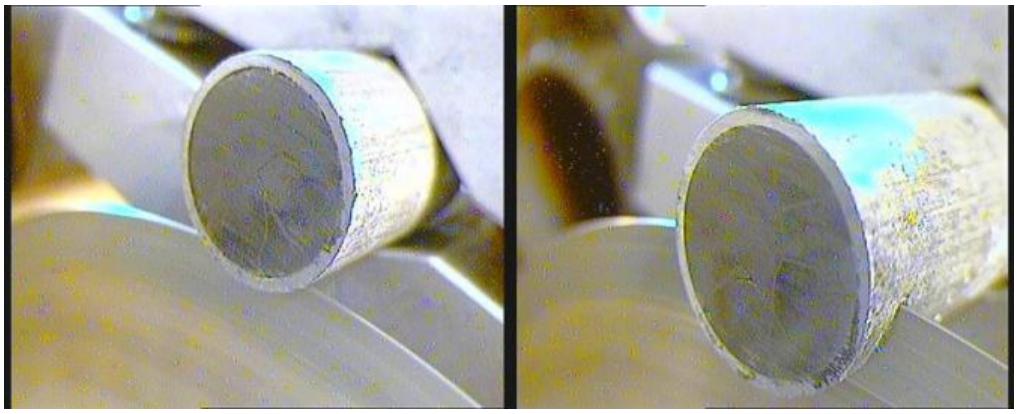


Figure 2.2.1: cutting of MOx pellets (a) MOx-H (b) MOx-L

Seven samples have been cut from a Cr-doped UOx fuel with an average burn-up of 58 GWd/T_{HM}. Two will be used to prepare de-cladded fragments for leaching, one for chemical inventory and burn-up and one for microscopic characterisation. Others will be held in reserve. The leaching autoclave has been extensively tested for H_2 tightness and confirmed at less than 0.3 bar per annum at a pressure of 50 bar. Optical and ceramography

characterisation for both MOx and Cr-UOx spent fuels is likely to be significantly delayed due to a failure in a hot cell where the equipment is housed. As it will exceed the deliverable (D2.1) deadline this will be addressed by a revised deadline for this characterisation to be reported in the updated WP2 deliverables report.

2.3 Spent fuel samples WP 2.1(c): Hot cell work at NNL

Fuel	Burn-up	Forms
UOx	21.2 GWd/T_{HM}	Solid pellet
UOx	7.3 GWd/T_{HM}	Hollow pellet

Twelve samples from intact fuel pins exposed to water in pond for >40 years have been cut. Two of these will be used in DisCo and the exposed surfaces will be subject to examination with state-of-the-art gamma scanning optical and scanning electron microscopy and Raman spectroscopy as part of a capability upgrade. The replacement of a shield window in the cave has delayed work thus far. This cave is now operating and the work is in progress. The results of the initial characterization will be presented in the update of this report. More detailed information resulting from the analyses performed at NNL will be documented in a separate deliverable (D2.2 Failed fuel report: Characterisation and secondary alteration products).

3 Characterisation in WP2.2: alpha glove boxes

3.1 WP 2.2(a): Alpha glovebox work at SCK-CEN/Jülich

Fuel	Doping (Laboratory)
UO_2	Reference (Jülich)
Cr-UO_2	Reference (Jülich)
UO_2	^{238}Pu (SCK-CEN)
Cr-UO_2	^{238}Pu (SCK-CEN)

Sample preparation techniques for the reference materials have been established at Jülich to optimise the production of alpha doped material. A method of wet-chemical synthesis was adopted to achieve a homogenous distribution of Cr. The principal scheme of the two developed routes is presented on the Fig 3.1.1.

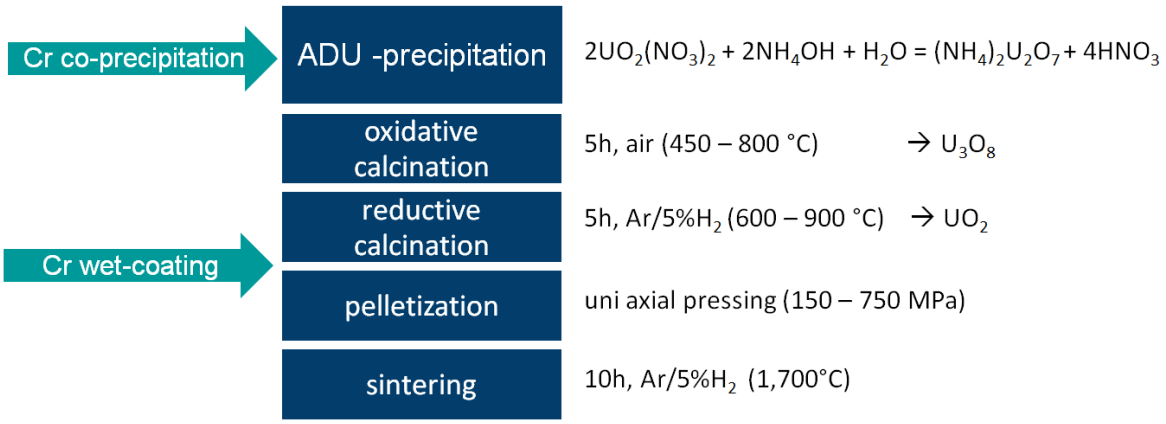


Figure 3.1.1. Principal scheme of wet chemical synthetic rout for pure and Cr-doped UO_2

As it can be seen from the Fig. 3.1.1, Cr can be added on different stages of the synthesis and this plays an important role in the pellets micro-structures (grain sizes) and the Cr distribution (in grains and on the grains boundaries). To avoid contamination in the production of Pu-doped pellets at SCK CEN, we adopted the method which minimises grinding or milling steps. In order to archive higher densities of the final pellets, the oxidative calcination (stage 2, Fig. 3.1.1) was made at 600°C. The porosity of U_3O_8 obtained at this temperature is higher than that for samples oxidised at 800°C and 900°C as it can be seen from Fig.3.1.2.

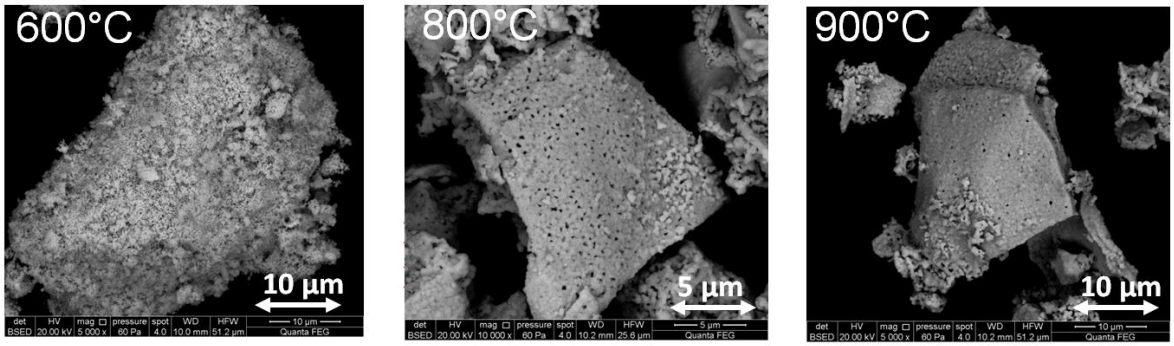


Fig.3.1.2. TEM images of U3O8 after oxidative sintering at different temperatures

The optimal density of the pelletized materials can be archived after reductive sintering at 600°C (step 3 on Fig. 3.1.1) and pressurizing above 250 MPa (Figure 3.1.3).

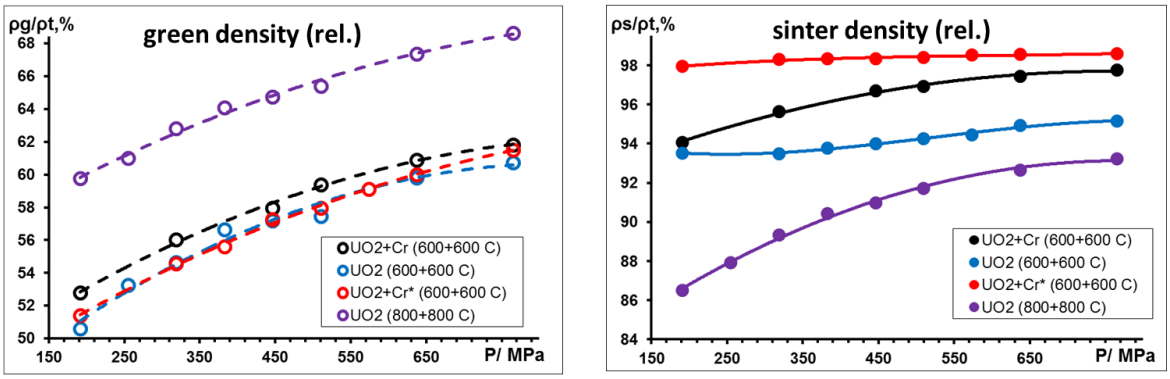


Figure 3.1.3. *Density of UO_2 pellets as a function of calcination temperature and pressure. The temperatures of stages 2 and 3 (Fig.3) are given in brackets for each experiment set.*

Cr-doping changes the microstructure of UO_2 pellets as it is shown in Fig. 3.1.4. The co-precipitation (adding of Cr at the first stage, Fig 3.1.1) has a minor influence on grain size and speculatively most of Cr is dissolved within the grains. The wet-coating method (Cr adding after stage 3, Fig. 3.1.1.) increase the density of the materials (Fig.3.1.3) and grain size (Fig. 3.1.4).

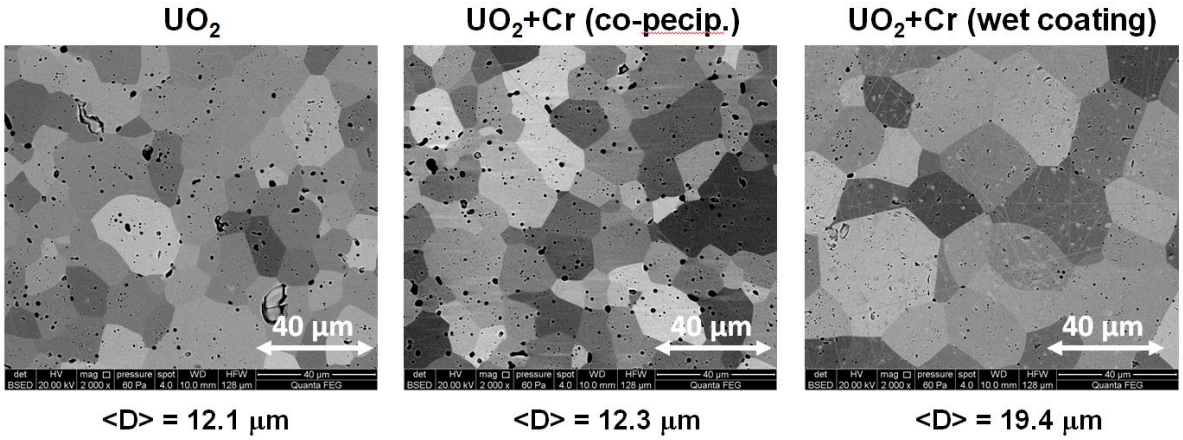


Figure 3.1.4 : Microstructure of pure and Cr-doped UO_2 pellets

Electron back scatter diffraction (EBSD) has been used to characterise the reference materials with focused ion beam (FIB) trenching of the measured area to allow post-dissolution examination of any differences in dissolution between different crystallite orientations. The sample preparation methods are ready to be transferred to SCK-CEN to produce alpha doped materials. When the alpha-doped samples are ready and characterized, they will be described in the update of this report.

3.2 WP 2.2(b): Alpha glovebox work at CEA Marcoule

Fuel	Description
24.1% U/PuO_2 MOx	unirradiated, homogeneous
7.3% U/PuO_2 MOx	unirradiated, inhomogeneous

Two materials existed for the experiment, but needed to be returned to t = 0 state of radiation damage and dissolution testing by thermal annealing and polishing. Pu, U and O maps were made of the materials before and after thermal annealing. These materials were also analysed for Pu, U and O content, which revealed measured Pu contents of 27 ± 0.5% Pu and a formula of $U_{0.73}Pu_{0.27}O_{1.990\pm0.004}$. This composition was also confirmed by the calibrated Raman shift of the principal mode of the fluorite structure. The α-activity of the pellet is 2.2 x 10^9 Bq/g, which is similar to a MOx fuel with a burn-up of 47.5 Gwd/THM that has been out of reactor since 1985 (22% ^{238}Pu of total Pu). The two (homogeneous and inhomogeneous) samples have been released for dissolution studies.

3.3 Alpha glovebox work at VTT

Samples doped with U-233 are already available at VTT, and these samples have been described elsewhere (*Dissolution Rate of Alpha-Doped UO_2 in Natural Groundwater* (2013) Ollila, K., E. Myllykyla, M. Tanhua-Tyrkko, and T. Lavonen, Journal of Nuclear Materials 442, 320-25.) Other alpha-doped samples used by VTT will come from the same batch of materials synthesized at SCK CEN, and these will be available and described in the update of this report (see above).

4 Characterisation in WP2.3: U/Th Laboratories

4.1 WP 2.3(a): U/Th lab work at USFD

Fuel	Dry synthesis method	Wet synthesis method I	Wet synthesis method II	HIP synthesis
UO_2	✓	✓	✓	×
UO_2 + Cr	✓	✓	✓	×
UO_2 + Al	✓	✓	×	×
UO_2 + Cr/Al	✓	✓	×	×

A series of reference materials of UO_2, UO_2 doped with between 150 to 5000 ppm of Al, Cr, and Al+Cr have been prepared by three different synthesis routes, including one dry synthesis and two wet synthesis methods. Wet synthesis methods were not planned in the original project scope, however dry synthesis methods were found to give inconsistent doping

concentrations. Samples have been characterised by electron probe microanalysis, helium pycnometry (to determine density), scanning electron microscopy (grain size analysis), energy dispersive spectroscopy, X-ray diffraction and Raman spectroscopy (stoichiometry and defect content). Additionally, U L_{III}-edge and Cr K-edge extended X-ray absorption fine structure spectroscopy, to determine the local oxidation state and coordination environment of the dopants, was performed at the National Synchrotron Light Source II and Diamond Light Source.

Figure 4.1.1a compares the microstructure of UO_2 prepared by wet synthesis route I, with of Al-doped UO_2 prepared by the same method. The UO_2 grains have an average size of 5.3 ± 0.2 µm (Fig. 4.1.1b). When 150 ppm of Al is added, the grain size increased to 8.3 ± 0.4 µm, however, above this dopant value, the grain size decreased. This is due to the precipitation of Al_2O_3 particles at the grain boundaries, as shown by the darker z-contrast phases in Figure 4.1.1a. These data are consistent with EDX measurements, which show that no Al was incorporated into the UO_2 lattice, and Rietveld-refined XRD data that showed no change in the UO_2 lattice as a function of Al-doping (Figure 4.1.1c). Similar data were obtained for Cr-doped UO_2, where a maximum grain size is observed at a dopant concentration of 300 ppm, however no Cr_2O_3 precipitates are observed; these samples will be analysed in September at the Swiss Light Source by µ-focus XAS methods to ascertain whether such precipitates are present. XRD analysis of Cr-doped materials showed a lattice contraction, consistent with the incorporation of Cr in the UO_2 lattice, with a solubility limit of between 300 and 600 ppm.

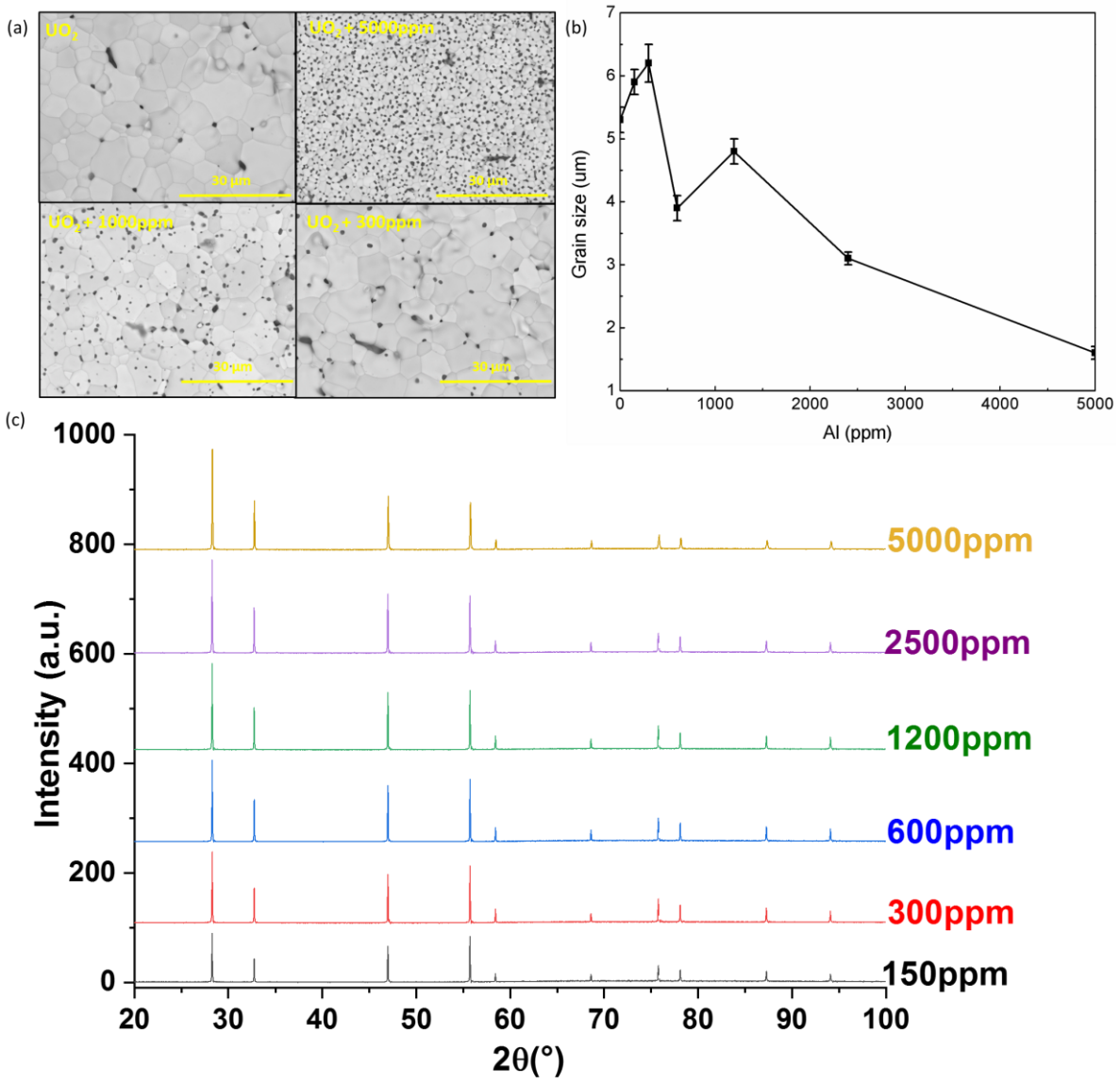


Figure 4.1.1 Analysis of Al-doped UO_2 prepared via wet synthesis route I, showing: (a) images of the UO_2 and Al-doped UO_2 microstructure as obtained by SEM; (b) average grain size as a function of Al dopant concentration, as analysed by image processing using Fiji software (minimum number of grains analysed was 500); and (c) X-ray diffraction patterns for Al-doped UO_2. Rietveld refinement of these data showed no influence of Al-doping on the lattice parameter of UO_2.

Further work will include finalising the synthesis matrix by performing further wet synthesis using method II (with Al and Al+Cr), and selecting several samples for synthesis by Hot Isostatic Pressing (HIP) to produce high density materials. The materials will be described in the update of this report.

4.2 WP 2.3(b): U/Th lab work at CIEMAT

Dry route preparation of the four model samples has been completed at CIEMAT. The selected compositions of additives are listed in Table 4.2.1 Additionally, Cr-doped UO_2 samples were also prepared with the same % of dopant that Al-doped UO_2 discs.

Table 4.2.1 UO_2-based fuel compositions selected for investigations at CIEMAT.

Fuel	Description
UO_2	Dry route, pressed pellet
UO_2+Al_2O_3	0.02 wt%, 0.06 wt% Dry route, pressed pellet
UO_2-Cr_2O_3-Al_2O_3	0.05 wt% - 0.02 wt% Dry route pressed pellet
UO_2-Gd_2O_3	4.5 wt% Dry route pressed pellet

The starting oxide powders (Al_2O_3, Cr_2O_3, Gd_2O_3) were commercially available (Alfa-Aesar). Natural UO_2 was provided by ENUSA. Prior to manufacture of the disks, all the raw material were previously characterized (Table 4.2.2) and/or thermally treated if needed, particularly Al_2O_3, in air at 1100 ºC to get nano α-Al_2O_3 and UO_2 in 4.7%H_2-N_2 atmosphere at 1100ºC to attain stoichiometric $UO_{2.0}$.

Table 4.2.2 Raw material characterization

Property	Powder UO_2	Powder α-Al_2O_3	Powder Cr_2O_3	Powder Gd_2O_3
Lattice parameter (nm)	a = 0.546920(4)	a = 0.7944(6) b = 0.7980(4) c = 1.1722(6)	a = b = 0.49586(7) c = 1.3592(2)	a = 1.08141(4)
SSA (BET) (m^2 g^{-1})	0.95 ± 0.01	37.6 ± 0.1	3.47 ± 0.02	14.6 ± 0.01
Density / g·cm-3	10.97 (TD)	3.95	5.22	7.41
D(v, 0.5) / μm	19.6	23.5	2.09	11.8

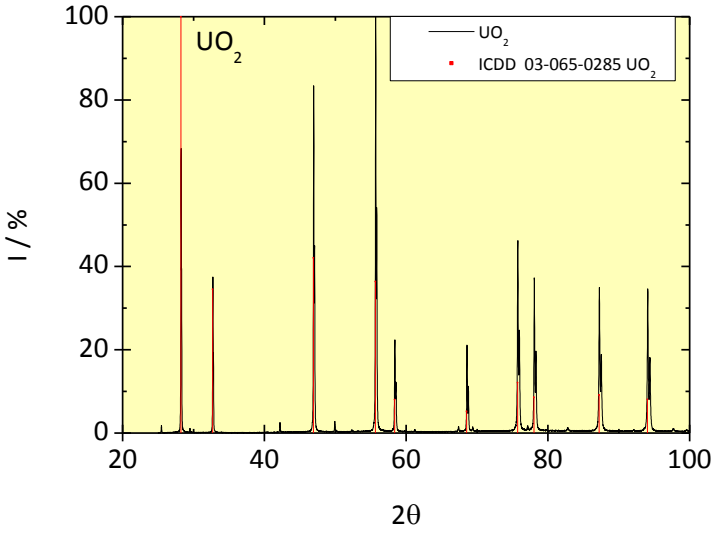
The sintered pellet densities have increased from ~ 80% for UO_2 to ~90% of theoretical densities for pellets containing additives. X-ray diffraction and Archimedes density measurements have been made on pellets. Samples have also been characterised by Raman spectroscopy in anticipation of post dissolution surface analysis. The most significant outcomes obtained are found in Table 4.2.3. The grain structures were examined by SEM and grain sizes were calculated by the linear intercept method. The highest density is obtained in the sample with the greatest amount of Cr_2O_3.

Table 4.2.3 Measurements obtained from the analysis of the doped UO_2 samples.

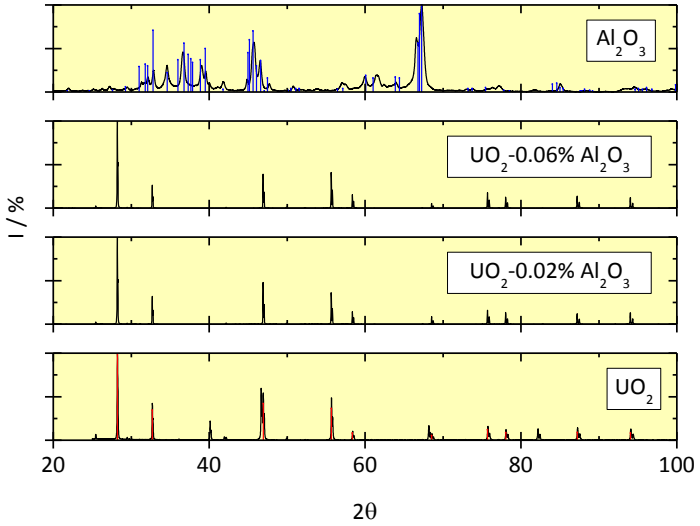
Sample / %wt	**Lattice parameter / nm**	**SSA (BET) / $m^2 \cdot g^{-1}$**	**Density / $g \cdot cm^{-3}$**
UO_2	0.547174 (6)	0.36 ± 0.01	8.93 ± 0.07
UO_2-0.02 Al_2O_3	0.547123 (8)	0.36 ± 0.01	9.85 ± 0.14
UO_2-0.06 Al_2O_3	0.547108 (7)	0.33 ± 0.01	9.96 ± 0.17
UO_2-0.02 Cr_2O_3	0.547108 (7)	0.28 ± 0.01	9.80 ± 0.12
UO_2-0.06 Cr_2O_3	0.547113 (7)	0.63 ± 0.02	9.83 ± 0.07
UO_2-4.5 Gd_2O_3		0.63 ± 0.01	9.81 ± 0.11
UO_2-0.05 Cr_2O_3 – 0.02 Al_2O_3	0.547198 (5)	0.25 ± 0.01	9.80 ± 0.43

Each sample's average grain size increased compared with pure UO_2, excluding Gd_2O_3 doped samples, which remained unchanged. Addition of higher contents of Cr_2O_3 boosted the grain size of Cr-doped UO_2 samples. On the whole, no precipitates were identified in any sample by XRD (see Figure 1a to Figure 1e) and Raman Spectroscopy, in the sense that dopants are well solubilized into UO_2 grains confirmed by SEM-EDS which showed a homogeneous distribution of dopants, especially those in solid solution of U mixed oxides containing Cr and Cr-Al samples. Uniquely for Gd-doped UO_2 samples, more than three types of Gd solid solutions in urania lattice with different Gd content have been observed (Figure 4.2.1e).

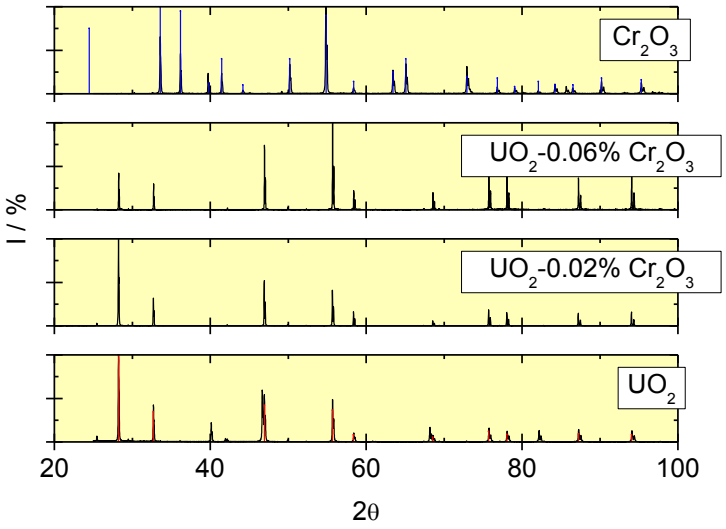
New doped UO_2 discs with the same additives are in progress to improve physical properties. The description of these new discs will be found in the update of this report.


UO2
UO2
ICDD 03-065-0285 UO2
I / %
2θ

a)


Al2O3
UO2-0.06% Al2O3
UO2-0.02% Al2O3
UO2
I / %
2θ

b)


Cr2O3
UO2-0.06% Cr2O3
UO2-0.02% Cr2O3
UO2
I / %
2θ

c)

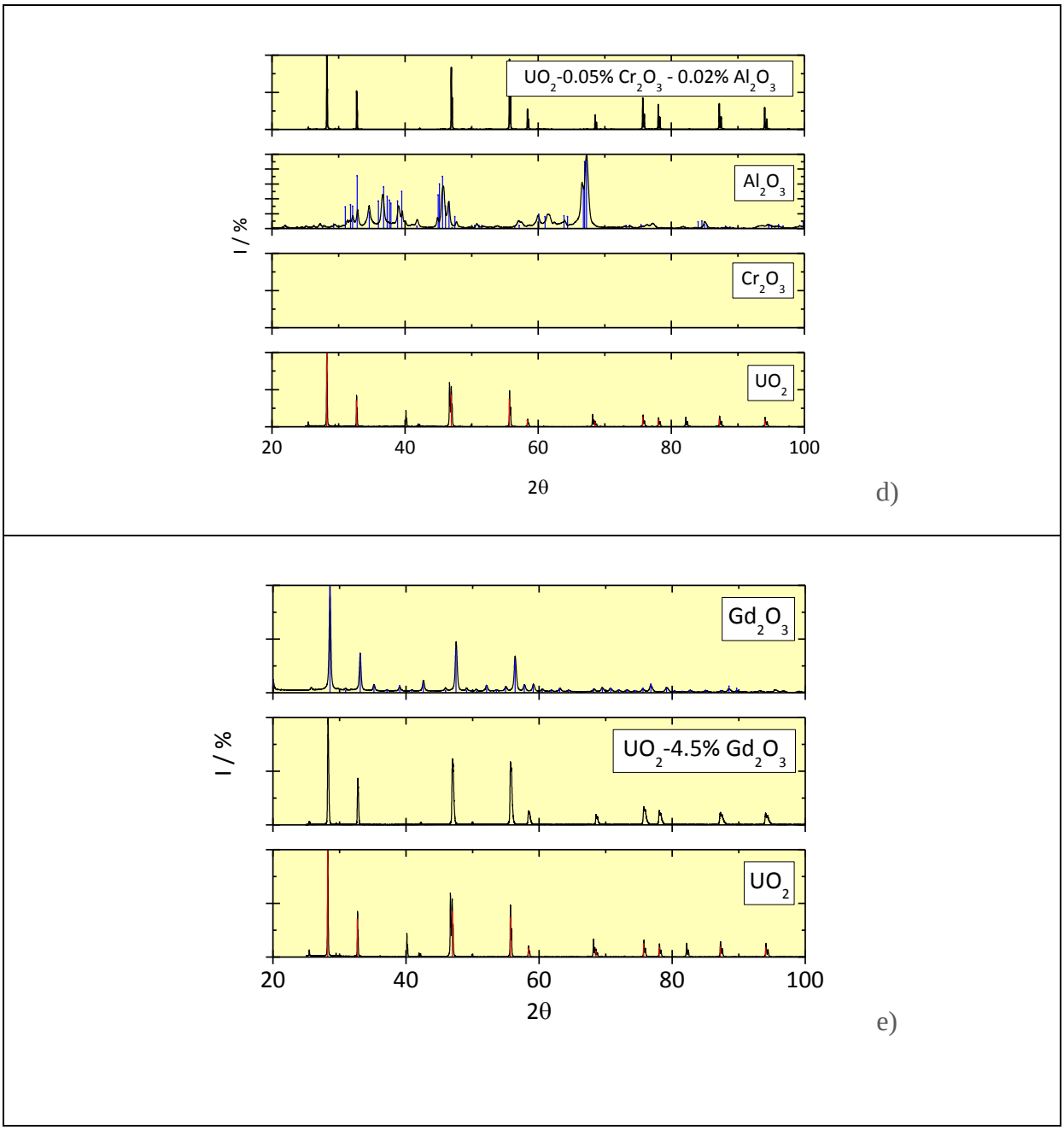


Figure 4.2.1 X-ray diffractograms of a) natural UO_2; b) UO_2- xAl_2O_3; x = 0.02 & 0.06 wt%; c) UO_2-xCr_2O_3; x = 0.02 & 0.06 wt; d) UO_2-0.05 wt%Cr_2O_3-0.02 wt% Al_2O_3 and, e) UO_2-4.5 wt% Gd_2O_3 disc fabricated at CIEMAT.

4.3 WP 2.3(c): U/Th lab work at UCAM

Fuel	Description
U/Th MOx 75:25	Wet route, pressed pellet (homogeneous)
U/Th MOx 90:10	Dry route, pressed pellet (inhomogeneous)

Work on project began in March. For the homogeneous $U_{0.75}Th_{0.25}O_2$, uranyl and thorium nitrate solutions have been used as starting materials. The uranyl nitrate solution has been reduced by purging with 5% H_2/Ar gas in the presence of a platinum catalyst. Stoichiometric volumes of the nitrates were mixed and then oxalic acid was added to the mixture to precipitate a U/Th mixed oxalate. The oxalate was decomposed at 570˚C and then the powder was pressed into pellets. These 'green' pellets will shortly be sintered at 1700˚C in controlled atmosphere of Ar/5%H_2 gas to obtain a dense material. This material will be characterised and used to prepare the two dry-milled (inhomogeneous) samples. Some samples of thin (100 nm) films of U/Th/Ce oxides are also being sourced to support the project.

When the U/Th samples are available, these will be characterized and described in the update of this report.