Introduction

TRANSCEND

Magnox nuclear reactors, using metallic uranium as fuel operated in the UK from the 1960's until just a few years ago. The metallic fuel was encased in a Magnesium alloy 'Magnox' cladding, which along with the U metal, is susceptible to corrosion by water. Until 1992, a significant volume of Magnox waste materials, including spent fuel assemblies, had been accumulated in the storage ponds at Sellafield in Cumbria [1]. These ponds were maintained at a high pH (above 10.5) to minimise corrosion [2]. However, considerable corrosion has still occurred over extended periods, raising concerns about the safe decommissioning of the facilities [3]. Corroded Magnox Sludge (CMS) arising from long-term corrosion of the cladding material is a prevalent residual material amongst others (e.g. fuel fragments and wind-blown debris) [4]. Corrosion of Magnox forms brucite (Mg(OH)₂) and liberates hydrogen. Embedded uranium metal fuel is also expected to have been exposed to water throughout the storage period. Uranium reacts with water to form uranium hydride (UH₃), uranium dioxide (UO₂) and hydrogen, presenting potential uncontrolled thermal hazards during decommissioning.

Flange U rod Sludge

Feasibility trials on uranium corrosion in sludges using in situ X-ray Computed Tomography Haris Paraskevoulakos, Tom Scott HH Wills Physics Laboratory, Bristol, BS8 1TL

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Figure 1: Experimental Analogue



Experimental Approach

A miniature analogue of storage pond conditions was experimentally replicated to investigate the behaviour of uranium while embedded in CMS (**Figure 1**). Powderised CMS–simulant was diluted in water to produce a thick slurry, resembling pond conditions. The sludge was poured into a cylindrical stainless steel cell. A single uranium specimen (1 mm x 1 mm x 20 mm) was then encapsulated in the CMS and the system was allowed to dry in air for 3 days before being sealed. At distinct time intervals, X-Ray Computed Tomography (XCT) was used to probe the evolving interior state of the sample and investigate the corrosion behaviour. Primary results are shown in **figure 2**. It can be observed that there is a notable change in the morphology around the

embedded uranium specimen, attributed to progressive corrosion. The morphology of the developing corrosion layer at the uranium–CMS interface suggests the formation of UH_3 based on a morphology very similar to experiments performed in uranium–grout systems [5]. The progress of uranium corrosion can also be observed in **figure 3** where the residual metal has been segmented from the rest of the materials.

Figure 2: XCT scans exhibiting uranium corrosion evolution within a CMS environment. The "age" of the sample at each different scan is shown in green letters.

Summary–Future Plans

Feasibility trials have proven that XCT is a powerful non destructive method for investigating complex corrosion systems. Corrosion of the uranium, based on morphology change, has been observed to progress over more than a year since sample preparation. Using relevant software, a quantification of the corrosion percentage over time is now possible. Confirming the phase of the corrosion product (UH₃ versus UO₂) is now of **significant importance** for the project. Synchrotron X-ray Diffraction may provide a method to characterise the interacting materials without breaking the sealed containment. Thus, potential formation and persistence of the pyrophoric UH₃ could be validated.



20 days





50 days



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Figure 3: 3D views of the uranium specimen. Threshold segmentation allowed separation of the non–corroded metal.







The Safe Disposal of Advanced Nuclear Fuels

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Project Background

The UK government has proposed a preliminary policy to re-use the UK's stockpile of plutonium as Mixed Oxide (MOX) fuel formed of a blend of plutonium oxide and uranium oxide. This would see the vast majority of UK's 138 tonnes of plutonium converted into fuel for use in new UK nuclear reactors.

In line with current government policy, this used MOX would not be reprocessed; rather, it would be sent to disposal within a geologic disposal facility (GDF)(See Figure 1). This spent MOX fuel is assumed to be a stable wasteform with reactivity largely comparable to more established and well-studied uranium oxide (UOX) spent fuels. As such spent MOX is expected to display high chemical stability when contacted by groundwater in a geologic disposal facility, with fuel dissolution and thus radionuclide release rates to the environment being very low. However, these assumptions need validating.

In order to do this, MOX simulant pellets will be produced from UO₂, CeO₂ (as a non-radioactive surrogate for plutonium) and fission product surrogates in the first instance. The dissolution behaviour of these pellets will then be investigated through a mixture of electrochemically accelerated corrosion studies and bulk pellet dissolution experiments under GDF-relevant solution conditions.



Figure 1. Artists impression of a GDF [1]

Raman and SEM of CeO₂ Pellets

A precursor CeO_2 powder, with no additives, (Particle size <5µm) was loaded into a pellet die of 13mm diameter and pressed with a pressure of 8 tons with a hydraulic press. After being removed from the die and placed in a crucible it was heated, at a heating rate of 5°C/min to 1100°C and held there for 12 hours and allowed to cool. The resultant pellet was analysed using SEM, the resultant image being shown in Fig. 2. As can be seen from this image, only limited sintering of the powder into agglomerates had occurred and this was reflected by the fragile nature of pellet.

Fig. 4 depicts the full Raman Spectrum recorded from the surface of the pellet. It is dominated by a high intensity band at 464 cm⁻¹ which is characteristic of the vibrational mode (F_{2a}) of the cubic fluorite lattice of CeO_2 . The sharpness of this band indicates that this sample is highly crystalline.

Fig. 5 depicts the details of the lower intensity features of the spectrum with a band appearing at 1170 cm⁻¹. This can be assigned to one of two second order bands which originate from the mixing of A_{1q} , E_q and F_{2q} CeO₂ modes with a third band reported at 592 cm⁻¹; however in this Raman Spectrum, the band at 592 cm⁻¹ is difficult to resolve due to the intensity of the 464 cm^{-1} band. [2]





LU Engineering

Figure 2. SEM of slightly sintered CeO₂ pellet surface

Raman Spectra





BES 10kV WD10mmSS50 x200 100µm LU Engineering

Figure 3. SEM of fully sintered CeO₂ pellet surface





Raman Shift (cm⁻¹)

Figure 4. (Above). CeO₂ Raman Spectra

Figure 6. (Left). CV of CeO₂ pellet in 0.1 M NaCl pH 9.5 solution sparged with air for 1 hour. Scan Rate 0.01 V/s , IR Compensation 2.0 kΩ (Max)

Raman Spectra Raman Spectra 400 (j. 30000 ने 350 छ 25000 Ē 300 Intensity sity 250 20000 200 15000 150 10000 Raman 100 Rama 5000 50 2000 3000 4000 1000 0 200 400800 0 Raman Shift (cm⁻¹) Raman Shift (cm⁻¹) Figure 7. Raman Spectra of CeO₂ pellet doped with Figure 8. Eu₂O₃ doped CeO₂ pellet Raman Spectra for

1200

4000 50025003500 200030001000

Raman Shift (cm⁻¹)

Figure 5. CeO₂ Raman Spectra for lower intensity features

Electrochemistry of CeO₂ Pellets and Raman of Eu₂O₃ Doped Pellet

IR compensation provided a value of 194.8 k Ω which is more than 100 times greater than the 1.567 k Ω for a UO₂ electrode. This combined with Fig. 6 demonstrates that a bulk CeO₂ pellet has too high a resistance to pass a current through in a simple groundwater analogue.

A CeO₂ pellet doped with 10 wt.% Eu_2O_3 , to decrease resistance, has been produced. Fig. 8 shows the lower band of the standard Eu_2O_3 doped CeO_2 pellet Raman spectra which demonstrates some features of interest:

- 1) What may be a very weak signal at 600 cm⁻¹ which has been attributed to the presence of intrinsic oxygen vacancies which occurs due to the presence of Ce^{3+} ions in the material. This however is very difficult to confirm due to its appearance as a dip between the two directly adjacent peaks with the bottom point occurring high enough that it may not just be due to noise.
- 2) The peaks observed between 525 and 540 cm⁻¹ which is assigned to extrinsic oxygen vacancies the formation of which can be explained as the vacancy compensation mechanism where one oxygen vacancy is created to balance the charge when Eu^{3+} substitutes Ce^{4+} . [3]

3) The CeO₂ F_{2a} band occurring at 466 cm⁻¹ (Figure 7).

Future Work

 Eu_2O_3

In the near future it is planned for the fabrication of fission product doped CeO₂ pellets will commence to begin investigating the influence on the inclusions of dopants on the Structure and Corrosion properties of the pellet.

Voltammetry studies of Eu_2O_3 doped CeO₂ pellet in solution in order to examine the effect of the doping on electrochemical properties.

low intensity features.

A UO₂ electrode will be coupled with a (doped) CeO₂ Electrode in order to carry out a range of electrochemical experiments for an introductory study of the behaviour of MOX in groundwater.

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Drying Advanced Gas Reactor Fuel

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Background

- Fuel currently stored in ponds.
- 25 years experience with this storage.
- Geological Disposal Facility (GDF) not expected till 2075.
- Need alternative in case long term wet storage becomes unviable.

Experimental Plan

- DET used to crack stressed stainless steel strips.
- Process will be carried out as shown in figure 1.
- After samples undergone DET CT scans will be used to obtain an image of the crack network.

Process Model

Currently assuming a constant volume and an idealised crack with constant width (see figure 3). This will be changed as the model is developed [1].

$$0 = \frac{2u}{\rho} \left[\frac{12 \cdot \mu \cdot l_{eff}}{d_{eff}^2} \right] - \Delta P \tag{1}$$



UNIVERSITY OF LEEDS

- All fuel will need to be dried before disposal.
- Especially failed fuel to prevent corrosion of the cladding.

Drop Evaporation Test (DET)

- Sample is placed under stress.
- Heated to 120°C.
- One drop of solution dripped every 10 seconds.
- Each drop evaporates causing an

- DET will be carried out on cylindrical sections of stainless steel.
- These samples will be subjected to first, fluid permeability tests.
- The drying rig shown in figure 3 will be used to test cracked samples.
- Here the samples can be loaded with water to be evacuated.





increase in the chloride concentration.

 Chloride used to induce cracking in stressed material.



flow.

Cracks found in the cladding are not expected to exceed this.

Future Process Model Work

- Adapt the initial code to cope with the water level and therefore volume changing.
- Use CT scan data to provide crack dimensions.
- Develop code to take the dimensions and split the crack into multiple regimes.
- Calculate each section's flow rate to

determine the overall flow rate.

• Validate against experimental work.

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Relationship between Chromium Depletion and Grain Boundary Plane Orientation in Thermally Sensitised 304 Stainless Steel

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Introduction

- Spent AGR (advanced gas-cooled reactor) fuel cladding in cooling ponds can be susceptible to stress corrosion cracking (SCC)
- The overall aim of this PhD research is to develop micromechanical testing methods to examine SCC by using thermally sensitised analogues, i.e. 304 stainless steels
- In this poster we present a means for characterising SCC resistant grain boundaries
- One of the main factors affecting thermal sensitisation is the character of grain boundaries.

Grain Boundary Misorientation

Proposed Method

- A 304 stainless steel sample has been thermally sensitised by aging at 600 °C for 50 hours.
- An EBSD (electron backscatter diffraction) scan will be taken and analysed
- An area of interest with special grain boundaries will be selected from the EBSD map (Fig. 4).
- Several grain boundaries with severe



The misorientation of grain boundaries was considered one of the most important factors for thermal sensitisation [1]:

- Low angle grain boundaries (LAGBs) are considered < 15° and high angle grain boundaries (HAGBs) considered >15°
- Among HAGBs, some boundaries have special CSL (coincidence site lattice) numbers such as Σ3, Σ9, Σ27 or Σ≤29
- LAGBs and HAGBs with special CSL numbers are more resistant to sensitisation and SCC
- These boundaries also act as bridges for cracks during SCC propagation

Grain boundary engineering (GBE) method was developed based on this theory to increase the resistance to sensitisation and SCC by heat treatment to increase the proportion of special grain boundaries.



chromium carbide precipitation will be selected and scanned using TEM (transmission electron microscopy) to find the exact chromium depletion profile (Fig.5).

Fig. 4 EBSD of a thermally sensitised 304 stainless steel with CSLΣ3 boundaries shown in yellow



Fig. 5 TEM line scans scanning on a thermally sensitised 20/25/Nb stainless steel sample: (A) location of the scans; (B) composition profile [3]

 Finally, the boundaries with Cr concentration lower than 12% are selected to be FIB (focused ion beam) milled.



Fig. 1 Correlation between observations in the microstructure of 304 stainless steel: (a) optical image of an intergranular crack, (b) the EBSD map of the same area of microstructure, (c) the strain map obtained after 16 h, (d) strain map after 24 h. In (b), (c) and (d), the Σ3 boundaries are represented in red lines, Σ9 and Σ27 boundaries are green lines, low-angle grain boundaries (Σ1) are white lines and random boundaries are black lines [1]

Grain Boundary Plane Orientation

As Fig. 1 shows however, even special grain boundaries fail, so other factors may also play a part in this hypothesis.



Fig. 2 3D DCT grain map of a section from a wire sample: (A) crystallographic orientation of grains; (B) Low Σ CSL grain boundaries are shown in colour: LAGBs, orange; Σ 3, red; Σ 9, blue; other boundaries $\Sigma \leq 29$, purple [2]

A wire sample was examined using DCT (diffraction contrast tomography), and it was found that not these special boundaries that are resistant to sensitisation but grain boundaries located near to low {hkl} Miller Index planes [2].

- A trench is milled across the boundary and near the TEM scans.
- The plane of grain boundary then can be measured

Conclusions

Fig. 6 FIB trench milling across a grain boundary [4]

We are currently in the process of analysing EBSD data. With other experiments to be conducted later. TEM will be conducted by a technician from another department at the University of Bristol. FIB milling is proposed to take place at the Henry Royce Institute with plasma FIB.

The outcome of this research will give a better understanding of sensitisation and SCC for further experiments and modelling.

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 Fig. 3 Pole figures showing the frequency distribution of grain boundary planes in the sample; {hkl} poles are marked up to {221}. (A) All boundaries, (B) all boundaries excluding Σ3, and (C) boundaries forming the fracture surface [2]

Current research is inspired by this to develop a new method

^{1.4} verify this theory









Elucidating the Dehydration Mechanism of Studtite by **Time-Resolved Laser Fluorescence and Raman Spectroscopy**

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Introduction

Determining the provenance and history of radioactive materials is a key aim for the field of nuclear forensics to ensure safety and to inform decisions on future treatment and disposal options. It is possible that this can be achieved through the characterisation of each species' material properties using a range of complementary analytical techniques. One class of relevant materials is the uranyl peroxides, including the two naturally occurring minerals, studtite $(UO_2O_2(H_2O)_2 \cdot 2(H_2O))$ and metastudtite $(UO_2O_2(H_2O)_2)$. Great interest has been shown in these two minerals as they are predicted to form as alteration products on spent nuclear fuel (SNF). The thermal decomposition of studtite in air was explored using timeresolved laser fluorescence (TRLFS) and Raman spectroscopy. The results are being used to validate the mechanism and kinetics of studtite dehydration.

Samples and Characterisation Techniques

Studtite was formed by mixing uranyl nitrate solution with hydrogen peroxide at room temperature, filtering the product and leaving it to dry in air for 48 hours. Small amounts (< 0.1 g) were heated in a N₂ atmosphere at 10 K min⁻¹ to 100, 150, 250, 350, 450, 500, 535 and 550°C. This temperature range covers the dehydration of studtite into first, meta-studtite by 100°C, into an amorphous phase, between 150 to 250 °C, and finally transformation into α -uranium trioxide (500 - 535°C)¹. Two phases were identified in the 535°C sample which were separated and characterised separately. The crystal structures of metastudtite and α -uranium trioxide ^{2,3} are shown in Figure 1.

Raman Characterisation

Figure 2 displays Raman spectra for each sample. Two sharp peaks were observed during the initial dehydration from studtite (30°C) to metastudtite (100 and 150°C). These are characteristic of the symmetric stretch of the peroxide anion, $v_1(O-O)$, and the uranyl ion, $v_1(UO_2)^{2+}$. The $v_1(O-O)$ peak remains at roughly the same position (865 – 869 cm⁻¹) whereas the single $v_1(UO_2)^{2+}$ peak at 820 cm⁻¹ is gradually replaced by another at 832 cm⁻¹. Other features were detected for the studtite and metastudtite samples but these were all relatively weak in intensity. Overall, the studtite and metastudtite Raman spectra are in good agreement with those published in the 550 °C literature ^{1,2,5}.



Figure 1: Schematic crystal structure images of metastudtite (left) and α-uranium trioxide (right) using the visualisation software VESTA 3⁴.

Raman spectra were obtained using a 785 nm laser to detect the vibrational, rotational and other low frequency modes in each sample. The fluorescence excitation and emission behaviour was explored using TRLFS.

Further dehydration significant change the The $v_1(O-O)$ peak Raman spectrum. disappears whereas the $v_1(UO_2)^{2+}$ feature becomes significantly broader and shifts slightly to higher wavenumbers. Other broader peaks become detectable between 750 – 700 cm⁻¹. These changes in the spectra (four brown lines in Figure 2) suggests the amorphous phase evolves continuously over this temperature range.

The Raman spectra alter again between 500 to 535°C indicating decomposition into αuranium trioxide¹. The intensity of the $v_1(UO_2)^{2+}$ mode (now ~ 850 cm⁻¹) reduces to around the apparatus detection limit. Negligible differences were observed between hexagonal and orthorhombic α uranium trioxide phases or with the 550 °C sample.



Figure 2: Raman spectra for studtite (red line), meta-

Fluorescence Spectroscopy

Common features were observed across the whole temperature range in the excitation and emission spectra. These features were at 375, 394, 415, 432 and 442 nm for the excitation spectra (Figure 3, left) and 483, 490 – 510 and 555 nm (Figure 3, right). The most noticeable difference was the fluorescence signal intensity which gradually decreased with increasing temperature but it difficult to accurately distinguish between studtite, metastudtite, the amorphous phase or α -uranium trioxide. For all samples, the fluorescence signal was too weak to for fluorescence decay experiments.



studtite (blue), an amorphous phase (brown) and α -uranium trioxide (magenta).

Conclusions and Future Work

Studtite's thermal decomposition products were characterised by fluorescence and Raman spectroscopy. Significant differences were observed in the Raman spectra between studtite, metastudtite, the amorphous phase and α -uranium trioxide enabling each to be distinguished from the others. Negligible differences were observed in the fluorescence excitation and emission spectra.

A decomposition mechanism is proposed findings combined based on our with published thermogravimetry analysis ^{1,6}, that performed at the University of Sheffield and the known crystal structures ^{2,3} (Figure 4). It suggests the amorphous phase region reflects multiple bonds breaking before the uranium together. the fuse layers In future, computational techniques will be used to verify this hypothesis. Overall, the results suggest that Raman spectroscopy could be a



In the higher temperature region, the amorphous phase starts fusing together along all plane directions (including in and out of the page).

By 535 °C, α-uranium

trioxide is formed.



amorphous phase. As the temperature increases the bonded water, peroxide and some axial U-O bonds break.

By 100 °C, metastudite is

Above 50 °C, studtite starts to dehydrated.

Figure 3: Fluorescence excitation (left) and emission spectra (right) of studtite (30 °C, red) and heated studtite samples (see key, top left) where λ_{ex} and λ_{em} were held between 506.7 to 510.3 nm and 375.6 nm, respectively.

very useful characterisation technique for distinguishing these uranium oxide species.

Figure 4: Proposed studtite decomposition mechanism into α -uranium trioxide.

Studtite.

Acknowledgements

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Transformative Science and Engineering for Nuclear Decommissioning



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Predicting the Alteration of Spent Nuclear Fuels

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Introduction

Ensuring safe surface storage and deep geological disposal of spent nuclear fuel (SNF) over short and long timescales, respectively, is difficult. There is significant uncertainty around the mobilisation of uranium ¹. The alteration products of both metallic and oxide fuel are expected to be similar to naturally occurring uranium minerals, of which more than 250 are known to exist ². Understanding the alteration mechanisms of SNF is key to providing solutions for safe storage and disposal. This work aims to predict the alteration mechanisms and products of SNF. This involves experimental characterisation and computational modelling of SNF analogues and potential alteration products. A complication for metallic SNF from the UK is the alteration products from legacy Magnox SNF coatings, such as brucite (Mg(OH)₂), where it is possible for spectral and chemical interferences ³. This work begins with the evaluation of possible spectral interferences from brucite and continues with experimentation and computational modelling of the alteration mechanism for uranium dioxide fuel.

Experimental methodology

High quality natural samples were loaned from the British Geological Survey and University of Surrey collections, with manufactured samples from the University of Sheffield (Figure 1). Chemical composition was confirmed with scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX). Raman spectra were collected with four lasers (457, 532, 633 and 785 nm). Fluorescence excitation and emission spectra were obtained using the TRLFS apparatus below with a Xe lamp light source (Figure 1).



Computational methodology

Computational modelling of brucite (Figure 2) was performed using Density Functional Theory (DFT), specifically the Perdew–Burke-Ernzerhof (PBE) functional. CASTEP 19.11 was used for the modelling of brucite $(Mg(OH)_2^{4,5})$.



Figure 1: Photos of the Raman spectroscopy (left) and TRLFS apparatus (right). The samples are (from far right, top to bottom) uranium trioxide (UO₃), metastudtite (UO₄·2(H₂O)), becquerelite (Ca(UO₂)₆O₄(OH)₆·8(H₂O) and brucite (Mg(OH)₂).

Figure 2: Crystal structure of brucite.

The electronic structure (band structure), Raman and Infra-red (ID) spectra were computed ⁴. The Raman and IR modes were then compared with experimental data collected in this study.

A semi-core Mg norm conserving pseudopotential was used, with a cut-off energy of 1500 eV with 5x5x5 Monkhorst-Pack grid size

Computational results

The Raman and IR spectra for brucite were modelled with density functional perturbation theory and compared with experimental results from this study (Figure 4). For all known shifts, both experimental and computational spectra were found to agree within 3 % error.

Additional peaks observed in the experimental region, such as the weak Raman feature at 340 cm⁻¹ were found to be surface Raman features through computational modelling of



the brucite surface.

Figure 4: Raman (left) and IR (right) spectra simulations of brucite from DFT model with comparisons to experimental results from this study. Baseline offset for clarity.

Raman spectroscopy results

The most well-defined features were found with the 785 nm laser wavelength. The uranyl symmetric stretch mode, $V_1(UO_2)^{2+}$, is typically located between 900 700 cm⁻¹ and 3) highly (Figure and is sensitive its surrounding to environment resulting in the peak position shift ⁶. From this mode, the U-O bond length, force constant and the position the uranyl asymmetric Of bending mode, $V_3(UO_2)^{2+}$, were predicted ⁷⁻⁹.



Figure 3: Raman spectra of three UOH's (left) with literature comparisons highlighted (key bottom right). Illustration of three active Raman modes (top right).

References

Uranium dioxide (UO₂) and future work

Uranium dioxide used in Advanced Gas-cooled Reactor (AGR) and Pressurised Water Reactor (PWR) fuel, in the form of compressed ceramic pellets, makes up 2,730 tHM of the UK's currently stored SNF inventory ¹⁰. Adding to this fuel currently used to generate energy within reactors and the predicted future fuel usage, the inventory is expected to grow to 6,550 tHM ¹⁰.

The alteration mechanism of uranium dioxide will be explored both experimentally by a selection of techniques including Raman and TRLFS, and computationally by DFT and TD-DFT. Experimental work will begin on natural UO_2 samples and synthetic analogues. The experimental and simulated work will then be validated by performing select experiments on real samples of SNF.



Acknowledgements

The authors would like to thank Kay Green at the British Geological Survey and Nathan Thompson from the University of Sheffield for the loan of samples. We are grateful to John-William Brown, Sarah Heisig, Antoni Milodowski and Dr Carol Crean from the University of Surrey for their support in this study.



Disce Doce

The University

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Figure 5: Cubic fluorite crystal structure of uranium dioxide.

Transformative Science and Engineering for Nuclear Decommissioning



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In situ HT-ESEM and XRD studies of UO2 oxidation and phase transition into U3O8 Jacek Wąsik1,2*, Renaud Podor3, Ross Springell2 1 - Bristol Centre for Functional Nanomaterials, University of Bristol, Bristol BS8 1FD, UK 2 - School of Physics, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK 3 - ICSM, University of Montpellier, Site de Marcoule, Bât. 426, BP 17171, FR

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Thin films

The University of Bristol hosts one of the world's only physical vapour deposition systems that is dedicated to the synthesis of nuclear-related materials. The possibility of growing samples with Angstrom precision significantly reduces levels of radioactivity. This makes samples safe to work with and to transport within and outside the university. Another advantage offered by this system is the capability to grow metal, oxide and doped films, specifying the stoichiometry, crystal structure and crystallite size.



 $UO_2 (001) / YSZ (001)$ $UO_2 (110) / YSZ (110)$ $UO_2 (111) / YSZ (111)$

Difference in crystallinity across uranium dioxide fuel, due to high temperatures and radiation fields, can be mimicked by modifying polycrystalline YSZ substrate prior to deposition of thin films.

Before the oxidation experiment, an area of 200x200 μ m on the sample was marked (crosses) using Dual-beam microscope (FEI Helios NanoLab 600i Dualbeam), and EBSD mapping was conducted.



Figure 3. SEM image of the sample with visible grains before the in-situ oxidation



Figure 4. EBSD inverse pole figure map of the polycrystalline uranium thin film sample.



Figure1.DCmagnetronsputtering setup at the IAC, UoB.

Figure 2 Schematic representation of the epitaxial matches of the three principle UO_2 orientations (100), (110) and (111) with (100), (110) and (111) oriented YSZ substrates. The lattice mismatch is the same in each case at 6.3%. (S. Rennie PhD Thesis)



In-situ XRD and HT-ESEM oxidation

In-situ oxidation of a 160 nm thick UO_2 polycrystalline thin film was conducted in HTK 1200 chamber inside a Philips Xpert pro diffractometer, at pressure of 200mbar of oxygen. The transformation of UO_2 into U_3O_8 is a two step reaction $UO_2 \rightarrow U_4O_9/U_3O_7 \rightarrow U_3O_8$. At 150 °C (Fig 5a) only the first step was possible, in which regular cubic fluorite structure of uranium dioxide accommodates additional oxygen atoms in its structure. That leads to the displacement of lattice oxygen atoms from their ideal lattice position and this is observed until $UO_{2.25}$ (U_4O_9) [1,2]. Further oxidation leads to a distortion of the unit cell by interstitial oxygen atoms, and change of a unit cell from cubic to tetragonal (U_3O_7). The second step of the reaction (Fig 5b-c) was possible after increasing the temperature to 300°C, that allowed for higher accommodation of oxygen atoms resulted in a phase transition to



Figure 5. Changes in XRD patterns of polycrystalline thin film sample after oxidation in atmosphere of 200mbar of oxygen.

In-situ XRD and HT-ESEM oxidation



In-situ oxidation of polycrystalline thin film (Fig 6a) showed that the structure could not withstand the expansion of 36% [4] associated with phase transition from regular cubic fluorite structure of uranium dioxide to orthorhombic U_3O_8 and break into flakes. The majority of the cracks starts at grain boundaries (~75%).

Studies conducted on (100) (Fig 6c), (110) and (111) (Fig 6b) oriented UO_2 single crystal thin films showed that at the same conditions samples behave differently. The (100) sample phase transition to U_3O_8 starts at 505°C and does not lead to disintegration of the sample. Two remaining single crystals (110) and (111) disintegrate while transforming to U_3O_8 and first changes were observed at 528°C and 568°C.

Conclusions



Figure 6. In-situ oxidation of uranium thin films using a FEI Quanta 200 field emission ESEM (Environmental Scanning Electron Microscopy) equipped with a 1500 °C hot stage. Top row present images take for a polycrystalline sample, middle row shows images for (111) oriented single crystal, and bottom row shows data collected for (100) oriented single crystal.

The oxidation mechanism of uranium dioxide depends on the crystallographic orientation. The phase transition to U_3O_8 occurs only at temperatures above 300°C. Changes to the structure at oxygen pressure of 3.5 mbar are observed at 505°C, 528°C, 568°C and 628°C for (100), (110), (111) and polycrystalline sample respectively. The (100) oriented single crystal dose not disintegrate. Disintegration of in polycrystalline system start mainly at the grain boundaries.

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Building the Foundations of a Predictive Tool for Spent Fuel Behaviour

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Spent Fuel in the UK

As UO₂ comprises the majority of high level nuclear waste generated by modern society, it is crucial that we develop a safe and efficient storage strategy for this material. While many advances have been made to improve nuclear storage facilities, eventual failure of these systems will expose the surface of UO2 to ground water, resulting in the release of radionuclides [2].



Figure 1: Spent fuel storage pond at Sellafield. Taken from [1].

Figure 2: Artists impression of a Geological Disposal Facility (GDF). Taken from [1].

Examination of a safety case that covers operation and post-closure safety must be included in the licensing process for such a facility [3]. The sheer timescales at which the waste remains hazardous gives rise to high levels of uncertainty that must be mitigated. By building predictive models for the likely corrosion behaviour of spent fuel exposed to pond or groundwater this can be achieved.



Modelling Tools

Pvthon

Open source, coding language used for a variety of programming, fast build time but a slow computation time

Use - Random walk simulation of alpha, beta and gamma radiation through small spheres for the case study highlighted on the project outline

FACSIMILE

Modelling tool to solve differential equations, specifically for chemical kinetics.

Use - Radiolysis and chemical kinetics of dissolution process.

COMSOL

Multiphysics general-purpose

simulation software.

simulation

FACSIMILE

NATIONAL NUCLEAR

MOOSE.

Snapshot of Convective flux above a pit Use – Multi scale and Diffusive flux inside a pit modelled of a incorporating given chemical and species in COMSOL

Fiaure

8:

References



Thin Film Approach

Single crystal, thin films of UOx can be grown via reactive magnetron sputtering have been used to investigate the dissolution process. Yttria stabilised zirconia (YSZ) is used as a crystal substrate, giving a lattice strain of 6% (Fig 4) [4].



Figure 4: YSZ crystal lattice match with [001], [110] and [111] oriented UO₂ [4].

Exposure to an Intense X-ray beam at a synchrotron source in the presence of water, radiolysis was induced to a 40Å [001]-UO2 thin film. Modelling the electron density, surface roughness and change in oxide composition a dissolution rate was achieved at the Ångström level [4]







Figure 7: Model results of OH production in H₂O under a pulsed radiation source. Data taken from FACSIMILE code [6].



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University of BRISTOL





Figure 9: Spherical Dosimetry modelling

U Ar Plasma ~60mm Uranium Targe S Ν Magnets Negative Bias

Substrate

0,

Film

O₂

Figure 3: Reactive DC magnetron sputter deposition mechanism of UO₂





Project Outline

The current project outline is to develop a model incorporating dissolution studies that utilize thin films. The goal is to scale up, adding complexity iteratively to build a comprehensive model for spent fuel dissolution. This will be modelled in COMSOL. Radiolysis data will be developed using FACSIMILE and incorporated into the model

Case study: Size effects of leached spent fuel particulates to radiolysis and dissolution rates in fuel pond storage

To model size affects on radiolysis and hence H₂O₂ release rate from particle size. The rate of oxidation increases with reduced size. A predictive model on particle dissolution would be in partnership with Sellafield and NNL. This will be done using a random walk simulation of alpha, beta and gamma radiation through small spherical spheres of varying radius.