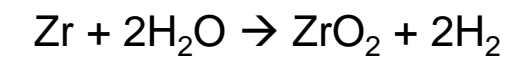


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1. INTRODUCTION

Zirconium alloy fuel cladding corrodes in the high temperature cooling water to form zirconium oxide and free hydrogen:



As the zirconium oxide grows, it creates thermal resistance, reducing the efficiency of heat extraction from the fuel. In addition, a proportion of the hydrogen generated by the above reaction is absorbed by the zirconium alloy, which can lead to embrittlement.

In the case of a Loss of Coolant Accident (LOCA), the cladding is required to survive as long as possible at a maximum temperature of 1200°C until cooling to the reactor can be restored.

Thin chromium (Cr) coatings on the zirconium alloy cladding potentially offer the following advantages:

- The formation of a thinner and more protective chromium oxide film during normal operations, offering reduced thermal resistance and longer fuel residence times
- Limiting hydrogen uptake by the zirconium alloy substrate, leading to reduced likelihood of hydrogen embrittlement affecting in-service performance and long term used fuel storage
- Increasing the oxidation resistance (and upper temperature) that the fuel cladding can survive during a LOCA to allow more time to restore cooling

2. OBJECTIVES

Cr-coated zirconium alloy specimens were provided by Manchester Metropolitan University covering a range of coating parameters and cleaning regimes. Complementary characterization performed by the University of Manchester and the National Nuclear Laboratory – see other posters.

- Undertake corrosion testing in 360°C simulated PWR water and 400°C steam to test integrity and performance of Cr coatings compared to uncoated control specimens
- Characterise the performance and hydrogen uptake with time
- Undertake high temperature air oxidation trials to elucidate potential performance during a LOCA

3. CORROSION AND OXIDATION TESTING

A variety of sheet, plate and tube specimens of Zircaloy-2, Zircaloy-4 and ZIRLO™ zirconium alloys were coated by Manchester Metropolitan University. Cladding alloy compositions given in the table below.

Element (wt%)	Zircaloy-2 ¹	Zircaloy-4 ²	ZIRLO ³
Zr	Bal.	Bal.	Bal.
Sn	1.2-1.7	1.2-1.7	0.7-1.5
Nb			0.5-2.0
Fe	0.07-0.20	0.07-0.20	0.04-0.28
Cr	0.05-0.15	0.18-0.24	
Ni	0.03-0.08		
O (typical values)	0.10-0.14	0.10-0.14	0.10-0.14

¹ ASTM Standard Specification UNS R60802; ² ASTM Standard Specification UNS R60804; ³ European Patent: EP0475159A1



Figure 1: Cr-coated fuel tube specimens suspended within the autoclave space awaiting lid placement.

Autoclave corrosion testing has been undertaken in autoclaves in in 360°C simulated PWR water containing Lithium Hydroxide and Boric Acid and 400°C steam aligned with the standard method of accelerated corrosion testing of zirconium alloys ASTM G2. High temperature air oxidation was undertaken in conventional furnaces. Figure 1 shows specimens suspended within the autoclave space, awaiting the lid installation.

Specimen dimensions and masses were measured prior to testing. Specimen masses were remeasured following periodic autoclave or furnace exposures, including photographs (Figure 2) to record visual changes.

Selected specimens were sectioned and prepared for microscopy. Hydrogen concentrations were estimated using Differential Scanning Calorimetry to determine the dissolution temperature of zirconium hydrides, from which the concentration could be estimated [Une & Ishimoto, Journal of Nuclear Materials, 2003].

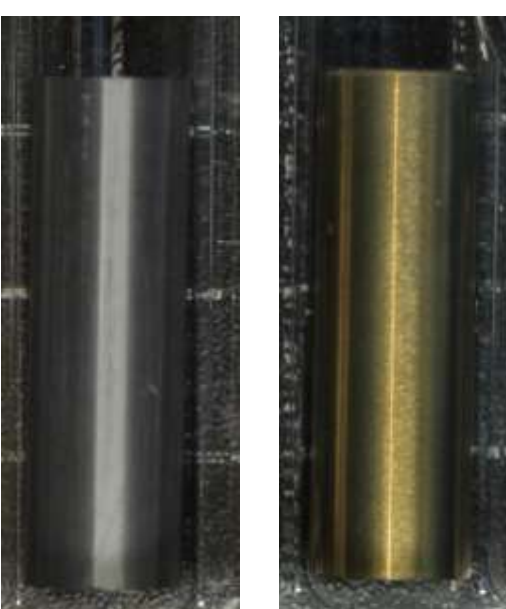
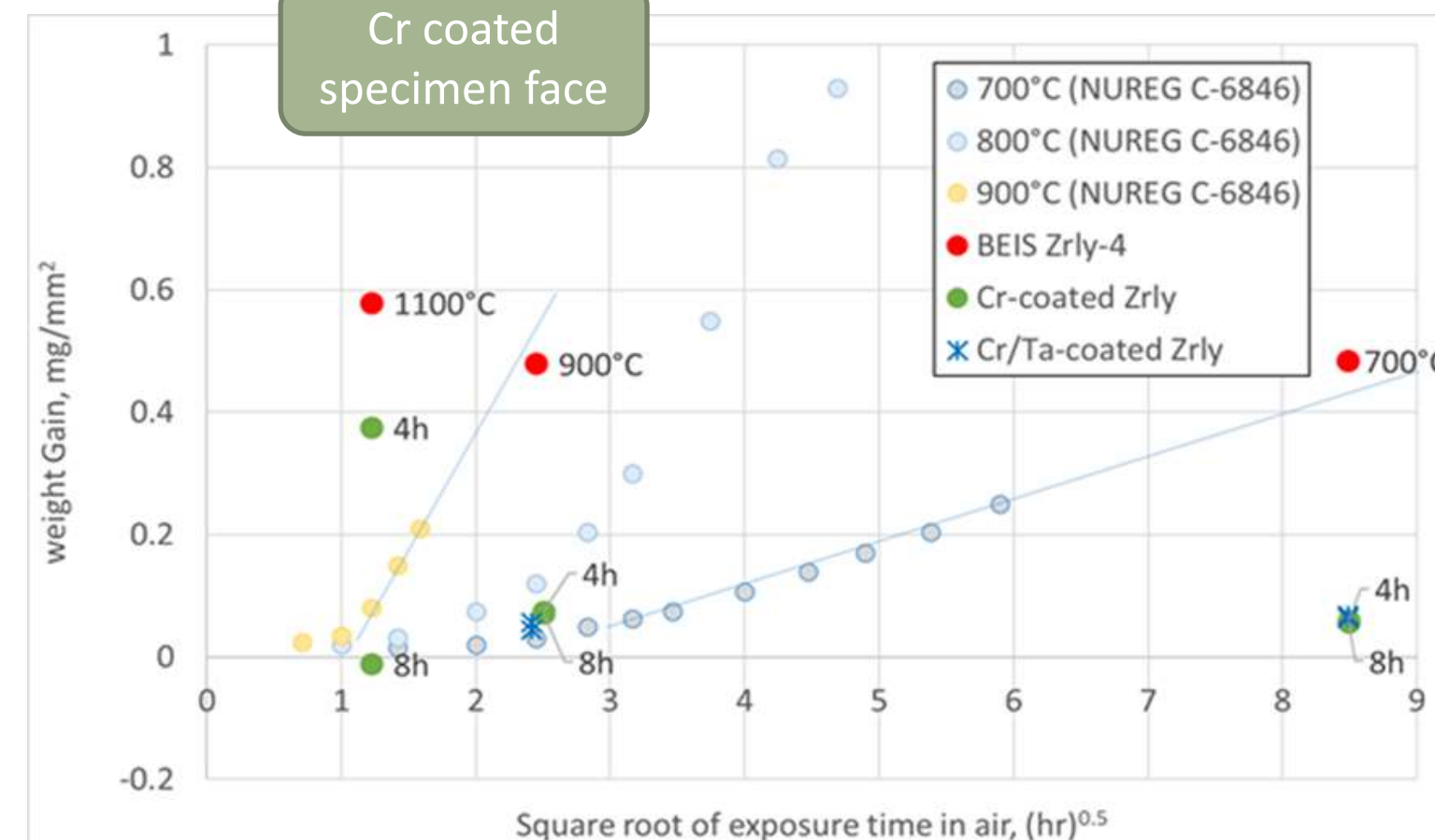
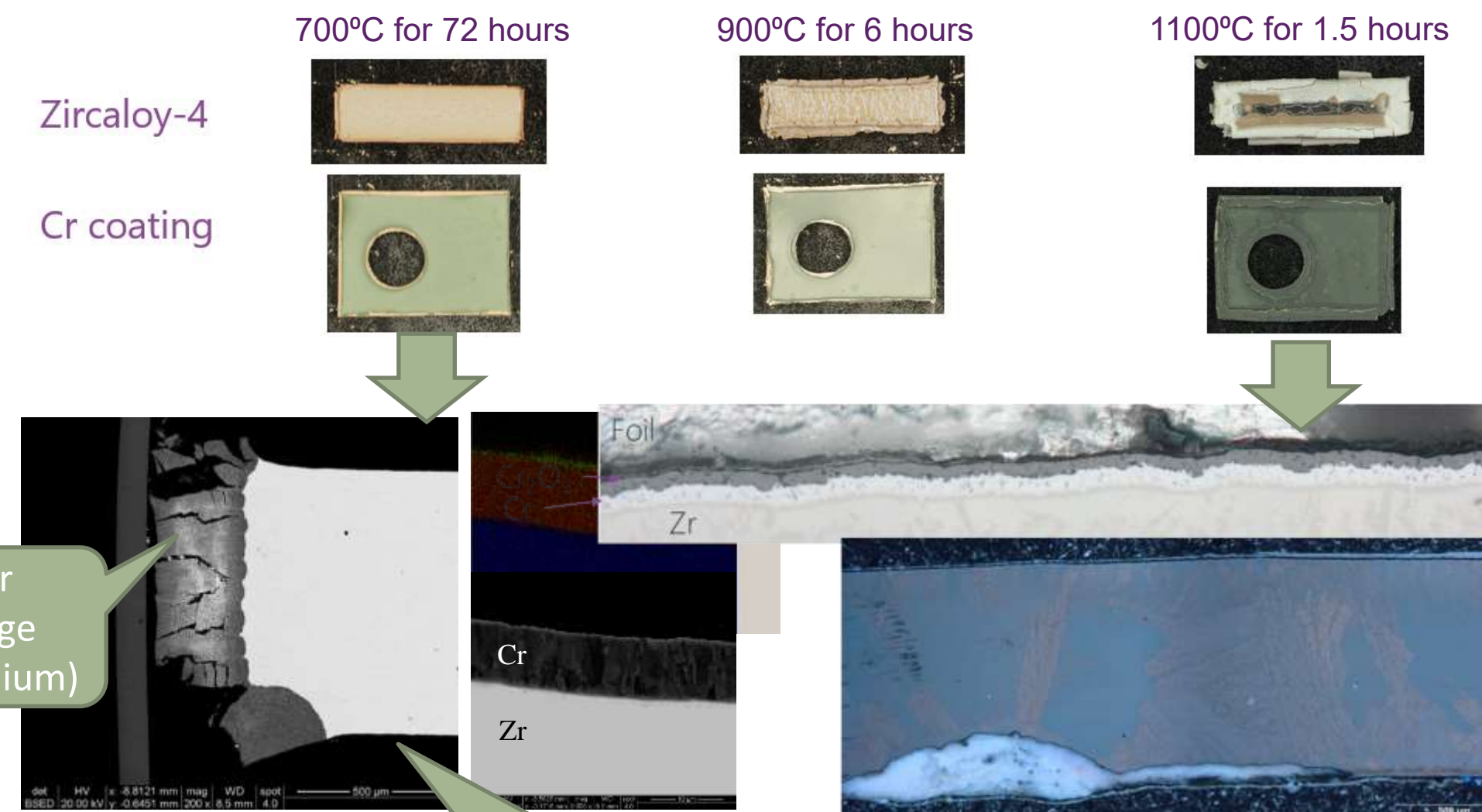


Figure 2: PWR water exposed uncoated and Cr-coated fuel tube specimens after 143 days.

4. AIR OXIDATION

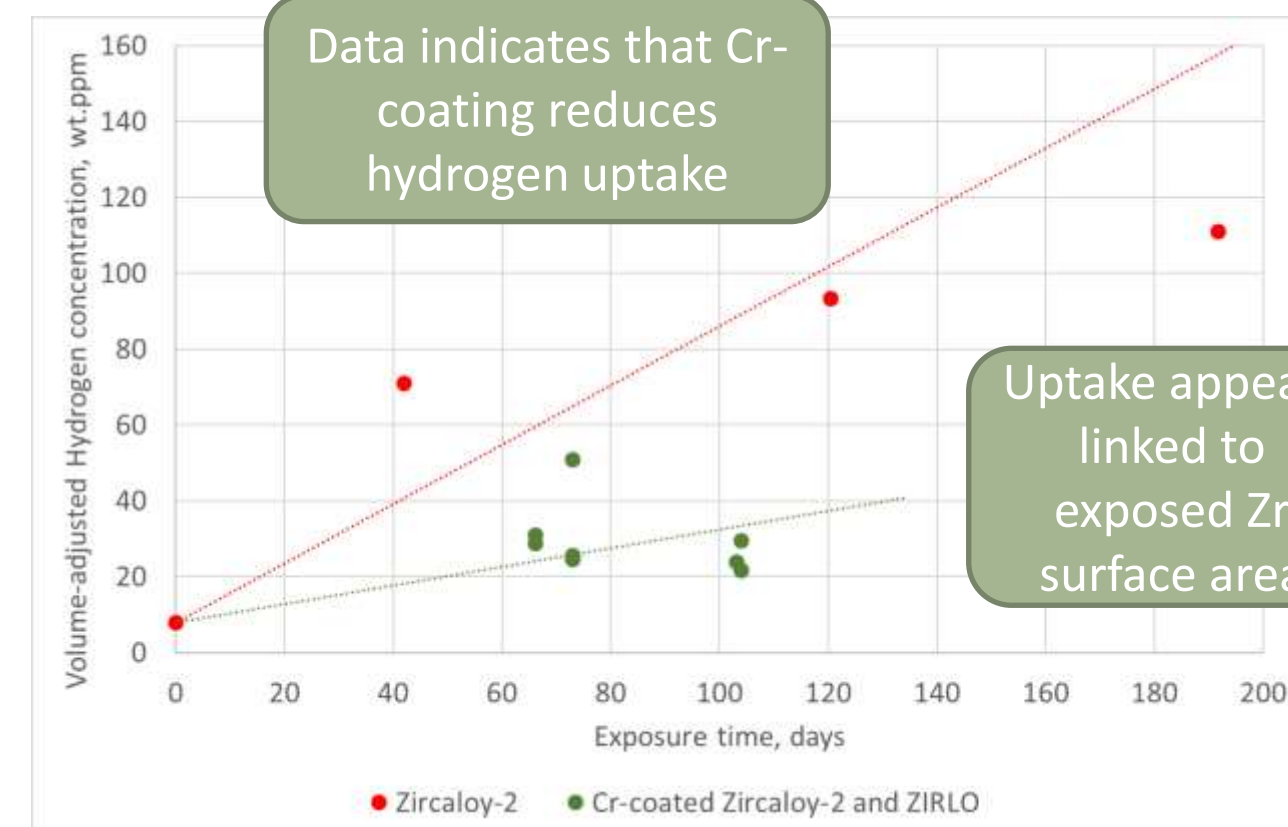


Reduced weight gain of Cr-coated samples means more cladding retained for longer during a hypothesised LOCA

6. HYDROGEN UPTAKE

Zr alloy substrate measurements from a number of samples undertaken. Both Opt. ZIRLO tube and Zircaloy-2 sheet substrates, exposed to 360°C water and 400°C steam. Data compared to Zircaloy-2 hydrogen measurements for specimens exposed to 350°C PWR water (Cole-Baker *et al.*, Topfuel 2019).

Hydrogen concentrations normalized to tube dimensions (assume hydrogen pickup proportional to surface area but dissolved in substrate volume, so need to account for differences in geometry)

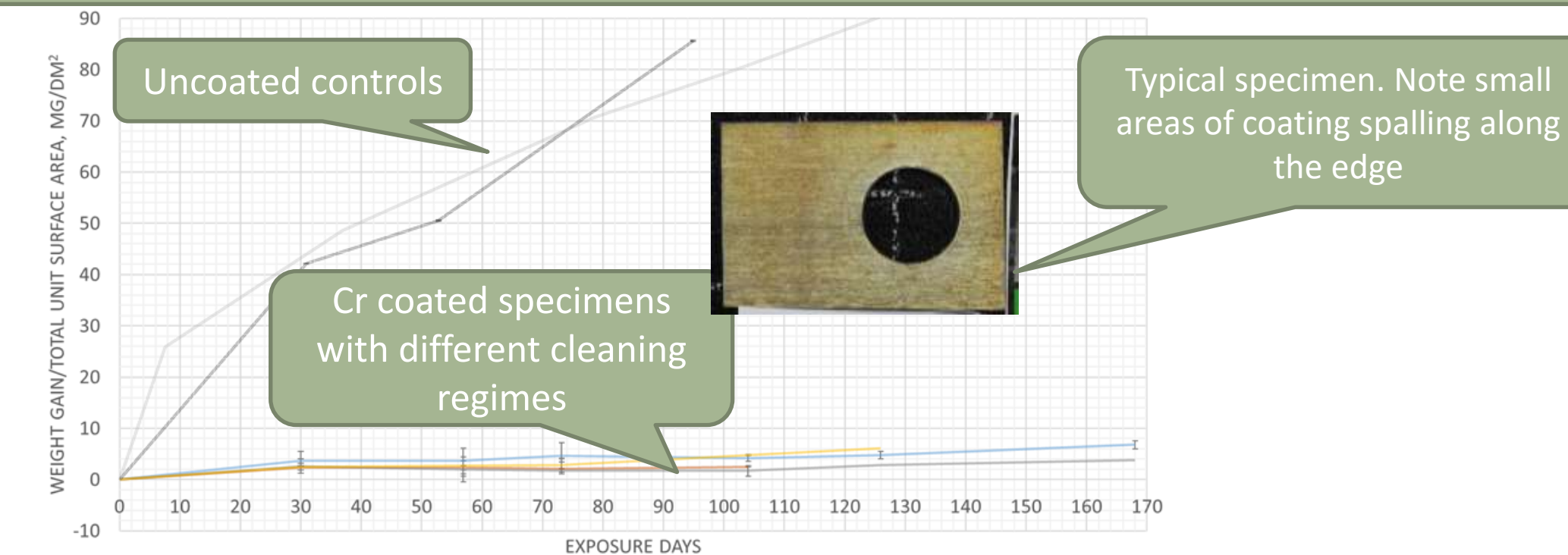


Data indicates that Cr-coating reduces hydrogen uptake

Uptake appears linked to exposed Zr surface area

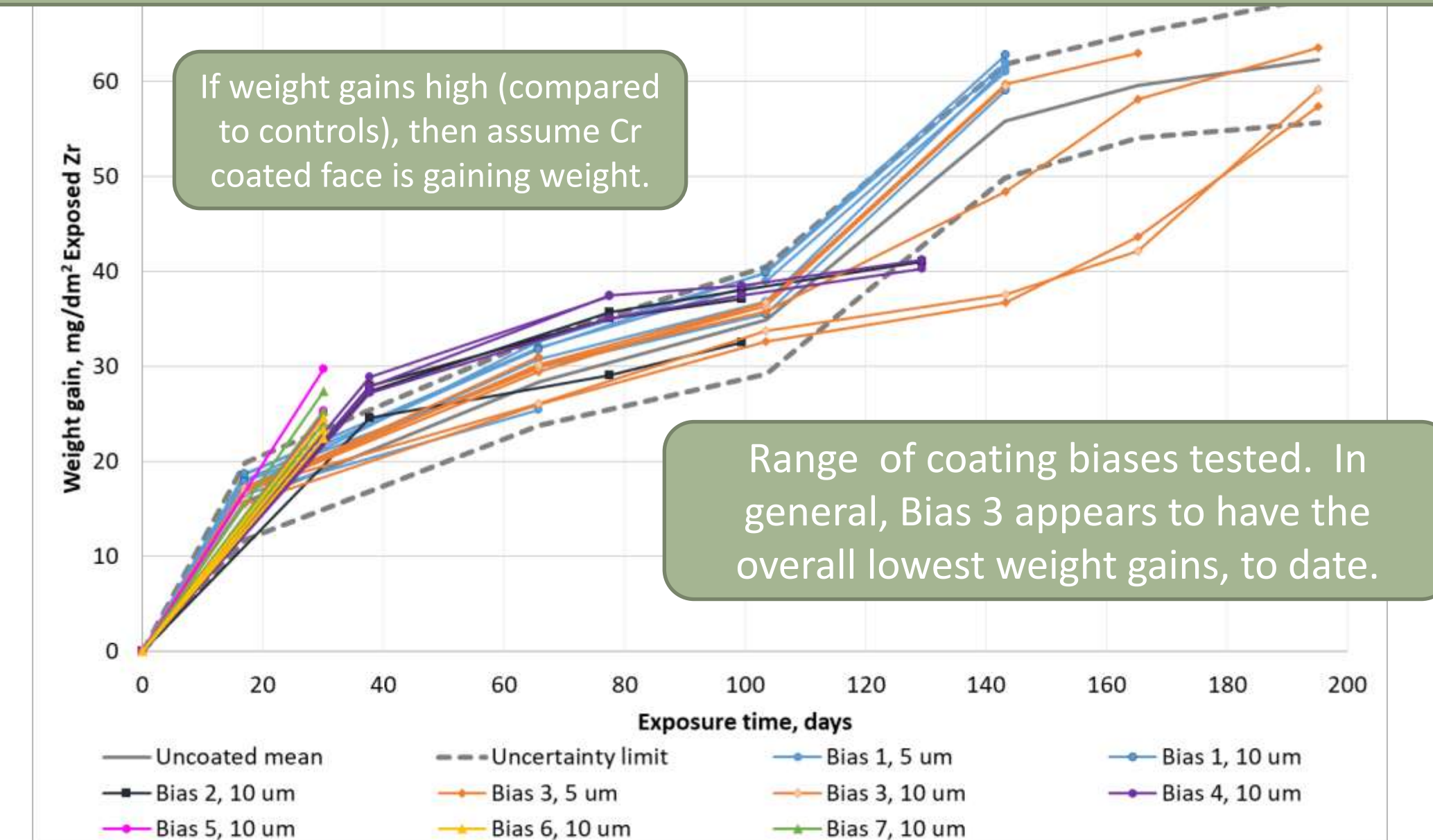
5. AUTOCLAVE CORROSION

400°C steam testing – Effect of specimen cleaning on sheet specimen weight gain (cleaned and coated on both sides)



Conclusion: Cleaning beneficial (better coating bonding, less spalling) but no specific cleaning parameters better

360°C PWR Water – Expected corrosion and, therefore, weight gain, on Cr so low, assume weight gain is entirely on the zirconium tube internals, which are uncoated.



If weight gains high (compared to controls), then assume Cr coated face is gaining weight.

Range of coating biases tested. In general, Bias 3 appears to have the overall lowest weight gains, to date.

7. CONCLUSIONS

Air Oxidation

- Clear benefit of Cr-coating demonstrated in air
- Small interfacial pores on 700°C specimen suggest improved bonding
- Intermetallic Cr₂Zr formed at interface
- Fe segregating to interface phase from Zr matrix

Autoclave corrosion

- Negligible weight gain attributable to Cr-coated surface – beneficial to normal operations through reduced thermal resistance, i.e. better heat transfer from the fuel.
- Ion cleaning beneficial, although specific parameters not critical
- Range of coating biases trialed, with some evidence to support optimum conditions from corrosion testing to date.
- Hydrogen uptake appears to be proportional to exposed zirconium surface area, thus Cr-coating not acting as a hydrogen window to date.

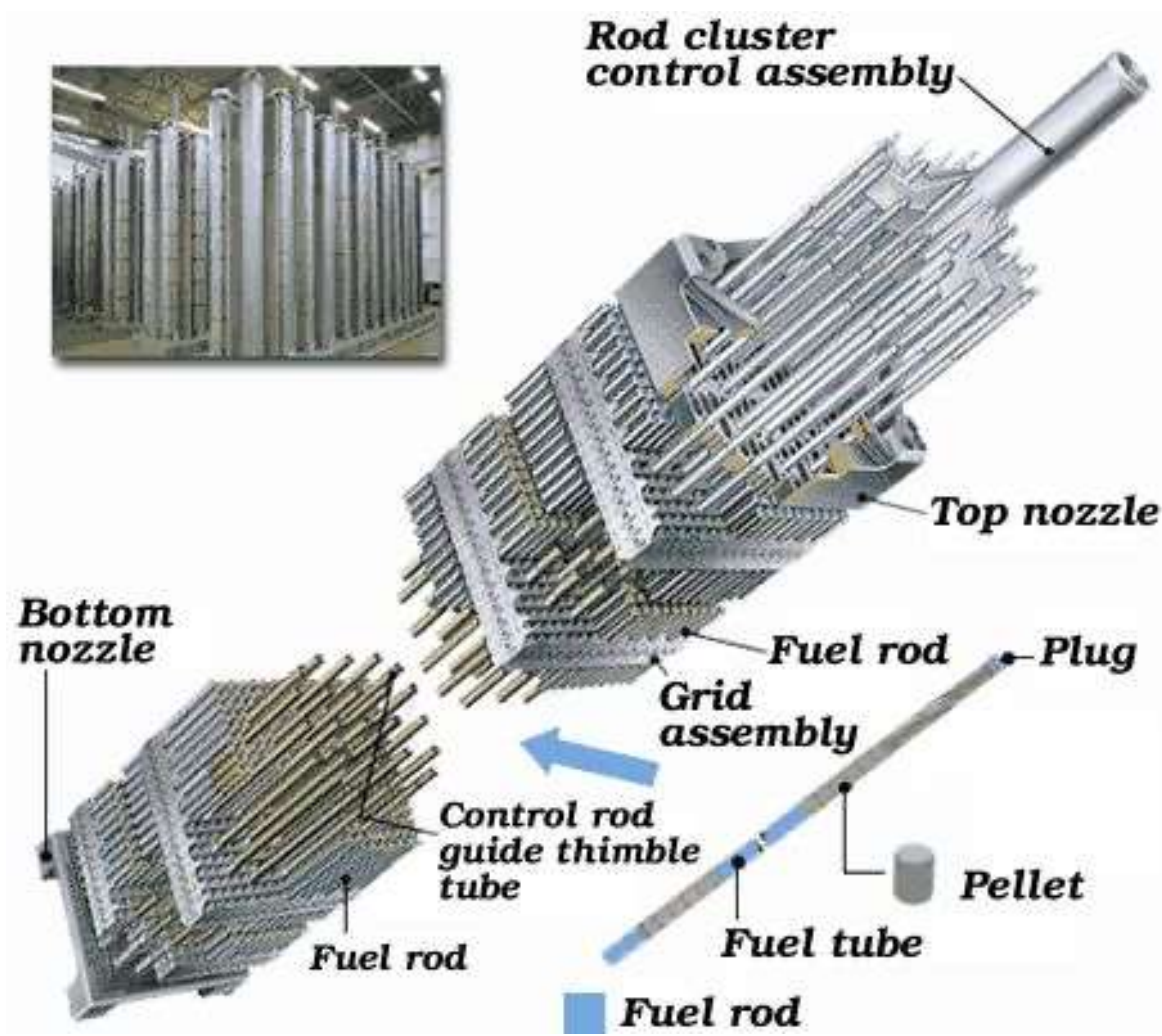
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INTRODUCTION

What is an Accident Tolerant Fuel (ATF)?

Accident tolerant fuels are a set of new technologies that have the potential to enhance safety by offering better performance during normal operation, transient conditions and accident scenarios



Coated ATF cladding aims to:

- Reduce oxidation by improving cladding reaction to high temperature steam
- Improve fission product retention
- Enhance mechanical strength at high temperatures
- Lower the generation of hydrogen gas when reacting with steam

Schematic view of a PWR fuel assembly

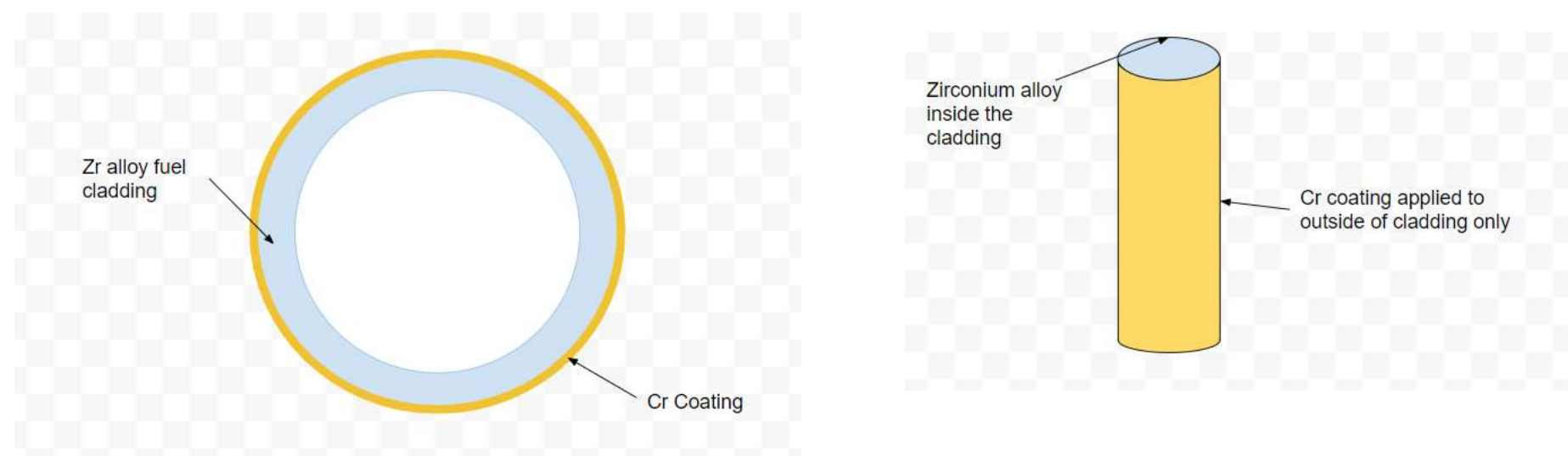
The deposition of a Cr coating onto a Zr alloy nuclear fuel cladding is the most advanced concept for deployment of an accident tolerant fuel. Through the UK Advanced Fuel Cycle Programme research has been conducted to investigate Cr deposition using magnetron sputtering, a coating technology which has been scaled up from coating flat coupons to small rodlets and has progressed to full length cladding.

OBJECTIVES

Research has demonstrated that Cr coatings reduce the oxidation of Zr alloys in normal operating conditions and high temperature Loss of Coolant Accident (LOCA) scenarios.

The objectives of this work were to:

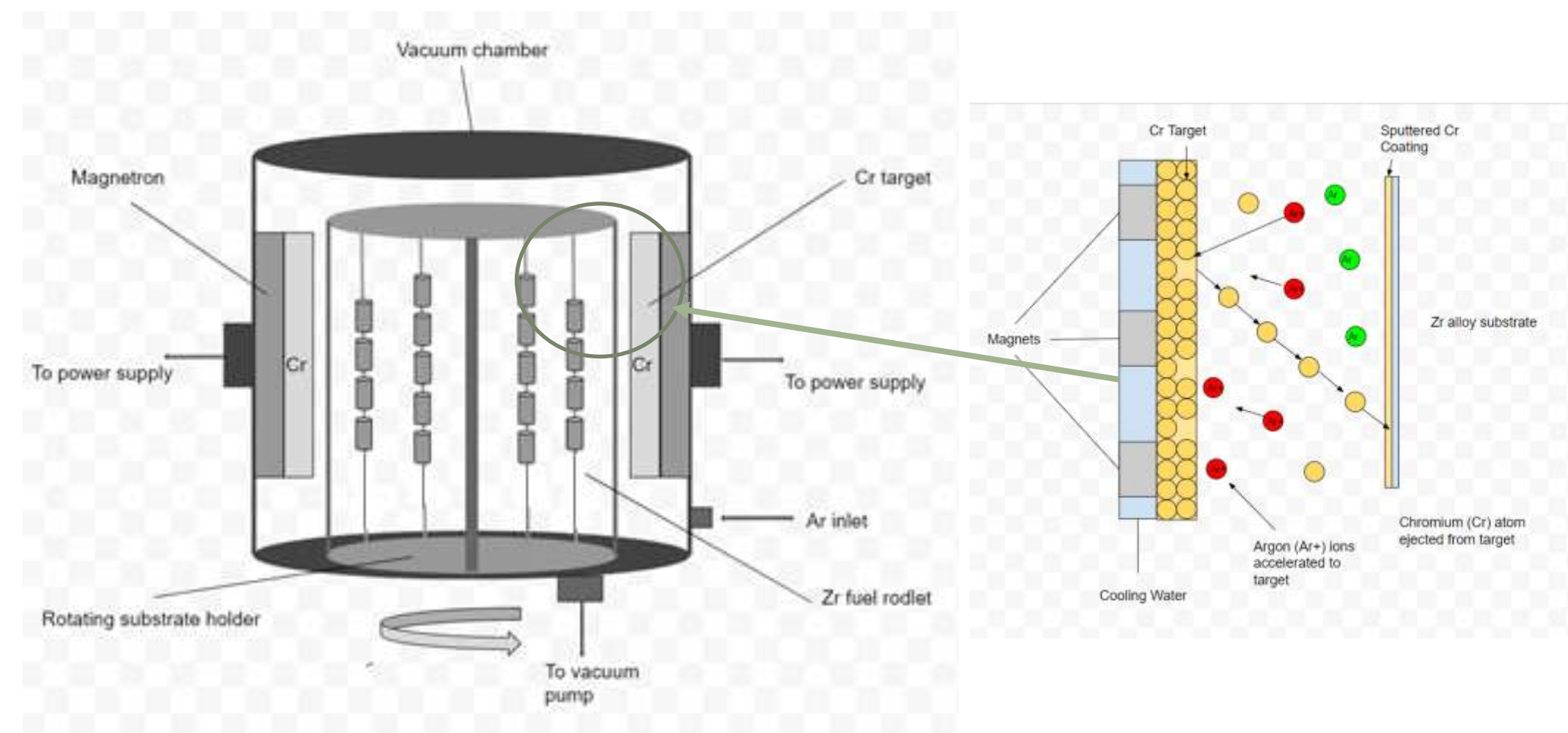
- Produce Cr coatings utilizing the PVD technique magnetron sputtering
- Vary process parameters to produce optimal coating performance
- Produce coatings with 5µm and 10µm thicknesses
- Demonstrate that the sputtering process was scalable to full length cladding



MATERIALS AND METHODS



Coating deposited by magnetron sputtering using UDP450 chamber from Teer coatings



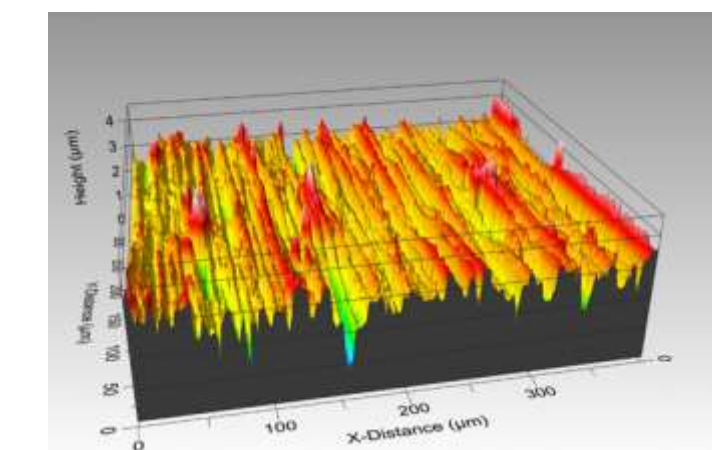
Sample substrate holder designed to rotate in a planetary motion

Magnetron Sputtering

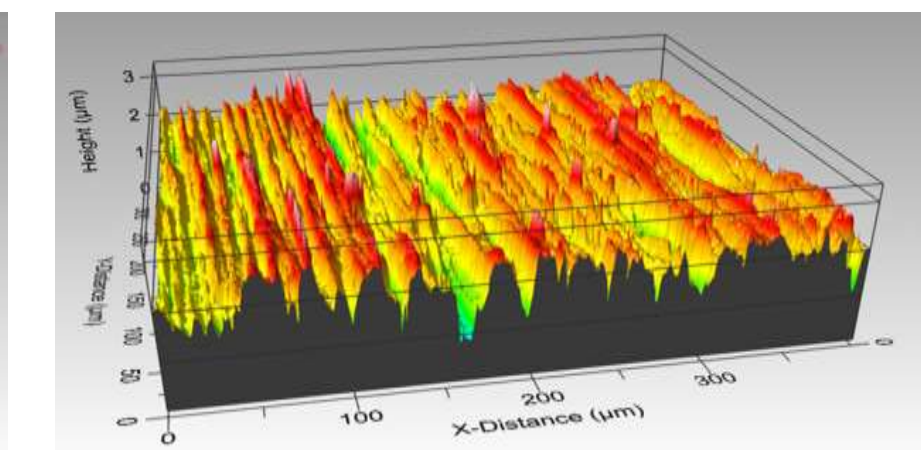
- Well established industrial method of applying coatings to plane surfaces and tubes
- Physical vapour deposition (PVD) method
- Plasma based deposition process
- Ions are accelerated towards a target
- Ions strike the target and atom are ejected from the surface
- Atoms travel to substrate and grow into a thin film
- Substrate temperature remains well below final annealing temperature of zirconium alloy
- The underlying topography is not adversely altered
- No post processing of cladding required

RESULTS

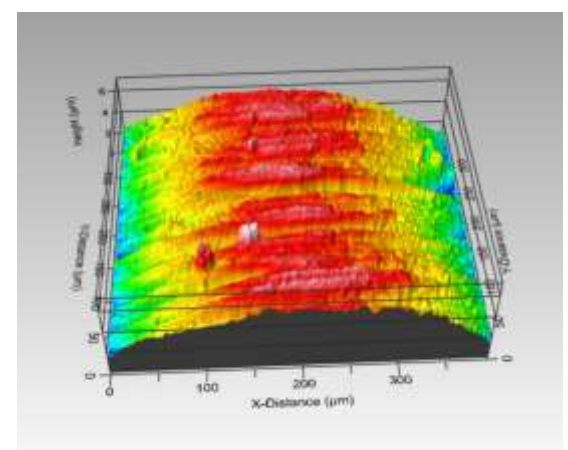
Following the deposition of the Cr coatings by magnetron sputtering the roughness of the samples was analysed by white light profilometry. The results showed that the coatings were conformal with the Zr alloy cladding substrate, with the data showing very similar measurements for all the bias settings and thicknesses examined



Uncoated ZIRLO™ cladding



Cr coated ZIRLO™ cladding

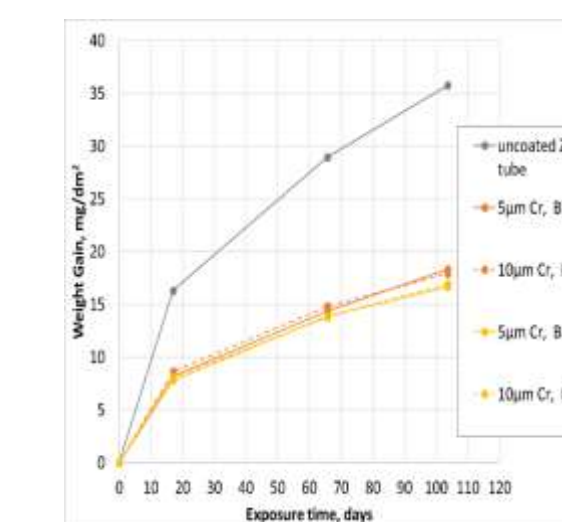


Circumferential finishing lines ZIRLO™ cladding

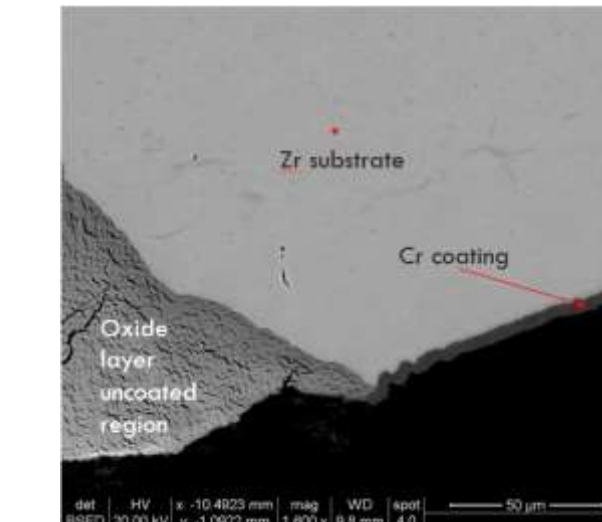
Table 1 Axial roughness measurement for Cr coated and uncoated ZIRLO™ fuel cladding

Substrate	Coating	Thickness	Bias	Ra (µm)
ZIRLO™ rod	Uncoated	-	-	0.24
ZIRLO™ rod	Cr	10 µm	Bias 1	0.25
ZIRLO™ rod	Cr	10 µm	Bias 2	0.26

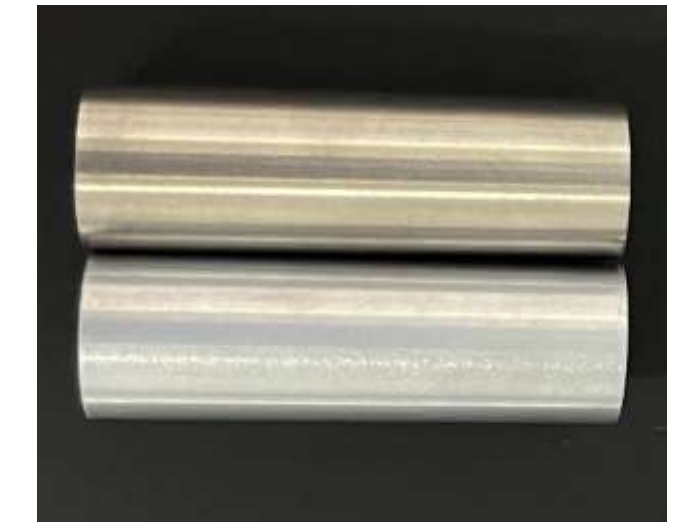
Autoclave results 400°C steam corrosion



Air oxidation at 900°C



Uncoated cladding (top) Cr Coated cladding (bottom)



CONCLUSIONS

Magnetron sputtering can provide a dense uniform Cr coating onto Zr alloy tubes. Changing deposition parameters has little effect on the roughness of the deposited coating. Autoclave tests supports the use of Cr coatings for ATF as weight gains were significantly reduced compared with uncoated specimens. Magnetron sputtering has been scaled up from a lab based system to an industrial scale coater for the application of Cr coatings to full length fuel claddings.

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CONTACTS

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This work was funded under the £46m Advanced Fuel Cycle Programme as part of the Department for Business, Energy and Industrial Strategy's (BEIS) £505m Energy Innovation Programme.

Introduction

UO₂ has many desirable properties as a nuclear fuel, high temperature stability, good radiation tolerance, and good coolant compatibility. Despite this, it has a poor thermal conductivity which results in high centreline temperatures, an important factor in an accident scenario. Advanced Technology Fuels (ATFs) are currently being developed with higher conductivities, but their behaviour is not fully understood.

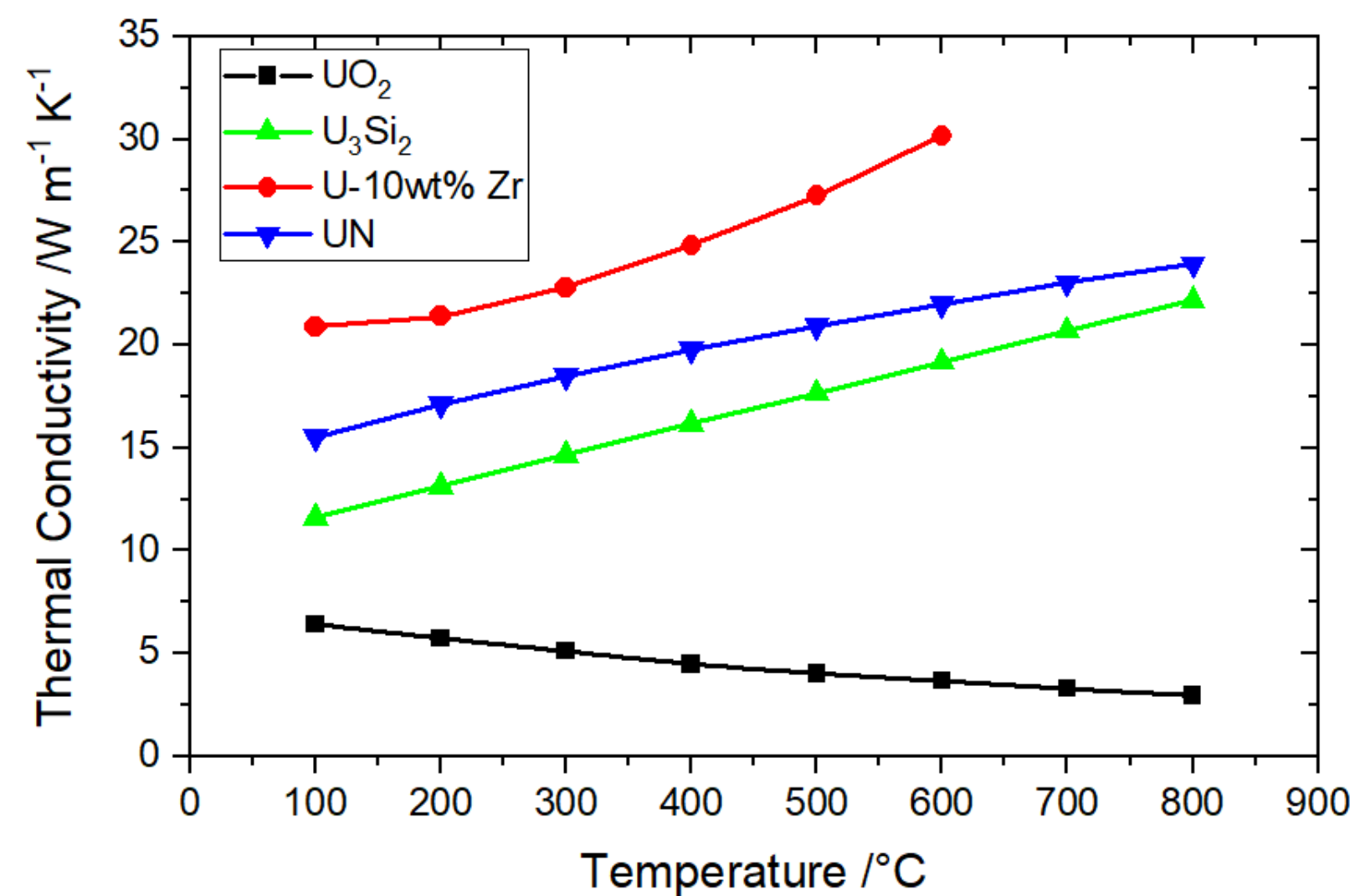


Figure 1 – Thermal conductivities of several ATF fuel forms and UO₂.

Figure 1 shows the poor thermal conductivity of UO₂ compared to some ATF and metallic fuels. With a minor modification to UO₂ such as adding a higher conductivity additive, the overall fuel conductivity can be improved, increasing its accident tolerance, rendering it a nearer-term ATF concept.

Objectives

A literature review highlighted several additive candidates, molybdenum (Mo), niobium (Nb), and aluminium nitride (AlN) and these were used to develop a set of project objectives.

- Fabricate UO₂ samples with selected additives and assess the resulting microstructure and improvements in thermal conductivity as a function of temperature.
- Investigate methods to introduce the additive in such a way as to maximise the thermal conductivity for the minimum incorporation of additive.
- Evaluate the reproducibility of the fabrication procedure and compare with a typical fuel specification.

Microstructural Results

Dispersed phase composites were prepared by simply mixing UO₂ and additive powders together whereas continuous phase composites were prepared by gently mixing additive powder and granulated UO₂. The combined mixtures were then sintered by Spark Plasma Sintering (SPS).

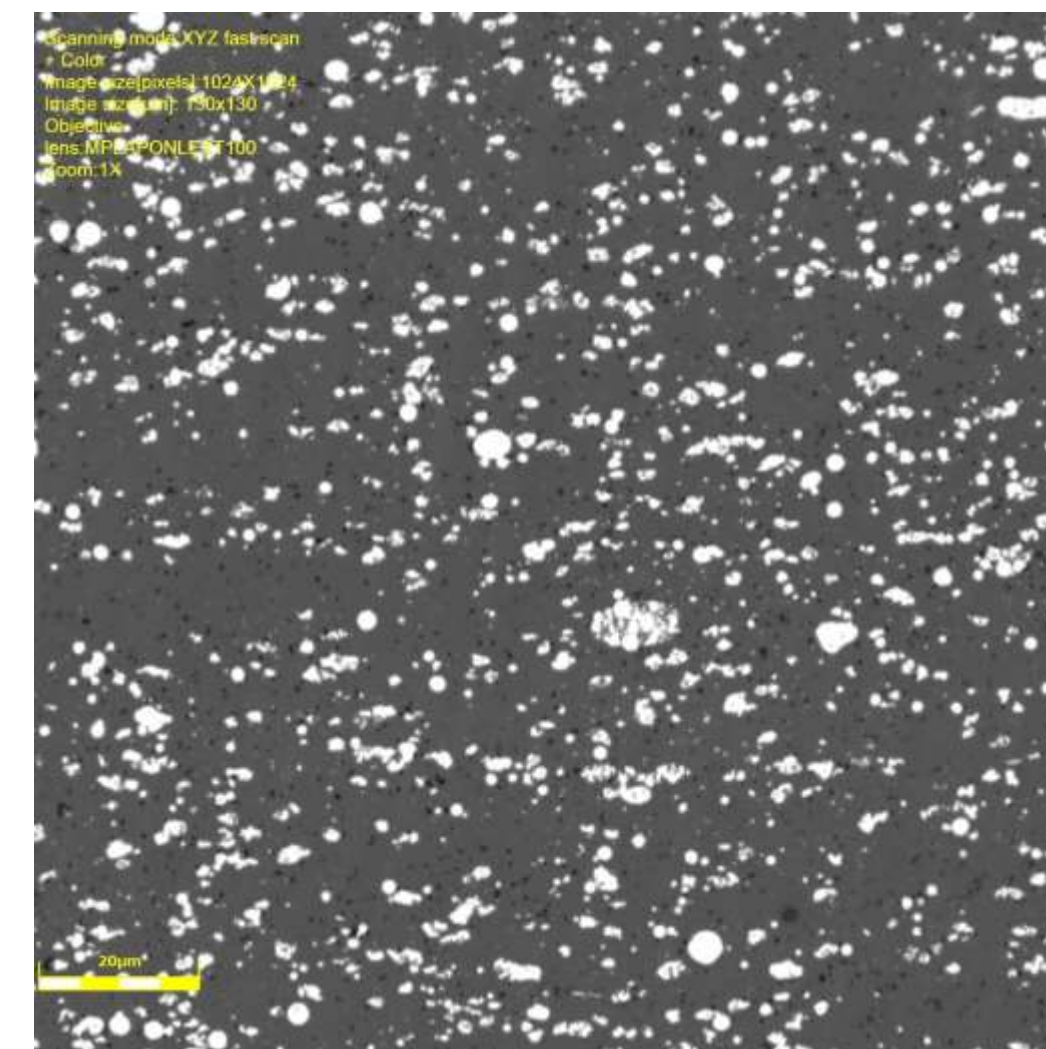


Figure 2 – Micrograph of composite with UO₂ and 10 vol% Mo powder.

Figure 2 shows the microstructure of a dispersed phase pellet of UO₂ and 10 vol% Mo where the additive is uniformly dispersed throughout the microstructure. Both Nb and AlN based composites showed similar microstructures.

Figure 3 shows the microstructure of a continuous phase pellet with 10 vol% Mo powder and UO₂ granules where additive is in an almost continuous channel structure.

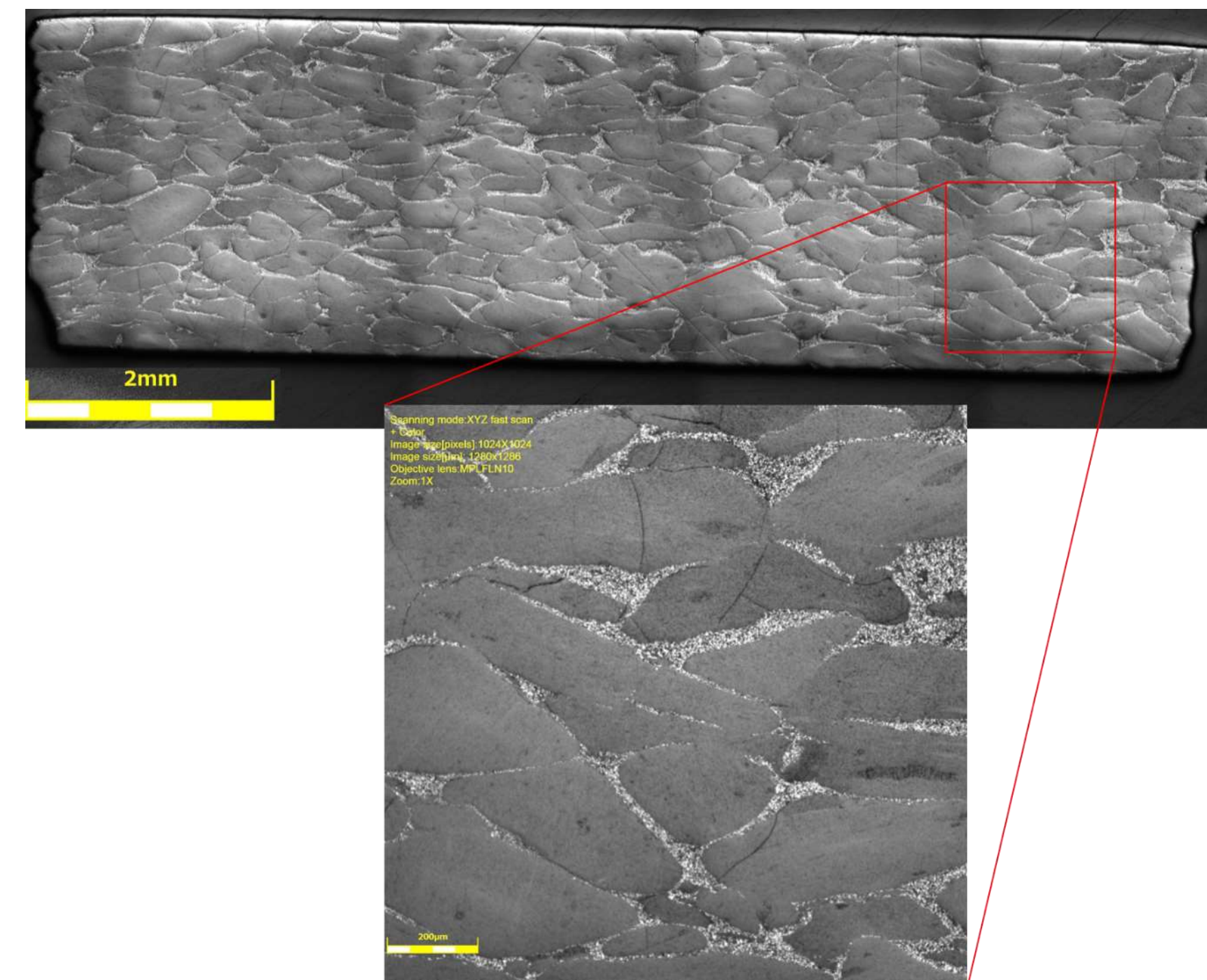


Figure 3 – Micrograph of continuous phase pellet with UO₂ granules and 10 vol% Mo powder.

Thermal Conductivity Results

Thermal conductivities were obtained by Laser Flash Analysis (LFA) on both dispersed and continuous pellet types for each additive.

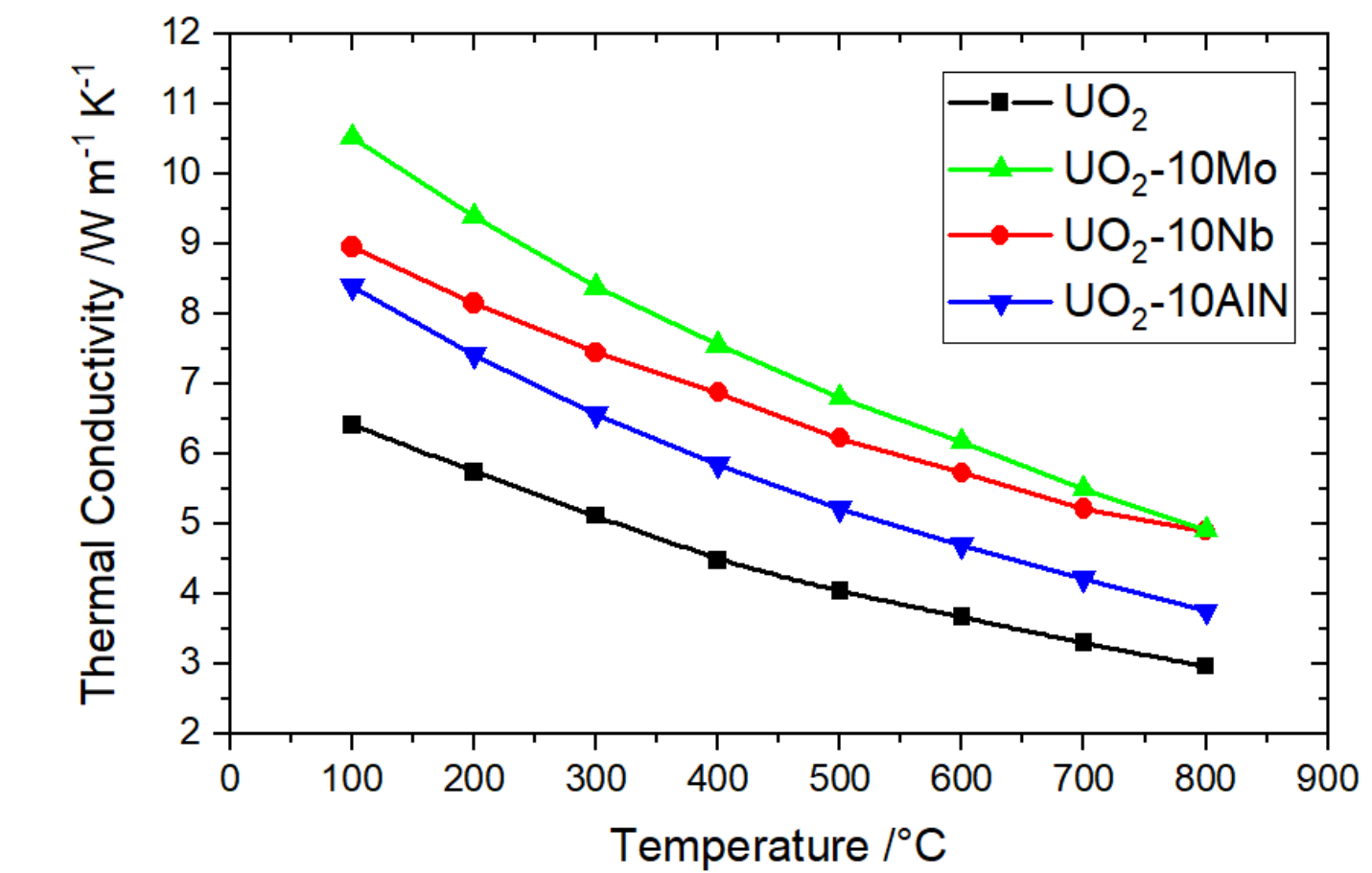


Figure 4 – Thermal conductivities of dispersed phase composites. Number in legend refers to volumetric percentage of additive.

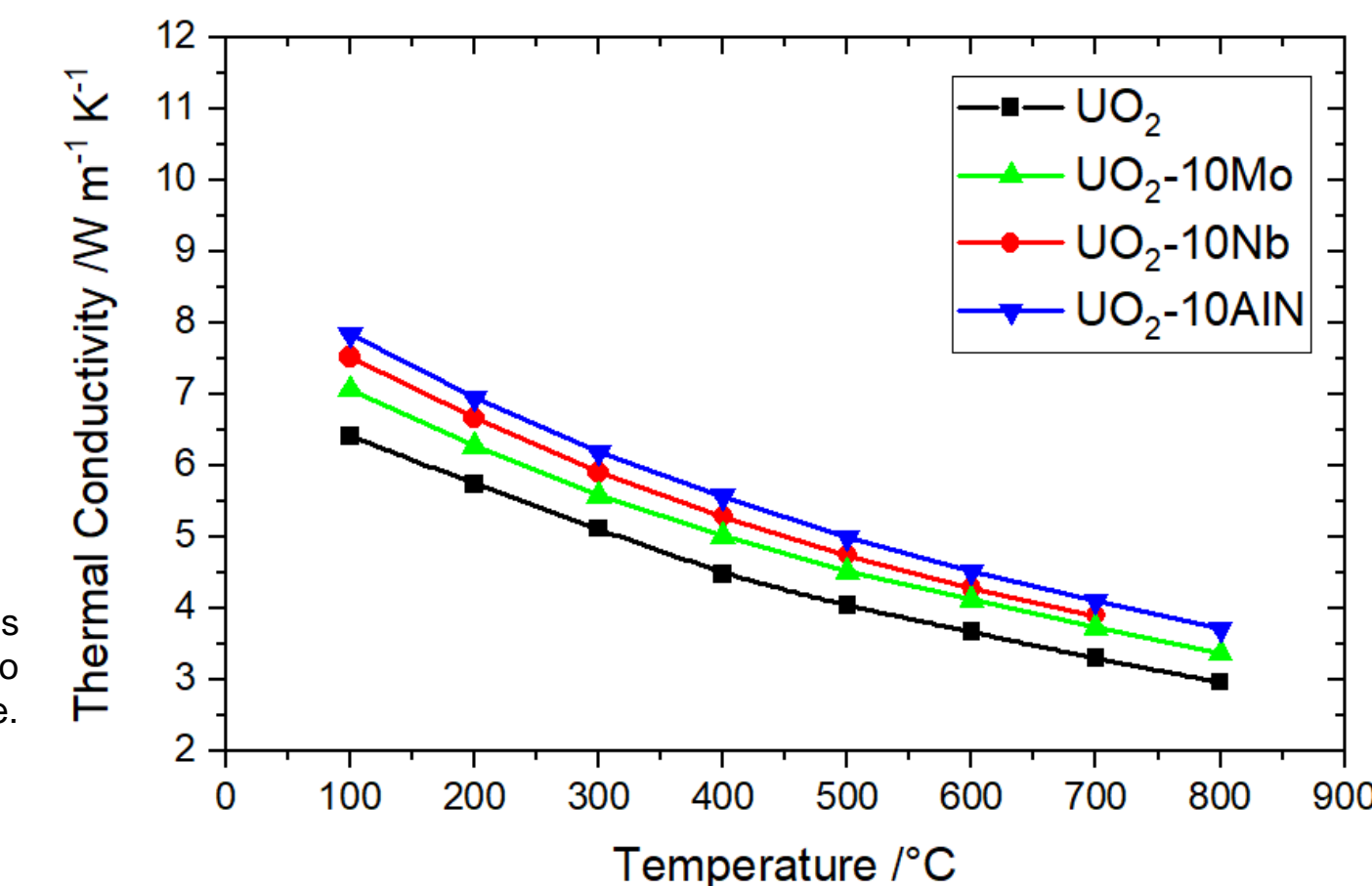


Figure 4 – Thermal conductivities of continuous phase composites. Number in legend refers to volumetric percentage of additive.

Conclusions

- Three additives, Mo, Nb, and AlN were investigated by incorporating into UO₂ pellets in dispersed form. Mo was shown to be most effective at improving the conductivity and AlN the least.
- Thermal conductivity of continuous phase composites showed only a marginal improvement, disagreeing with several other studies likely due to increased pellet cracking.

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3. Ragnauth, H. E. Uranium-Zirconium Nuclear Fuels and Methods for Improving Burnup Capability. (The University of Manchester, 2019).

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INTRODUCTION

Uranium mononitride (UN) is an Advanced technology Fuel (ATF) with potential applications in current and future reactor systems.

- UN could offer considerable economic and safety benefits over UO_2 when used as fuel in light water reactors, further improving the viability of nuclear as a solution to achieving net zero [1].
- UN is also applicable to next generation systems, with relevance to achieving net zero.
 - High temperature gas reactors (HTGRs)
 - Advanced modular reactors (AMRs)
 - Fast reactors (FRs)

This program of research has focused on developing lab scale synthesis and manufacturing capabilities at The University of Manchester to facilitate research into UN as a potential fuel form.

OBJECTIVES

- Develop UK academic capability to synthesise UN and fabricate representative fuel forms.
- Develop methodologies and techniques for characterisation of powder and pellet properties relevant to fuel manufacture and performance.
- Gain an understanding of how manufacturing parameters affect the final material.
- Facilitate parallel and future work on UN as a fuel material, both at the University and in the wider community.

METHOD

- Design, install and commission a furnace located within an atmosphere controlled glovebox, capable of hydriding, nitriding and denitriding uranium metal in accordance with the following reactions [2];



- Upgrade and utilise existing equipment at The University of Manchester to densify synthesised UN via cold-press then sinter (CP-S) and spark plasma sintering (SPS) methods.
- Utilise SEM, EDX, XRD, laser confocal microscopy and elemental analysis capabilities to understand the effect of manufacturing parameters on material purity and microstructure.

RESULTS

Synthesis

- Successfully demonstrated synthesis route.
- Scaled-up process to produce ~25 g batches of material (FIG1).
- Demonstrated the ability to produce material with low oxide impurity, <1 % UO_2 .
- Developed methods to understand and characterise carbon impurity content within the final product, confirming material to be: $UN_{0.96}C_{0.04}$.

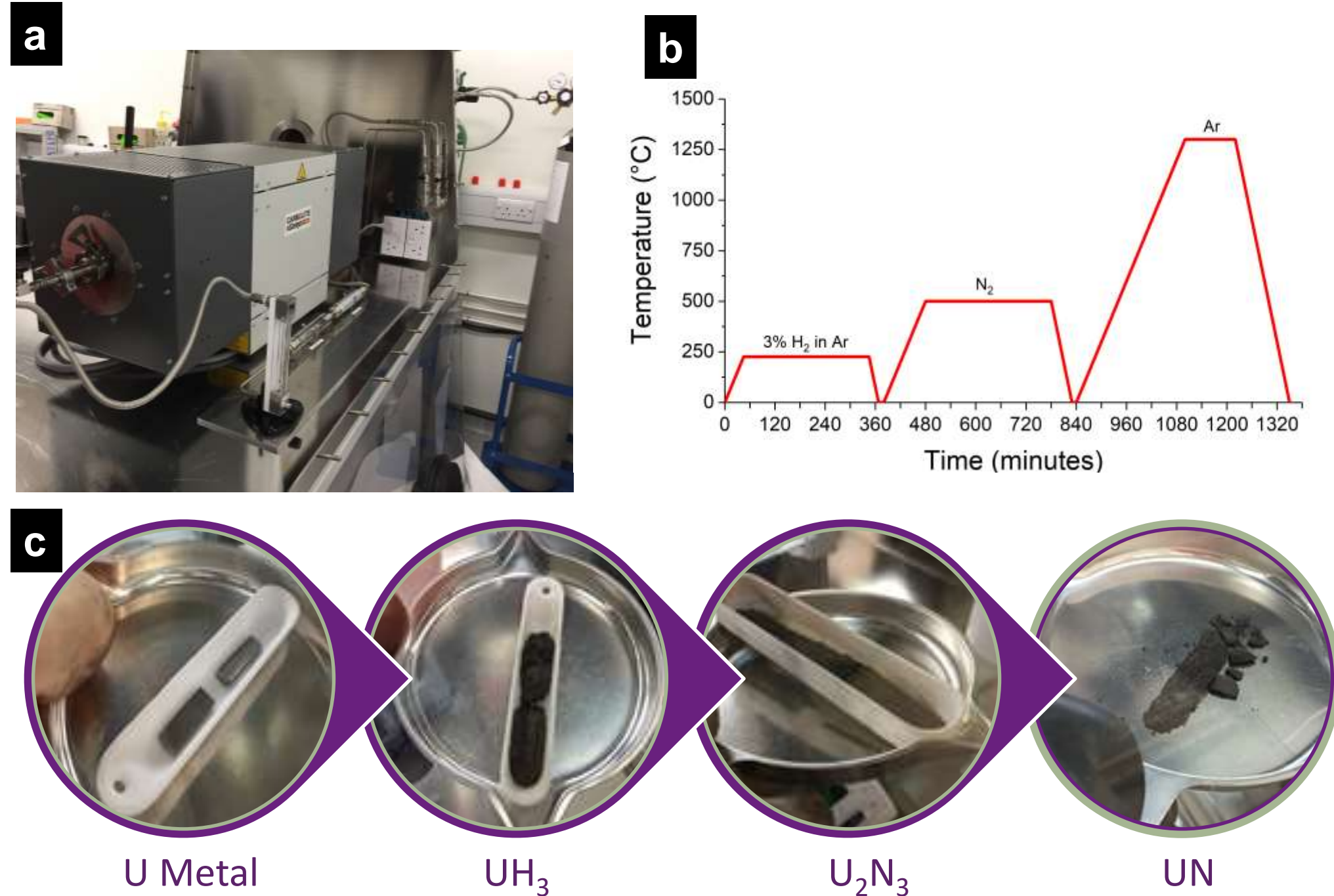


FIG1: a) Experimental setup developed for synthesizing UN, b) typical temperature profile employed to synthesize UN and c) schematic of material produced at each step of the synthesis process.

Fabrication

- Successfully employed conventional and novel sintering methods to densify UN powder to high densities, representative of fuel requirements (FIG2).
- Developed an understanding on how manufacturing parameters alter pellet microstructure (FIG3 a-c).
- Provided an understanding how elemental content of UK Magnox metal results in impurity content (FIG3d).



FIG2: batch of UN samples fabricated via SPS, samples are 10 mm in diameter.

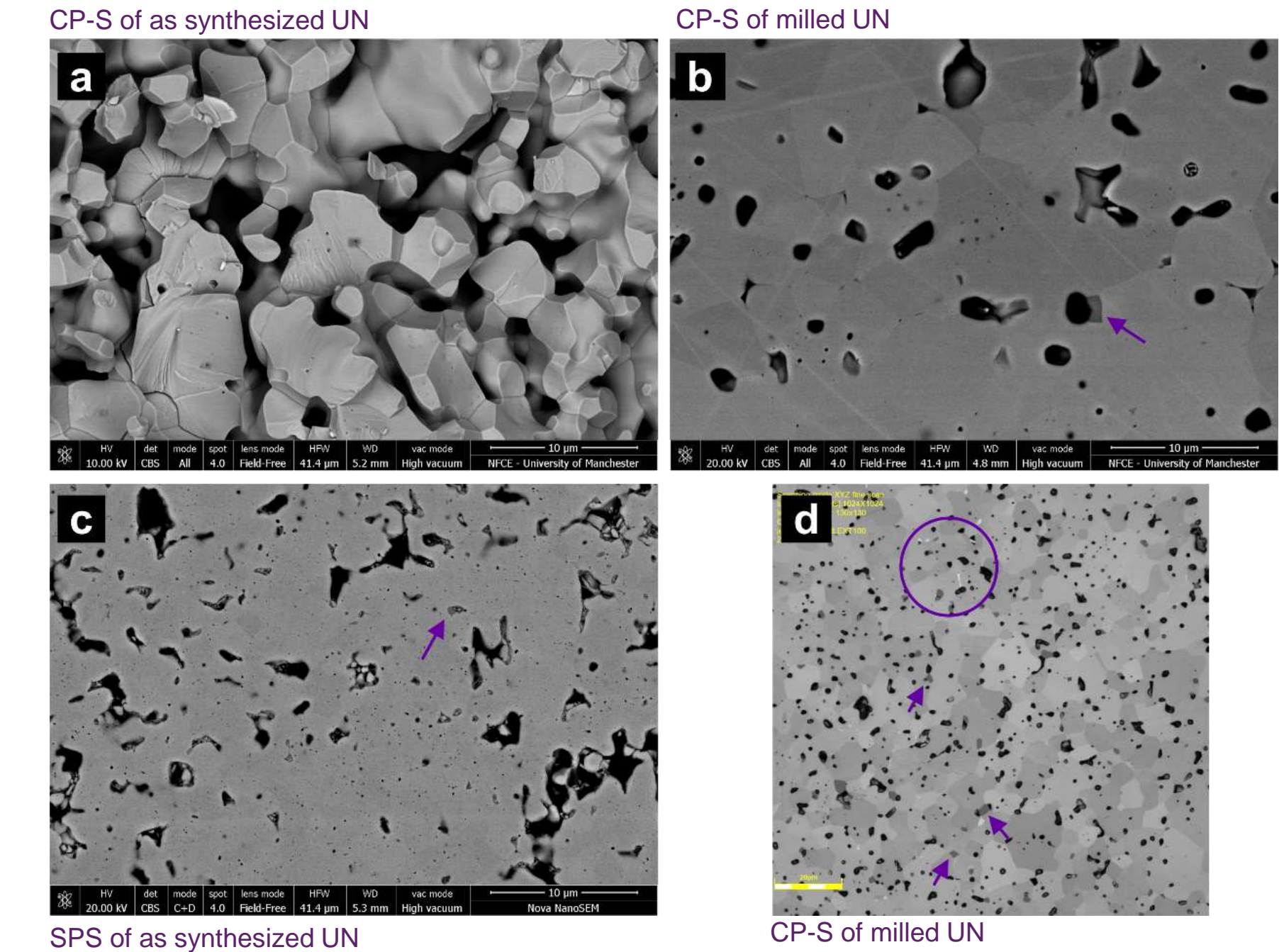


FIG3: a-c) Electron micrographs of UN microstructure produced with various sintering methods, d) optical micrograph of UN showing existence of Fe rich impurity phases (circled). Arrows highlight presence of UO_2 inclusions.

IMPACT

- This work has developed novel fuel manufacturing capabilities within the UK and provided the opportunity to understand how synthesis and fabrication parameters affect the final microstructure of this potential fuel form.
- Methodologies developed through this work are informing the development of scale-up facilities at NNL's Springfield site.
- Material synthesised through these capabilities has supported multiple parallel research projects within AFCP.
- These capabilities are now being utilised in research to support the UK's development of AMR technology.

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CONTACT

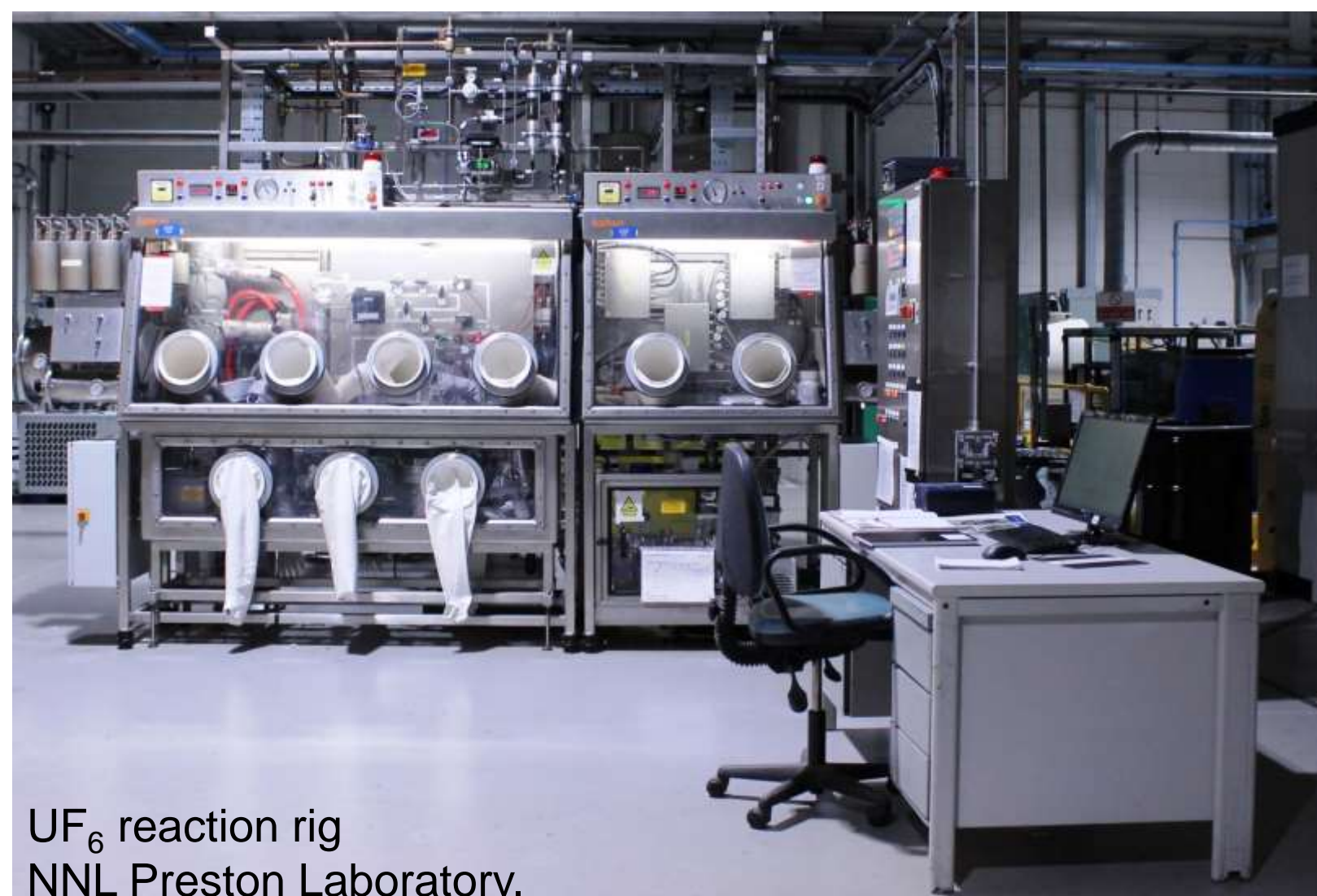
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This work was funded under the £46m Advanced Fuel Cycle Programme as part of the Department for Business, Energy and Industrial Strategy's (BEIS) £505m Energy Innovation Programme.

Introduction

Uranium nitride (UN) is proposed as an advanced technology nuclear fuel due to improvements in both uranium density and thermal conductivity in comparison to current technology fuels. Equipment has been constructed to allow uranium hexafluoride (UF_6) reactions with ammonia to be tested. Nuclear fuel production routes based on UF_6 are likely to be suitable for large scale production. The UF_6 conversion to UN occurs in three stages.

Property	Parameter
Reaction Temperature	120 – 950°C
UF_6 flow rate	0-120 cm ³ /min
NH_3 flow rate	0-5 l/min
Off gas Scrubbers	NaF and NaOH for abatement of off gasses
Safety	Automated safety trip circuits preventing over temperature and pressure. Non-flammable concentrations of ammonia are used to prevent explosive atmosphere hazard.
Atmosphere	Housed within an inert atmosphere glovebox <100ppm O ₂ and -60°C dew point.
Materials	High nickel content alloys (Monel & Inconel) are used for corrosion resistance.
Trace Heating	All pipework is trace heated to 120°C to maintain gas phase UF_6 throughout the process.

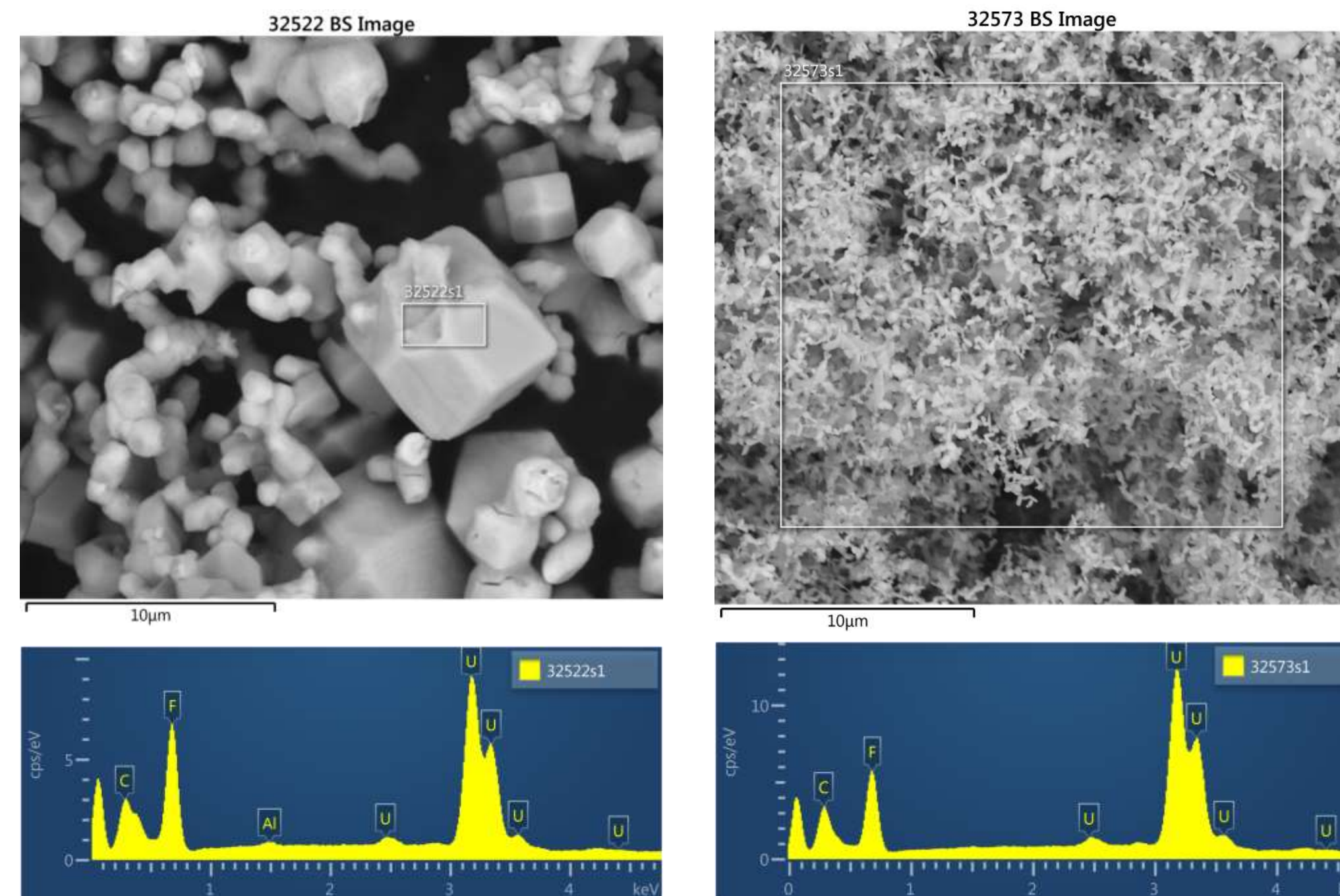


Stage 1: UF_6 Reaction with Ammonia (~300°C)

The first stage is the reaction of uranium hexafluoride with ammonia at approximately 300°C. This produces an intermediate product, ammonium uranium fluoride with off gasses of hydrogen fluoride and nitrogen.



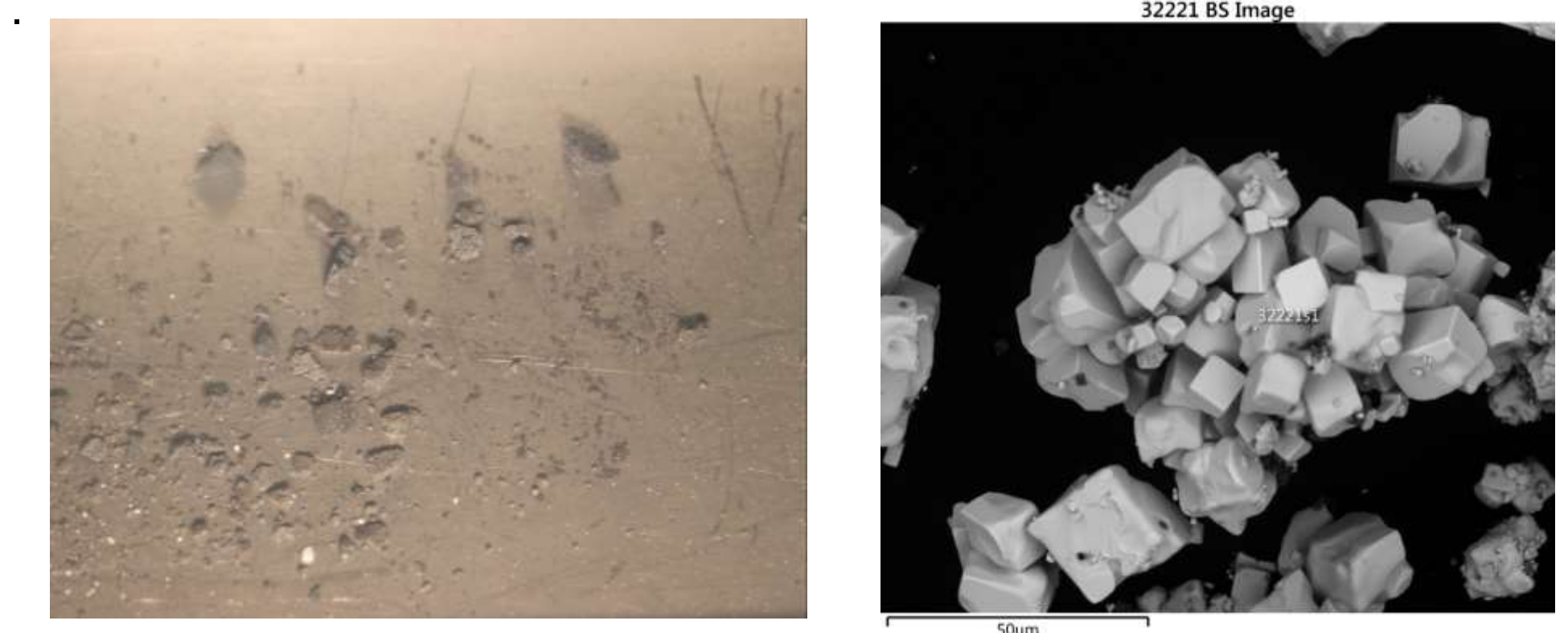
The reaction product produced from UF_6 reaction with ammonia at 200°C (Left) and 300°C (right)



SEM micrographs of the ammonium uranium fluoride compounds produced by reaction of UF_6 with NH_3 .

Stage 2: Ammonium-Uranium-Fluoride Reaction with Ammonia (~800°C)

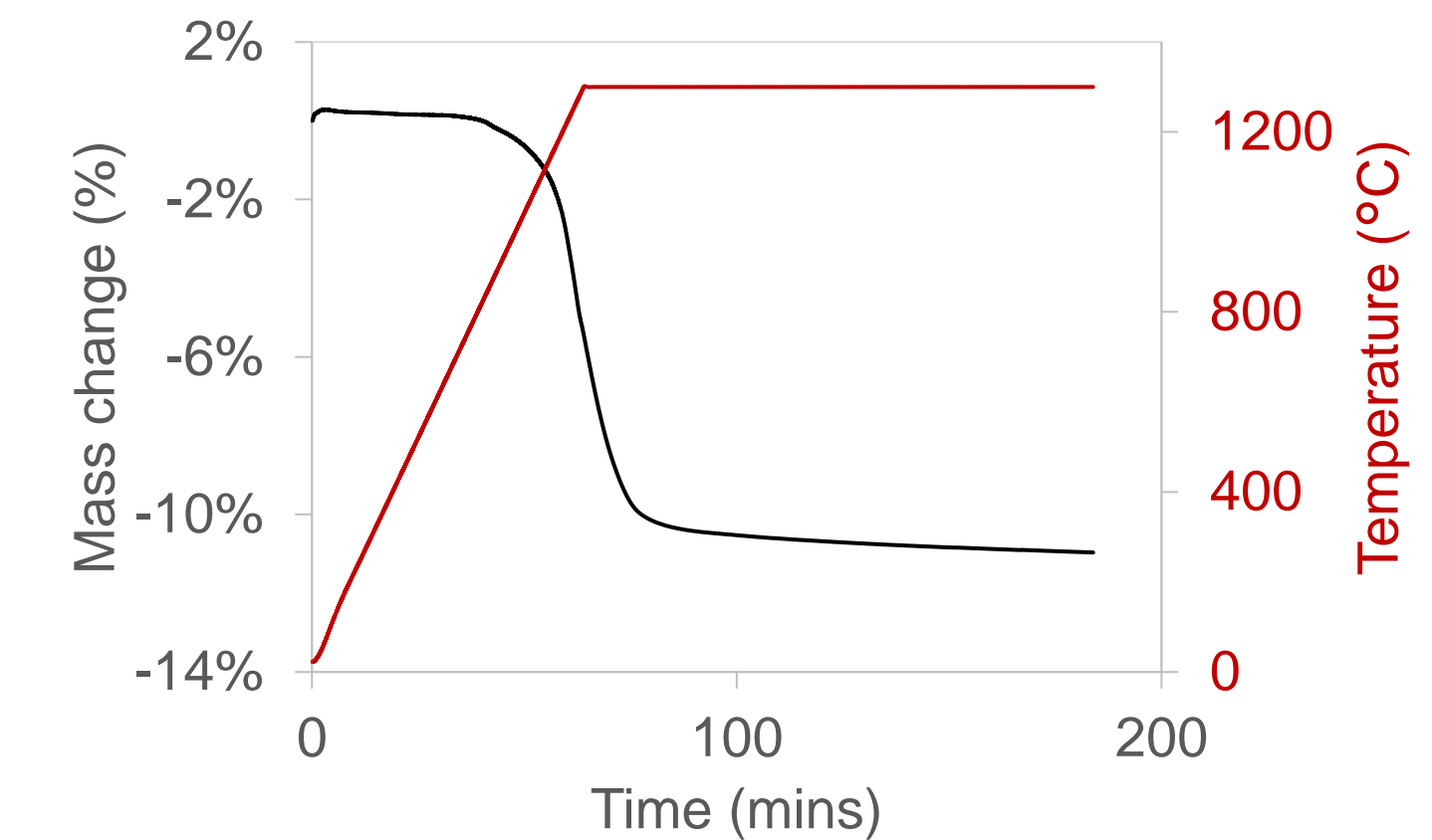
The second stage is the reaction of the intermediate ammonium uranium fluoride with ammonia at high temperature (approximately 800°C). This produces nitrogen rich uranium nitride compounds such as U_2N_3 or UN_2 and off gasses of ammonium fluoride and hydrogen.



Reaction product produced from ammonium uranium fluoride reaction with ammonia at 800°C (Left) and a micrograph of the U_2N_3 crystalline particles (right).

Stage 3: Reduction to uranium mononitride

The final stage is to reduce the nitrogen rich uranium nitride compound to uranium mononitride (UN) using a heat treatment. The product is heated in argon to 1300°C which removes excess nitrogen.



Thermogravimetric trace showing the reduction of U_2N_3 to UN.

Acknowledgement

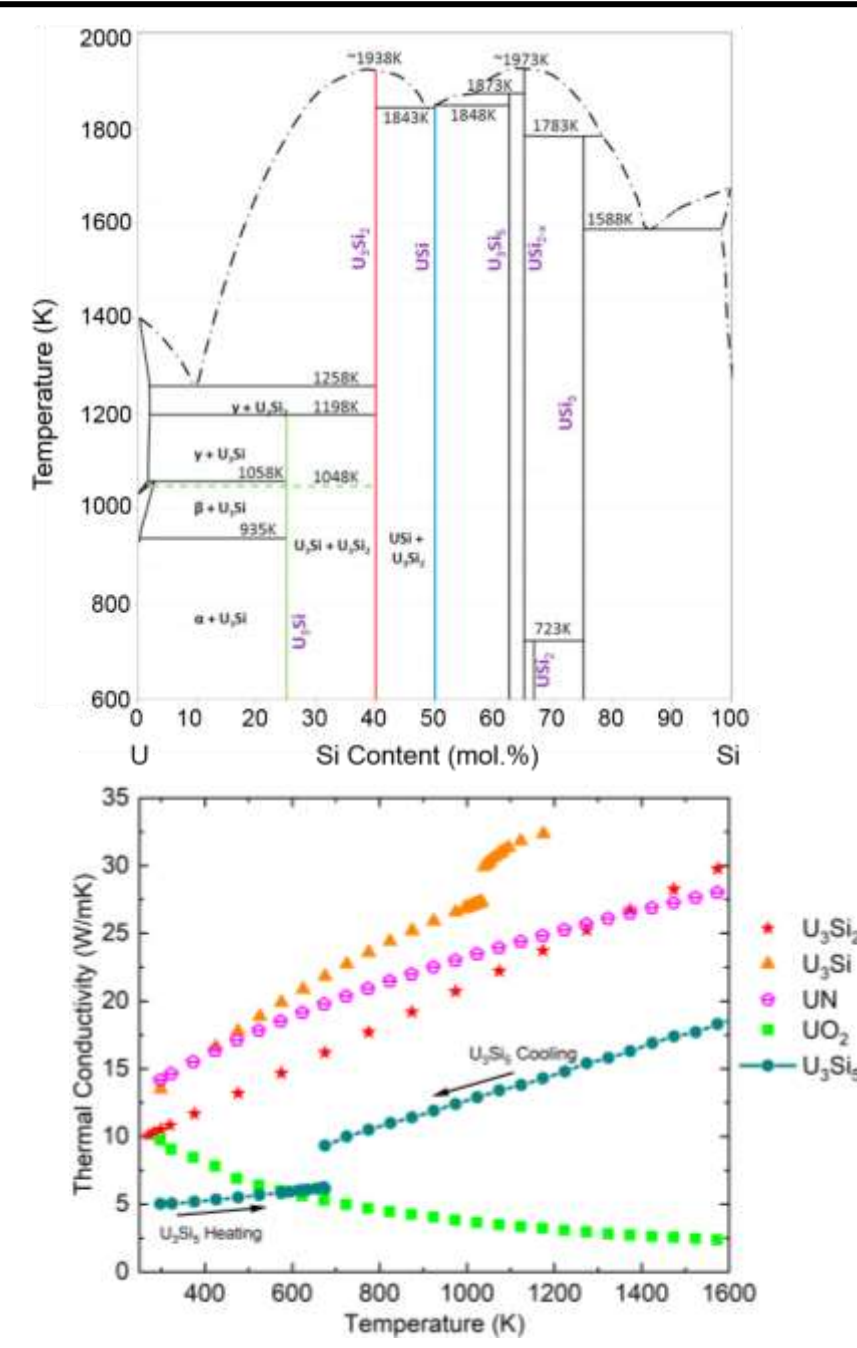
This research was initially funded under the £46m Advanced Fuel Cycle Programme (AFCP) as part of the Department for Business, Energy and Industrial Strategy's (BEIS) £505m Energy Innovation Programme. Research is continuing under the BEIS funded, Westinghouse led, Advanced Modular Reactors (AMR) Feasibility and Development Project.

Introduction

The 2011 Fukushima Daiichi Nuclear Power Plant accident revealed the limitations of the current UO₂-Zirconium alloy system. Following this, efforts have been made to improve the overall safety and economic of light-water reactors (LWRs). Uranium silicide phases, U₃Si, U₃Si₂, and U₃Si₅, have all been identified as **advanced technology fuels (ATFs)** due to enhanced thermal capabilities. Understanding the corrosion behaviour of these compounds is vital if they are to be implemented into the nuclear fuel cycle.

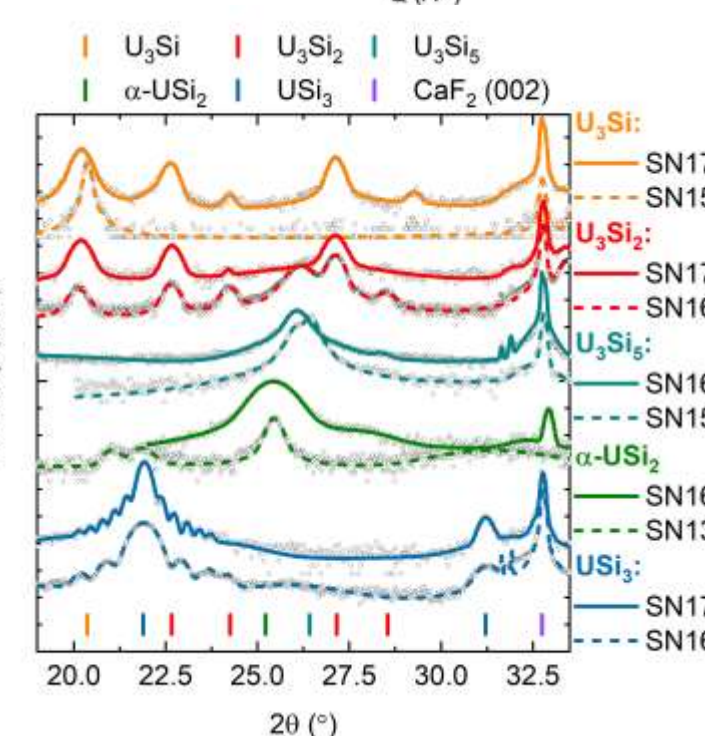
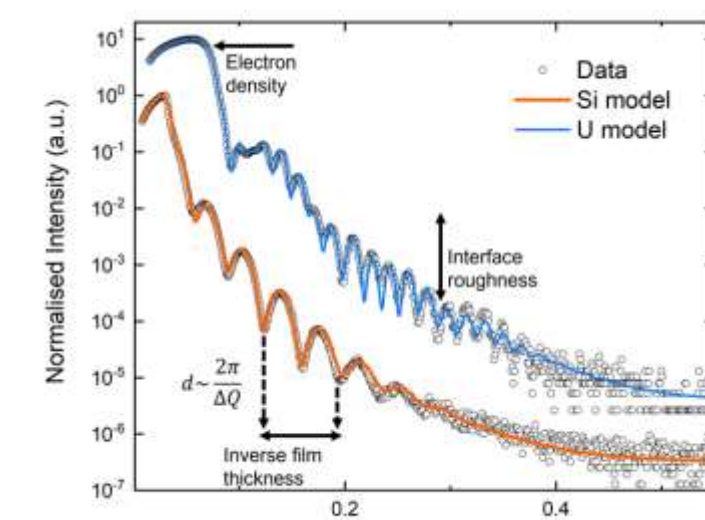
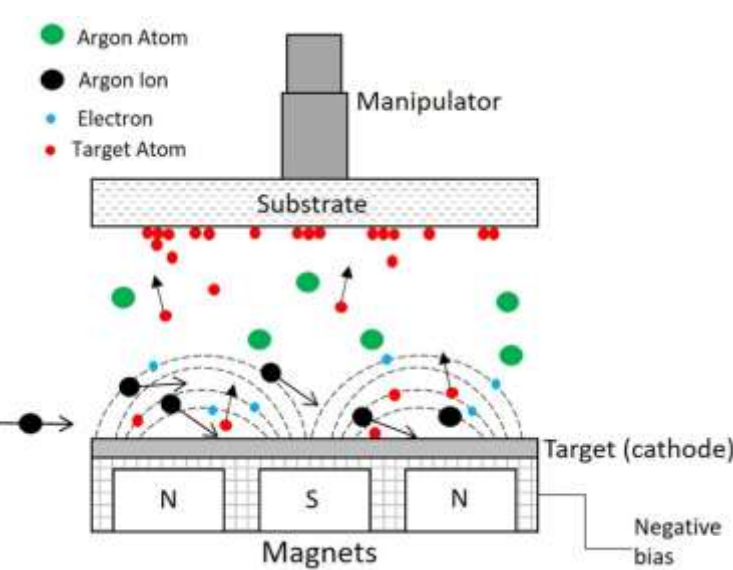
The uranium silicide phases have been utilised as nuclear fuels since their implementation into the RERTR Program in 1988^[2] as low-enriched uranium fuels (LEU) within test reactors. Therefore, these phases exist as spent nuclear fuels (SNF) which will require eventual disposal. There is a clear requirement that the dissolution processes of each uranium silicide phase must be understood.

Figure:(top) Binary phase diagram of uranium and silicon, taken from [1], (bottom) thermal conductivities of ATFs with comparison to UO₂



Sample Synthesis

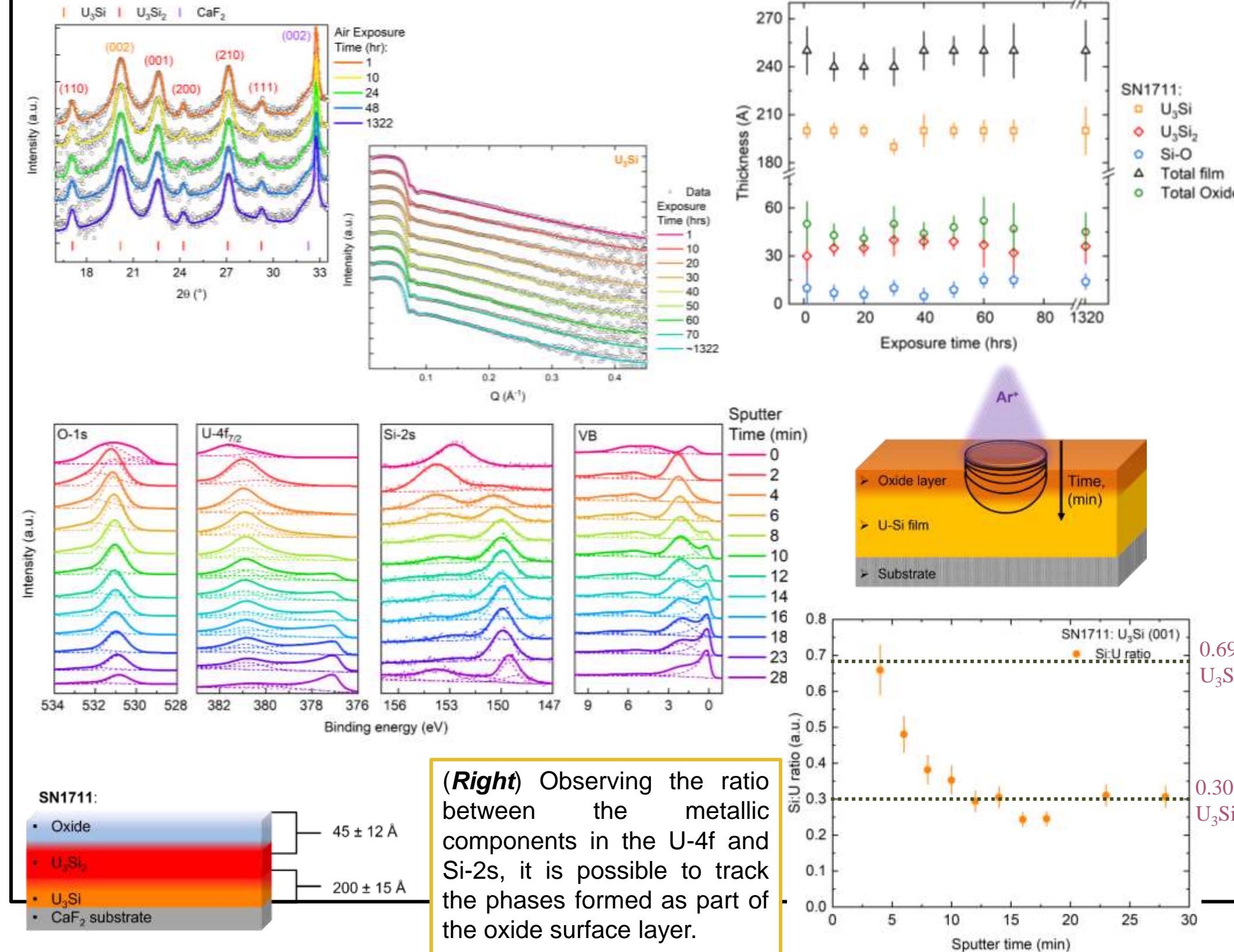
Single crystal, thin films of uranium silicide phases including, U₃Si, U₃Si₂, α-USi₂, and USi₃ were grown via DC magnetron co-sputtering from separate uranium and silicon target materials. These samples have been used to investigate the ambient oxidation of U-Si compounds as a function of silicon content. U₃Si₂ was engineered as a polycrystalline thin film. All phases were stabilised upon [001] CaF₂ substrates.



The ability to reproduce epitaxial U-Si thin films was possible through the use of DC magnetron sputtering. The figure to the right indicates the high angle XRD spectra collected from pristine (dotted line) and oxidised (straight line) U-Si thin films.

Oxidation Results

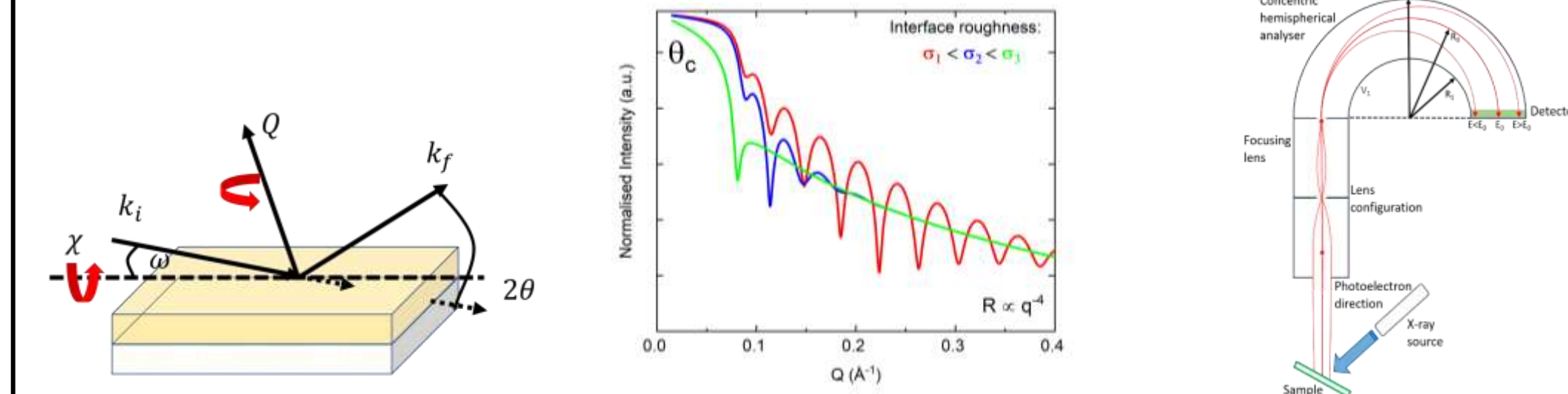
Through modelling data collected from **epitaxial U-Si surfaces** using XRD, XPS, and XRR, we can build up a comprehensive picture of the change in phase, structure, chemistry, and oxide thickness as a result of ambient oxidation. Data collected from (001) U₃Si presented below.



(Right) Observing the ratio between the metallic components in the U-4f and Si-2s, it is possible to track the phases formed as part of the oxide surface layer.

Experimental Techniques

The behaviour of U-Si phases within ambient atmospheric environments was probed using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR). XRD and XRR were used to characterise the structural changes inflicted on each U-Si phase as a result of ambient oxidation. A vast array of information can be obtained using these two techniques, including: composition, layer thickness, interfacial roughness and electron density profile. XPS provides information about the local electron bonding environments within each oxidised compound, allowing for the native oxide of each uranium silicide to be probed.

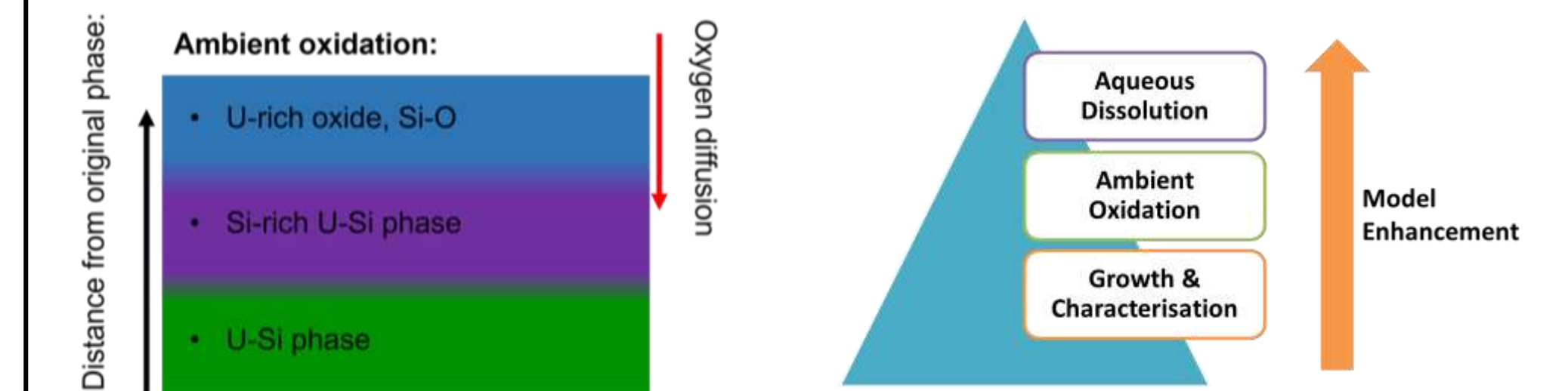


Conclusions

Using DC magnetron sputtering, U-Si phases were stabilised as epitaxial thin films. These engineered compounds provided idealised surfaces on which oxidation experiments could be conducted. Initially, the ambient oxidation was probed using XRD, XPS, and XRR techniques. This enabled the structure, chemical bonding and oxide thickness (**Table 1**) to be extracted from each sample. It was found here that the uranium sites have a higher affinity to oxygen uptake, resulting the formation of Si-rich U-Si compounds within the oxide (**below**).

Phase	Oxide Thickness (Å)	Oxide Compounds
U ₃ Si	45 ± 12	U ₃ Si ₂ , Si-O, U-O
U ₃ Si ₂	30 ± 5	U ₃ Si ₂ , Si-O, U-O
U ₃ Si ₅	110 ± 12	USi ₂ , Si-O, U-O
α-USi ₂	63 ± 5	USi ₃ , Si-O, U-O
USi ₃	50 ± 2	USi _{3+x} , Si-O, U-O

This multi-technique approach was applied to investigating the ambient oxidation of each stabilised uranium silicide phase (U₃Si, U₃Si₂, U₃Si₅, α-USi₂, USi₃). Tracking the Si-2s and U-4f metallic components from the XPS depth profile, it was possible to identify compounds that had formed within the oxide layer. Building this base model for the oxidation of U-Si phases, which extend across the phase diagram, it is now possible to further enhance the model, through adding more complex scenarios: *high temperature, pH, aqueous corrosion, steam*.



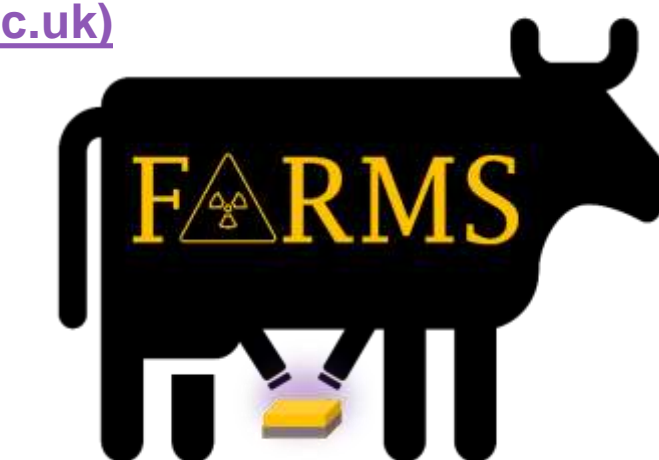
References

- [1] S. Middleburgh et al., JNM, 2015
- [2] A. Travelli., The RERTR Program, 1992

Acknowledgements and Contacts

Acknowledgements to: Jude Laverock (NanoESCA Facility Manager, University of Bristol) for XPS measurements.

For NNUF FARMS queries email: nnuf-farms@bristol.ac.uk or visit: [FaRMS | National Nuclear User Facility \(nnuf.ac.uk\)](http://FaRMS | National Nuclear User Facility (nnuf.ac.uk))



Introduction

Uranium Nitride



High thermal conductivity (15,8 W/m.K at 1000 K).



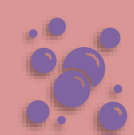
High melting point (2830-2850°C)



Uranium density of 13.5 g/cm³



Capable of running at lower operating temperatures



Reacts with water at elevated temperatures

Uranium nitride is an advanced technology fuel with preferable fuel economics and performance compared to conventional UO₂.

The main drawback of UN for use in LWRs is its rapid oxidation in steam or water environments, this results in pulverization of the pellet, as seen in Fig 1.



Fig1. Pulverised UN fragment

Aim and Objectives:

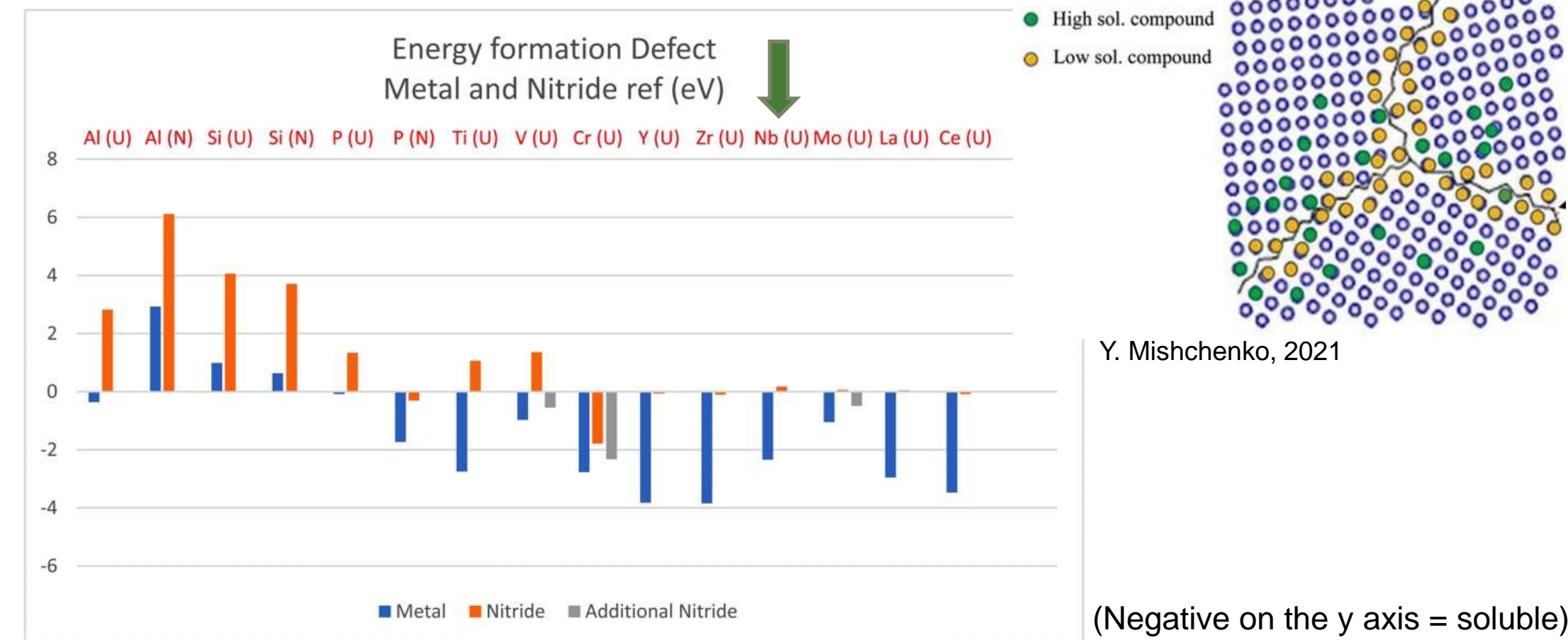
Aim:

To investigate methods for improving water tolerance of Uranium Nitride through use of dopants.

Objectives:

- Synthesise UN via the hydride-nitride-denitride route, utilising capabilities through AFCP.
- Fabrication of UN and UN-Nb pellets of differing Nb concentrations.
- High temperature water vapour tests on fragments of each pellet.
- Microstructural analysis using optical and electron microscopy.
- Phase examination using XRD analysis and EDS mapping.

Method



Additives were largely chosen on if they would be soluble in UN. If soluble, it is possible the rate of oxygen diffusion could be slowed down. If insoluble, the grains can be protected. DFT solubility calculations by Y.Mishchenko, 2021 as shown above, leave a number of candidates to be chosen from.

Niobium was chosen due to its strong solubility in the UN matrix. Additionally, a thermodynamic assessment of Nb has shown it not to take any nitrogen from the UN leaving uranium metal behind.

Final pellets fabricated using Spark Plasma Sintering (with densities)

UN	UN-2.5Nb	UN-10Nb	UN-20Nb
95%	93%	97%	95%

Results

Microstructural analysis results:

Figure 2 shows UN in light gray and the Nb being a darker shade, with signs that an interaction has occurred where the niobium is present, but still in discreet regions.

During sintering a phase of U-N-Nb was detected and confirmed by EDX analysis. Notably, some interaction has occurred but does not seem to be complete.

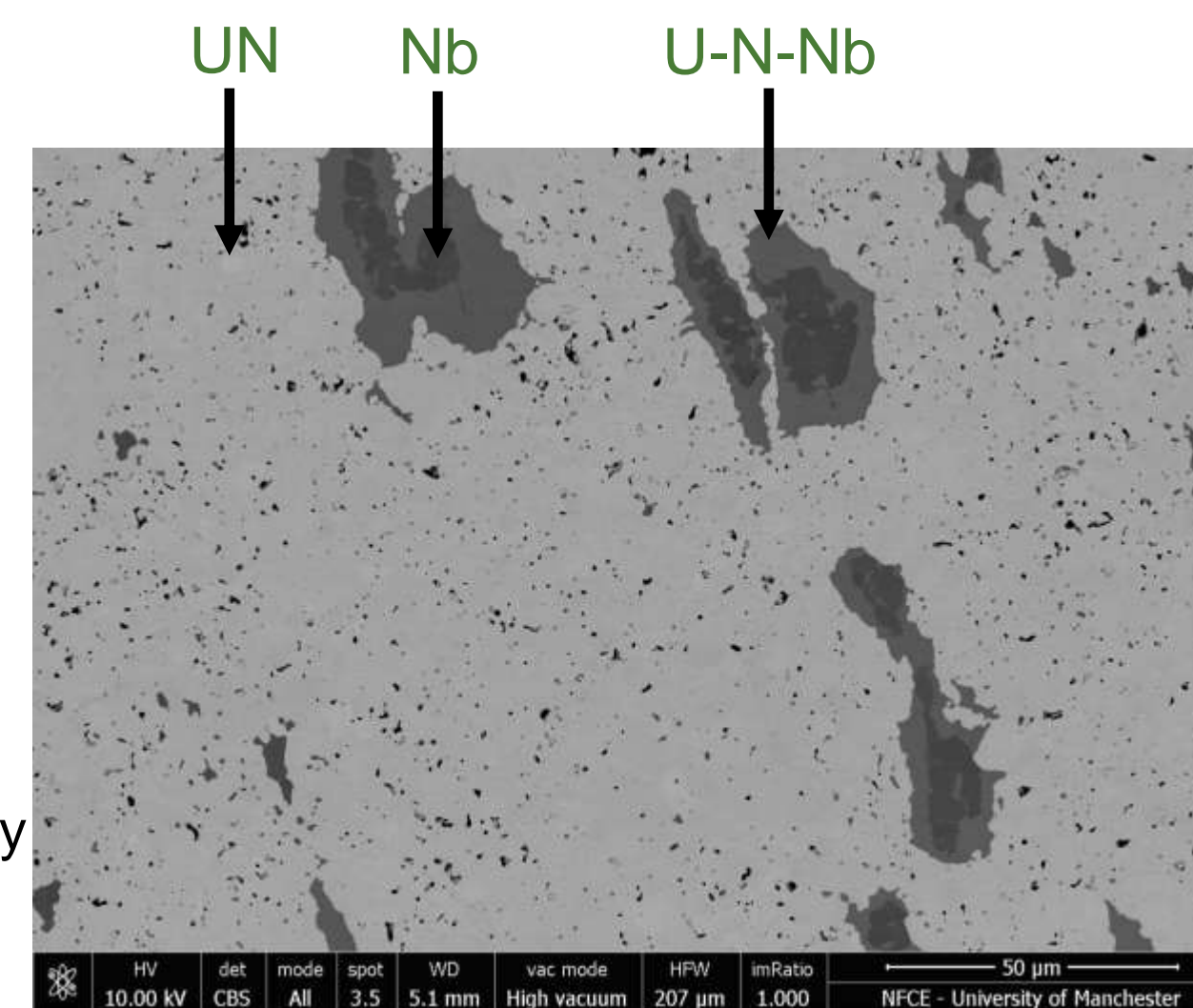
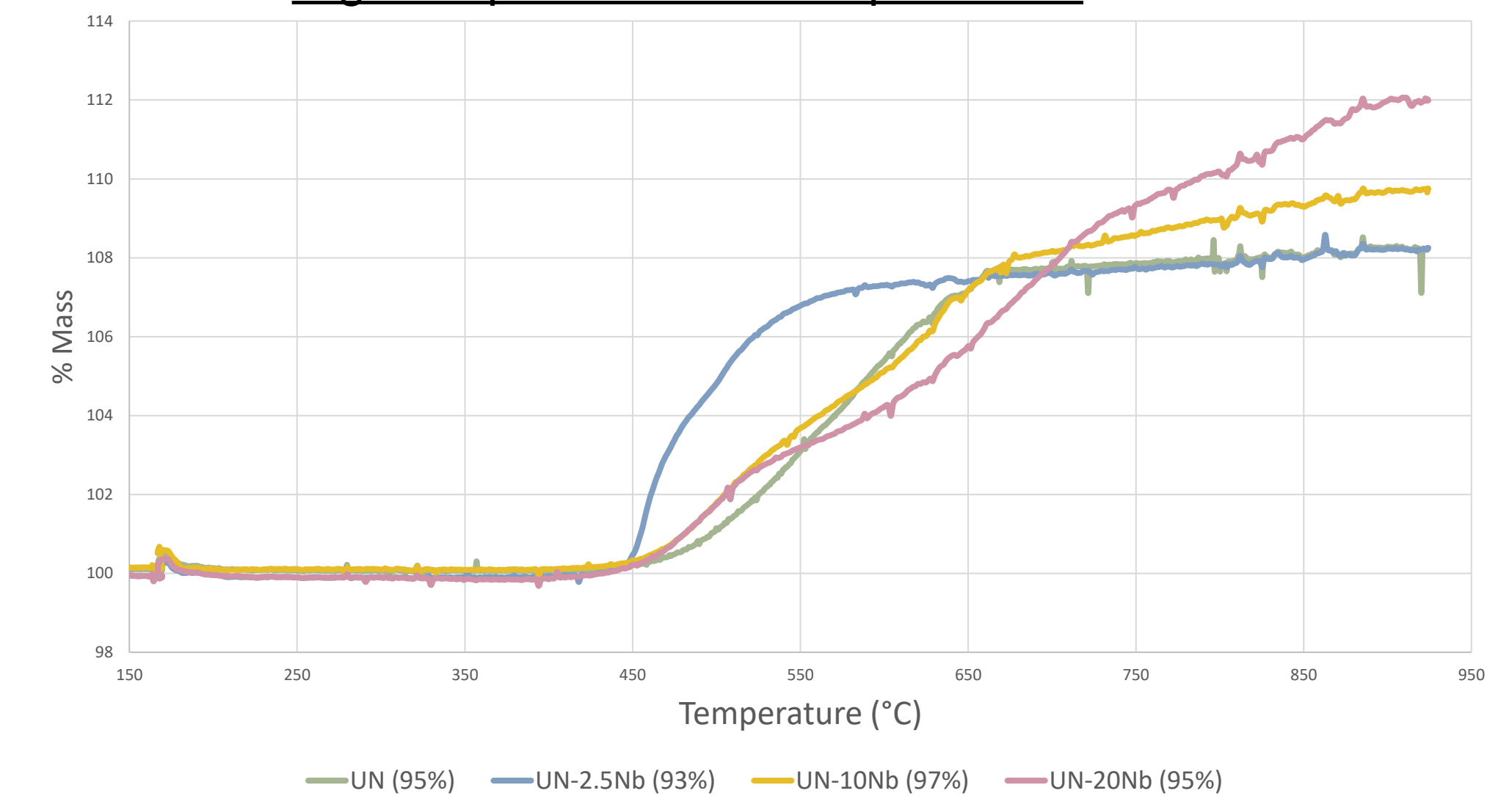


Fig 2. Micrograph of UN-10Nb pellet

High temperature water vapour tests



The graph above represents how the mass of each pellet changed during the water vapour oxidation, ranging from 150°C to 900°C.

The results show very small amounts of changes to the oxidation onset temperature between the samples, with the 2.5%Nb performing the worst, this could be a consequence of its low density. They did however show variation in reaction times and multiple stages in the reactions.

Conclusions

- UN-Nb composite pellets were successfully fabricated via SPS with high densities.
- Interaction between UN and Nb observed, with a phase of U-N-Nb detected.
- Nb showed no change to the oxidation onset temperature but did affect the reaction kinetics.
- The study has also offered an insight into niobium's incorporation within UN.

References

Y. Mishchenko, K. D. Johnson, J. Wallenius, and D. A. Lopes, "Design and fabrication of UN composites: From first principles to pellet production," *J. Nucl. Mater.*, vol. 553, p. 153047, 2021, doi: 10.1016/j.jnucmat.2021.153047.

Contact details and Acknowledgements

- Yulia Mishchenko and Denise Adorno Lopes at KTH for collaboration on additive selection.
- Colleagues at The University of Manchester for helping with the setup of the experimental equipment, training and understanding of UN.
- This work was funded under the £46m Advanced Fuel Cycle Programme as part of the Department for Business, Energy and Industrial Strategy's (BEIS) £505m Energy Innovation Programme.

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INTRODUCTION

The drive for change in nuclear fuel design is towards accident tolerance, which specifically relates to the absence or delay of high-temperature clad oxidation by coolant. Any replacement for UO_2 fuel must offer a combination of safer operation with lower fuel cycle cost; either longer cycles or lower enrichment. The candidate material that offers the greatest combination of these properties with the potential for industrial scale-up is currently uranium mononitride, UN. However, there is a major behavioural draw-back in that water and, more importantly, high temperature water/steam during operation, is significantly more corrosive to UN than to UO_2 oxide fuel currently employed in water moderated reactors. This PhD project will specifically address the two key issues that are driving research of accident tolerant fuels (ATF): thermal conductivity degradation and corrosion behaviour, with the main focus on the fuel-water interaction.

UN is an advanced technology fuel (ATF) that is touted for improvements in thermal conductivity and fissile density when compared with the common uranium dioxide (UO_2) fuel. Previous work at the University of Bristol suggested that whilst UN corrodes faster in water the radiolytic products in a nuclear reactor are much more corrosive [1] but previous polycrystalline UN films exposed to 0.1 M H_2O_2 had a lower reduction in film thickness than UO_2 [2].

A dopant added into uranium nitride acts as an effective corrosion inhibitor and as such it may be possible to reduce the thickness reduction rate further. A good dopant will form a stable oxide that passivates across the fuel surface in a wide range of pH and therefore prevent the easy corrosion of the uranium nitride fuel.

OBJECTIVES & METHODS

The work employs thin films which are 50 nm sputtered thin film samples. Sputtering is done using DC Magnetron Sputtering and by varying power, pressure and temperature it is possible to make ideal samples with selective properties including composition and orientation.

Comparison will be made by adding different dopants into the uranium-nitride system to study the effect of the dopant on the crystal lattice and the effect on corrosion degradation. Candidate materials include chromium, titanium and vanadium, with the current batch having used niobium, a metal that forms a stable oxide, Nb_2O_5 .

Corrosion will be completed in 3 different ways; by high temperature water, high temperature steam and by hydrogen peroxide, with samples analysed by X-Ray Reflectivity (XRR) to assess degradation of the sample structure. Chemical characterization by XPS, SEM-EDX and TEM will provide necessary information on how the dopant addition alters the crystal.

X-RAY REFLECTIVITY (XRR)

X-ray reflectivity (XRR) is a surface sensitive technique that is a form of reflectometry. The basic principle is the reflection of a beam of X-rays from a flat surface to then measure the intensity of the x-rays reflected in a specular direction, shown by the red arrow in **FIG. 1**. If the interface is not perfectly sharp and smooth then the reflected intensity will deviate from Fresnel's law of reflectivity and can then be analysed to obtain film thickness, a density profile and surface or interface roughness.

FIG. 2 is a schematic of how increasing the angle of incident X-rays leads to penetration of the film to give a specularly reflected wave of 2θ . Above the critical angle the reflected intensity begins decreasing with the reflectivity curve produced formed as a combination of Fresnel reflectivity and an interference pattern, called Kiessig fringes [3], from the scattering from different layers.

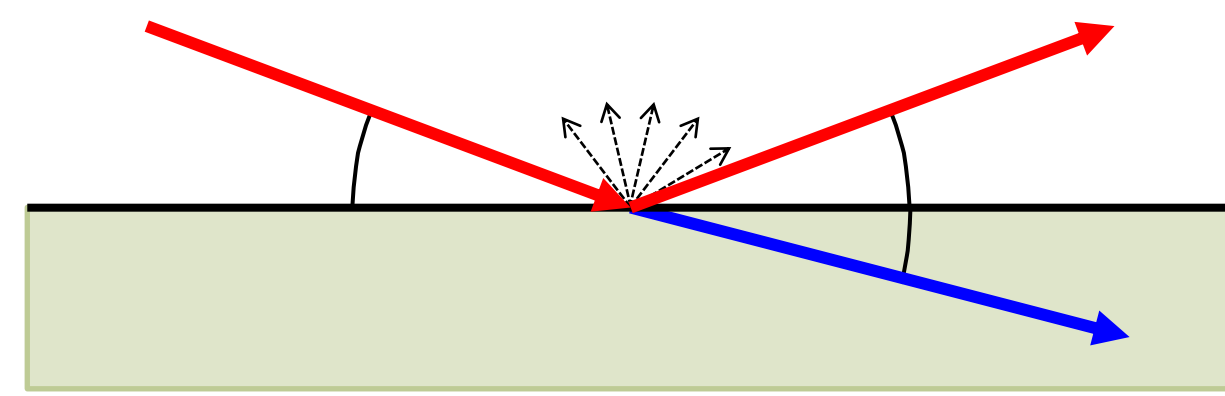
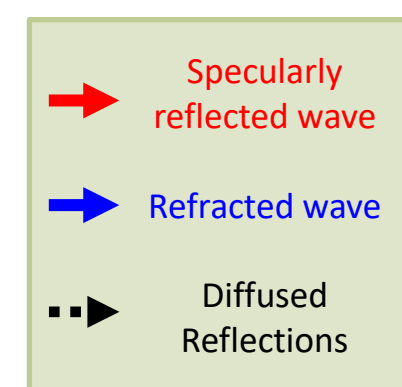


FIGURE 1: The principal of X-ray reflectivity on a surface with an incident beam of X-rays strikes a surface to produce a specularly reflected wave (red), a refracted wave through the material (blue) and diffused reflections (black) from off-specular reflectivity.

RESULTS

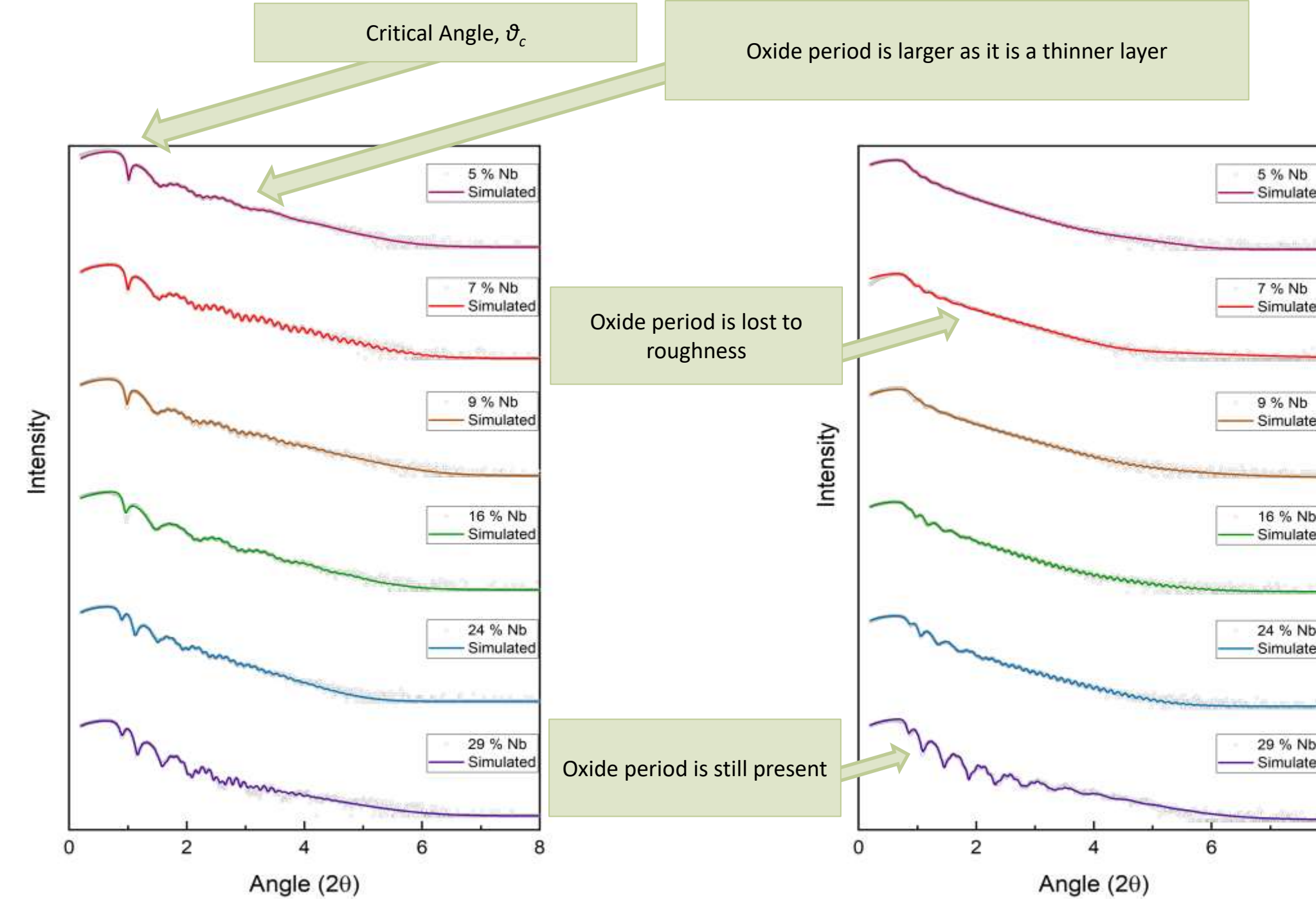


FIGURE 3: X-ray reflectivity curves of 6 niobium doped uranium mononitride with increasing niobium atomic percentage.

3a (left): When first made

3b (right): After passively oxidizing in room temperature air for 2 months.

The X-ray reflectivity curves in **FIG. 3a** and **FIG. 3b** are for the same niobium doped samples immediately after they were made (Left) and after being left to passively oxidise for 2 months (Right). The oxide layer for these samples appear as a larger peak compared to the nitride layers which have a higher frequency. It is therefore noticeable that for the high niobium content samples (24% and 29%) the oxide period is still visible which suggests a much more stable oxide has formed on the surface. The disappearance of the peaks in lower content samples is due to the varied rate of oxide formation increasing the roughness of the sample.

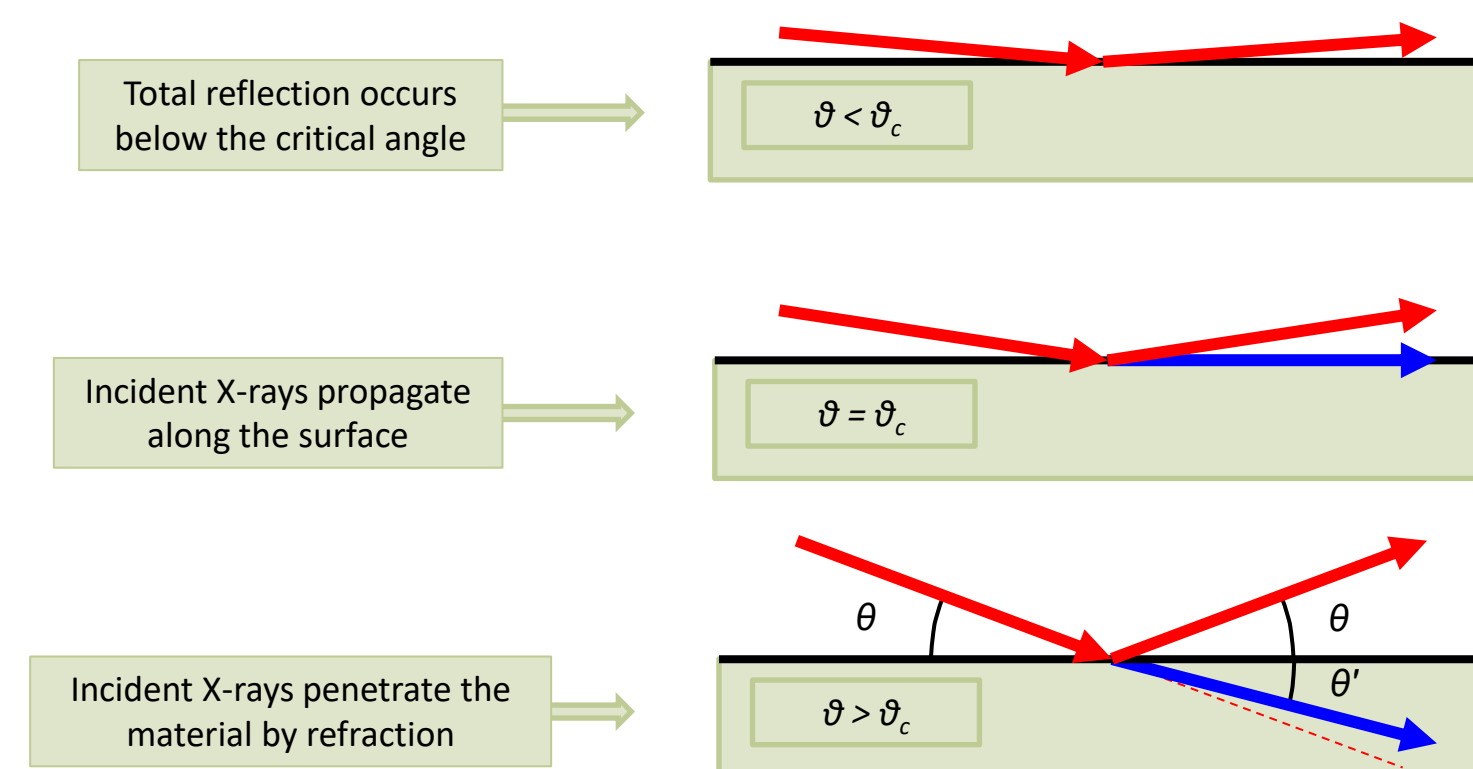


FIGURE 2: The critical angle of a material is the point where the incident x-rays propagate across the surface. Below this angle there is total reflection and above there is penetration and refraction.

X-ray diffraction (XRD) of the uranium nitride samples in **FIG. 4** illustrate an increase in 2θ angle as a higher gun power for niobium was used. The increased sputtering power of niobium leads to a higher atomic percentage of the atom within the system and the shift to a higher angle indicates that the crystal structure is becoming smaller as is confirmed in **FIG. 5**.

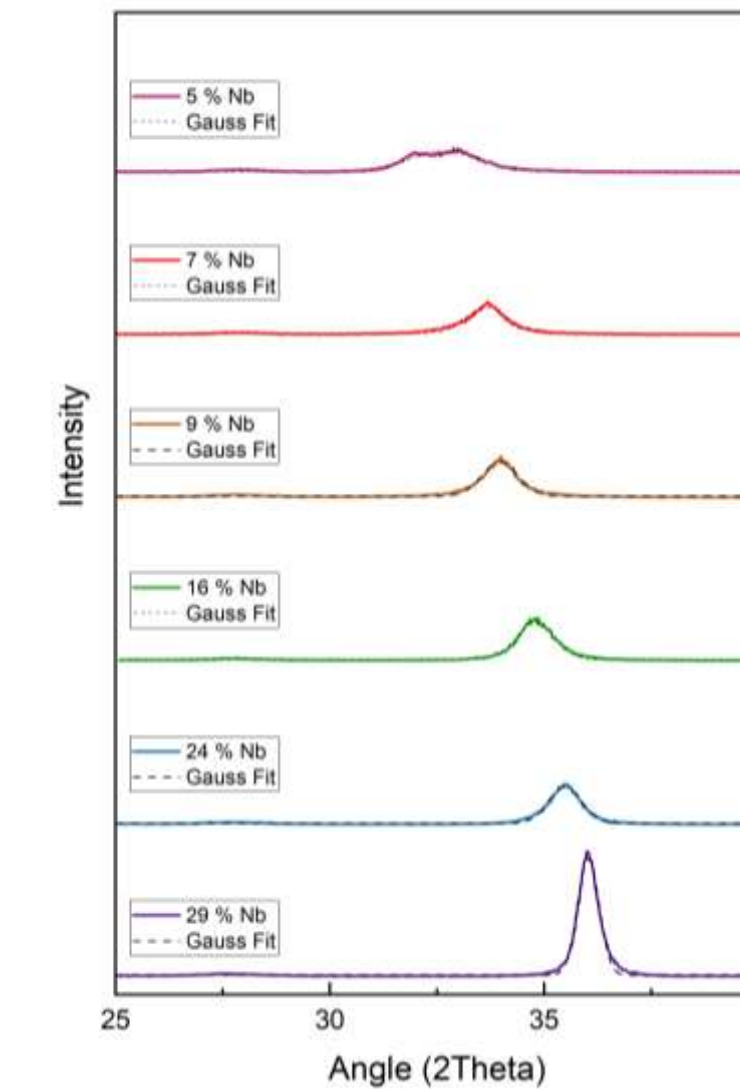
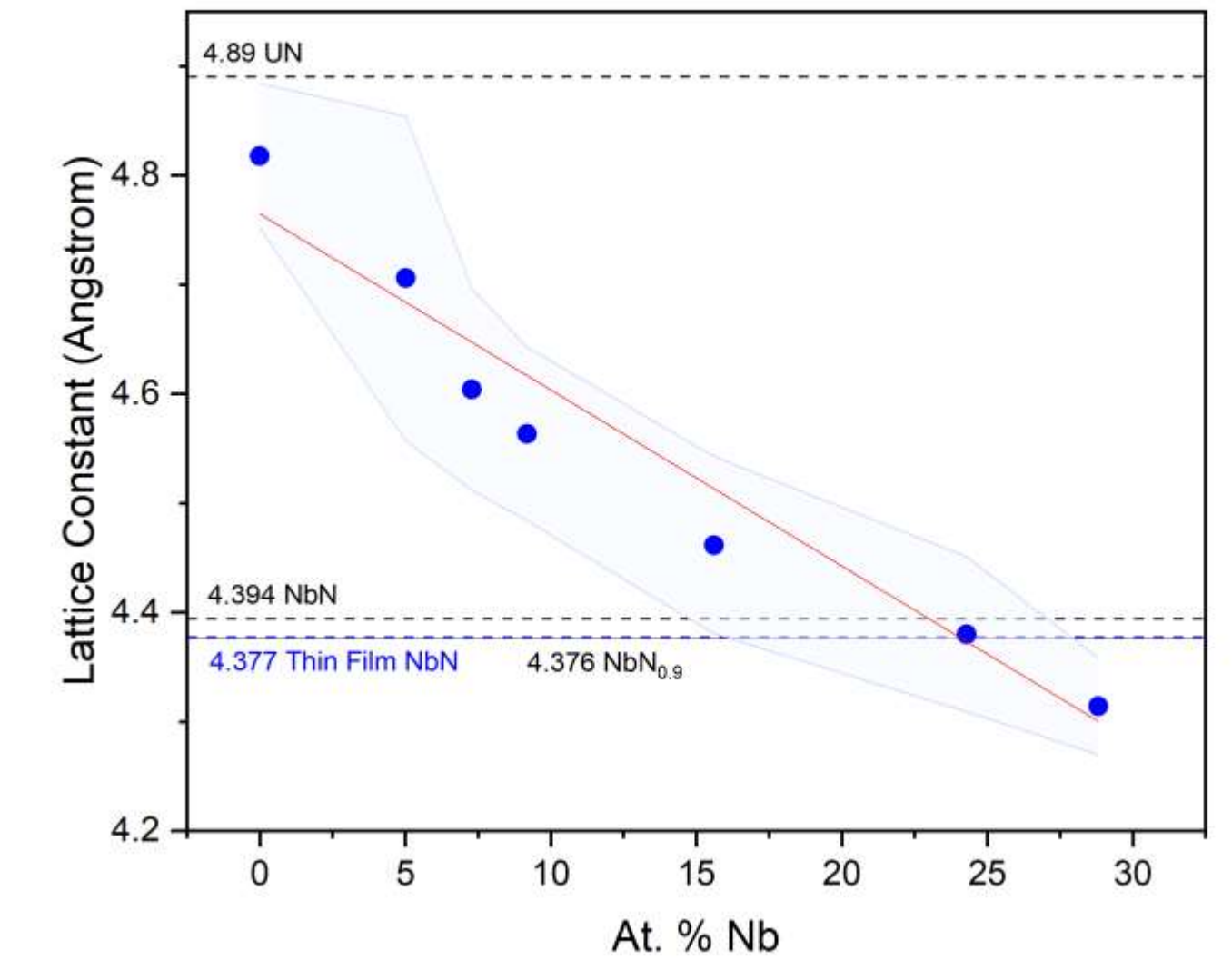


FIGURE 4 (left): X-ray diffraction of 6 niobium doped uranium mononitride with increasing niobium atomic percentage. **FIGURE 5 (right):** Lattice constant decreases with increased atomic percentage niobium. Literature UN is 4.89 Å and literature $NbN_{0.9}$ is 4.376 Å.



It had been predicted that the lattice would shrink in size as the expectation was that the smaller niobium atoms would replace the large uranium atoms. UN has a lattice parameter of 4.89 Å [4] and the shrinking of the lattice shown in **FIG. 5** should be occurring at a much slower rate as when the sample is 100% niobium in a nitrogen atmosphere it was expected to be NbN. However, the lattice parameter of NbN is 4.394 Å [5] or 4.376 Å for the non-stoichiometric $NbN_{0.9}$ [5] and the results see that the 24% Nb is already at this position.

CONCLUSIONS

The work completed so far suggests that crystal lattice formed by co-sputtering is more complex than initially thought. To understand the chemical bonding of the system XPS will be used to determine the covalency of the system. It is natural for crystal structures to have point defects where an atom is missing from a site so analysis by XPS should determine if this is occurring at what rate as niobium is added in larger quantities.

By growing single crystal thin films, it would allow comparison of off-specular reflectivity peaks like those in **FIG. 6a** and **FIG. 6b**. Finding these will give a clear indication of crystal that has been formed.

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- [1] R. Springell, et al., Faraday Discuss., 180 (2015) 301. [2] E. Lawrence Bright, et al., Thin Solid Films 661 (2018) 71. [3] H. Kiessig., Ann. Phys. 10 (1931) 36. [4] R. E. Rundle, et al., J. Am. Chem. Soc. (1948) 70, 1, 99–105. [5] A. N. Christensen., Acta Chemica Scandinavica, Series A: Physical and Inorganic Chemistry (1977) 31, 77-78.

ACKNOWLEDGMENTS

University of Bristol: Ross Springell, Lottie Harding, Jacek Wasik, Rebecca Nicholls, Jarrod Lewis
National Nuclear Laboratory: Dave Goddard

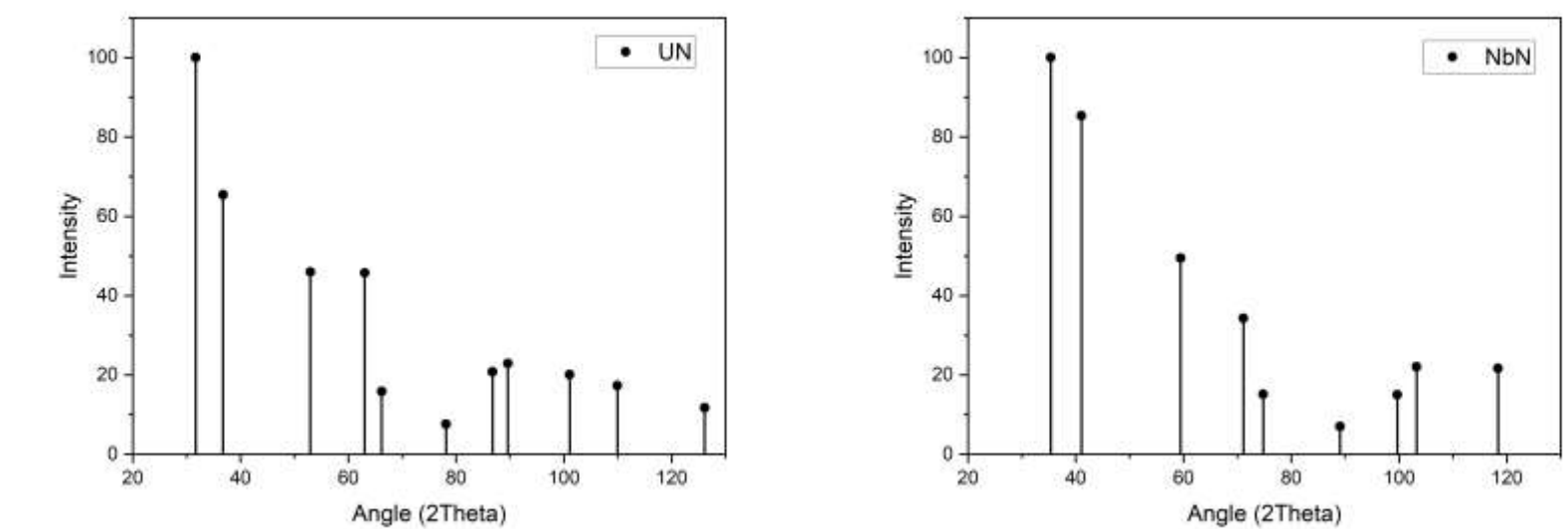
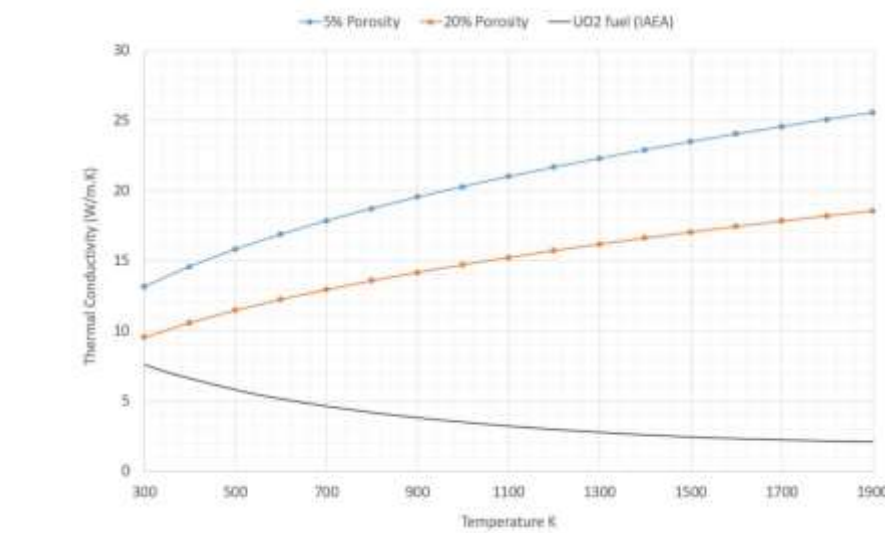


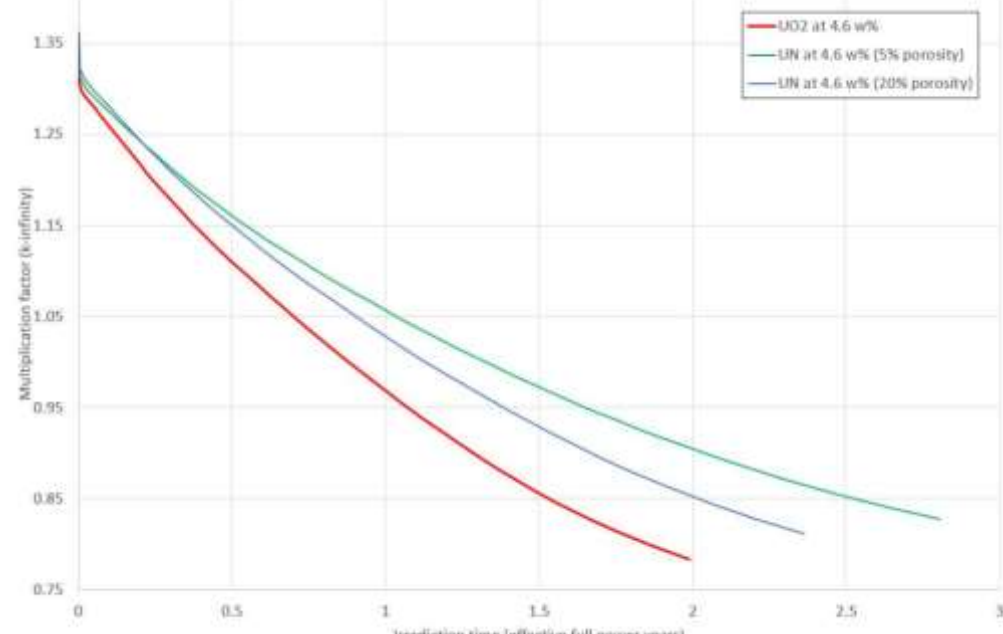
FIGURE 6: Off-specular peaks should be visible at multiple angles for single crystals. **6a (left):** UN off-specular peaks **6b (right):** NbN off-specular peaks.

Introduction – why develop UN fuels for PWR application?

- Beneficial thermal properties can significantly improve fuel performance during frequent and infrequent faults
- Higher fuel density can extend cycle length, significantly improving plant economics (higher load factor)



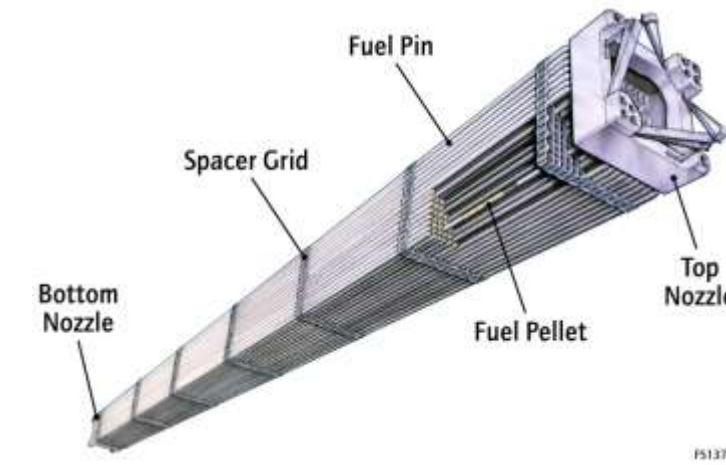
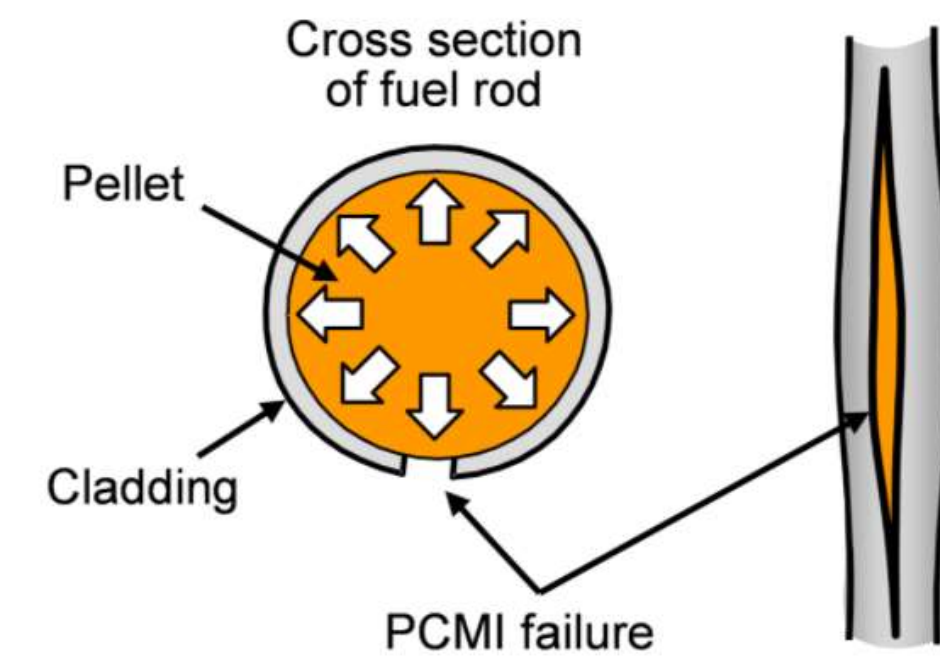
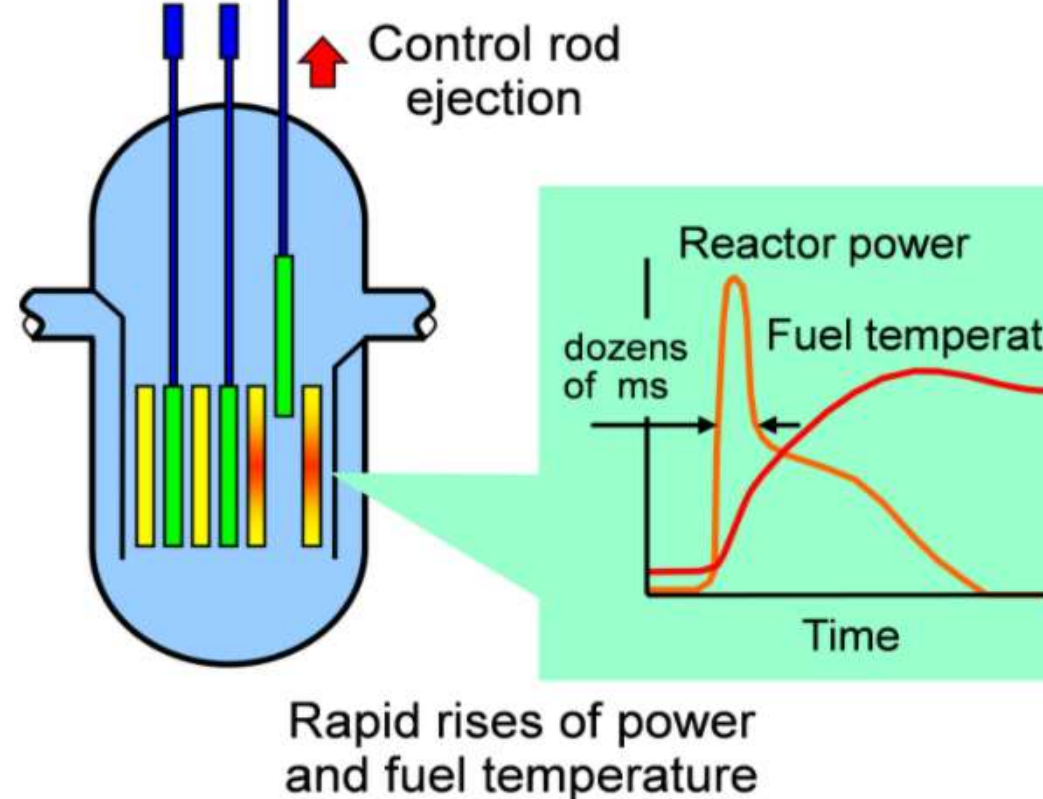
Thermal conductivity for UN and UO₂ fuels. Higher values reduce stored heat and improve heat transfer



Fuel reactivity versus irradiation time. The shallower gradient helps extend cycle length when utilising UN

Objectives of the study

- 1/. Assess the safety and economic impact of replacing UO₂ with UN fuel in a PWR
 - assuming a mature PWR assembly and core design
- 2/. Predict core behaviour during a limiting infrequent fault (rod ejection accident (REA))
- 3/. Calculate realistic pin power histories for further fuel performance assessments during normal and fault conditions

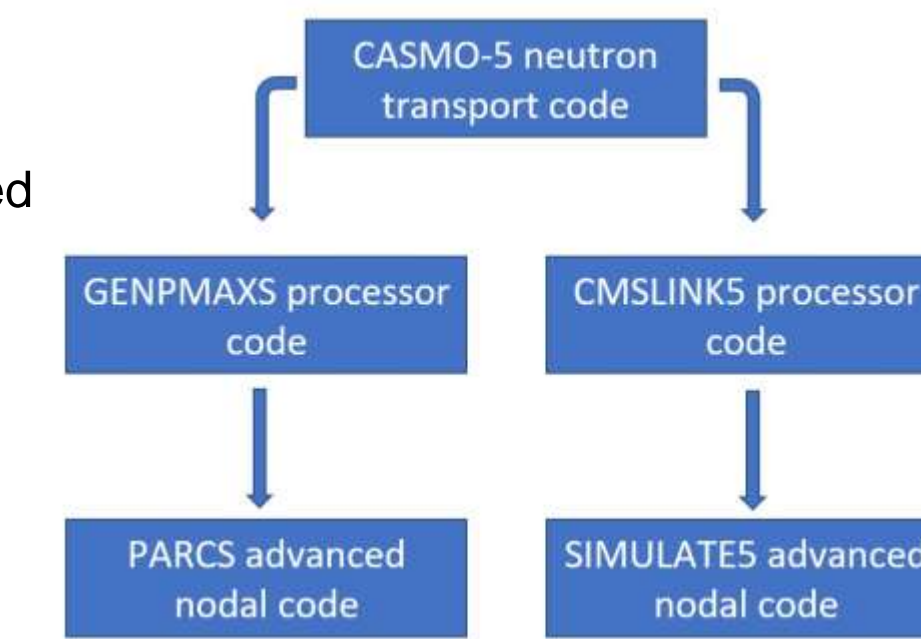


Typical (UO₂) fuel assembly and pellets (Westinghouse)

Neutronic methods used and core models developed

In order to predict core behaviour using UN or UO₂ fuel, industrial state of the art codes have been used. Optimised UO₂ PWR core developed as a comparator. Cores utilising UN at several densities, ¹⁵N enrichments and integral burnable poisons developed.

- 80% to 95% theoretical density fuels
- ¹⁵N enrichments ranging from 5% up to 99%
- Assembly designs using gadolinia doped UO₂ fuel pins or IFBA coated UN fuel pellets considered



Codes used for this study

Results

- Cycle length is strongly dependent on ¹⁵N enrichment (+1% enrichment extends cycle length by 2 days)
- Significant cycle length extensions are possible even for the lowest densities considered.
- Several safety parameters calculated including moderator temperature coefficient and boron coefficient (shown below)
- Increasing UN density adversely impacts safety parameters

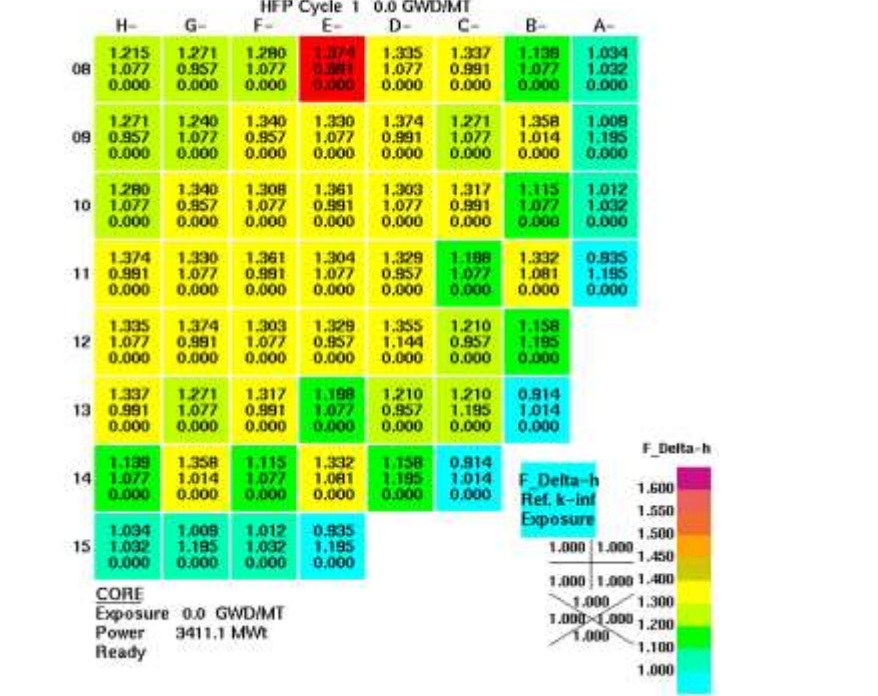
Core description	Fuel density	Cycle length (days at full power)	Moderator temperature coefficient at EOC	Boron coefficient at BOC	Shutdown margin (EOC)
UO ₂ core	95%	451 days	-66 pcm/K	-6.7 pcm/ppm	1565 pcm
UN fuel and gadolinia doped UO ₂ pins	80%	549 days (+22%)	-69 pcm/K	-5.5 pcm/ppm	2068 pcm
	85%	579 days (+28%)	-71 pcm/K	-5.1 pcm/ppm	1850 pcm
	90%	608 days (+35%)	-72 pcm/K	-4.8 pcm/ppm	1665 pcm
	95%	636 days (+41%)	-73 pcm/K	-4.6 pcm/ppm	1486 pcm
UN fuel with IFBA coating	80%	605 days (+34%)	-70 pcm/K	-5.3 pcm/ppm	1972 pcm
	85%	639 days (+42%)	-72 pcm/K	-5.0 pcm/ppm	1746 pcm
	90%	672 days (+49%)	-73 pcm/K	-4.7 pcm/ppm	1535 pcm
	95%	703 days (+56%)	-74 pcm/K	-4.4 pcm/ppm	1345 pcm

Cycle lengths for different UN fuel densities and integral poison types. Key safety parameters also displayed, with red values exceeding UO₂ safety parameter limits

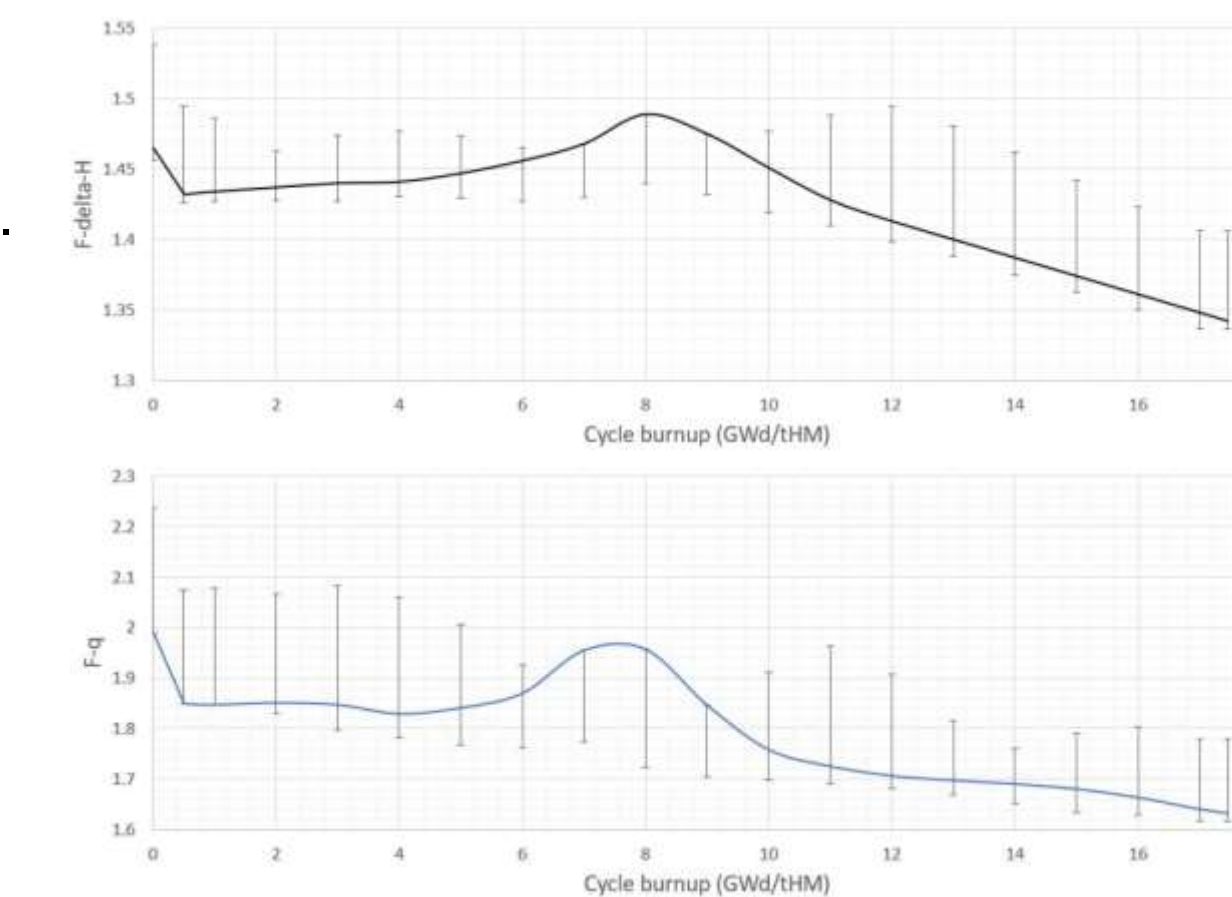
Conclusions

- Significant increases in cycle length are possible when replacing the incumbent fuel UO₂ with UN at the same enrichment
 - 22% and 34% for the lowest UN density assessed when using gadolinia and IFBA respectively
- Safety parameters for the lower UN densities considered generally within the (UO₂) limits assumed for this task.
- Neutron lifetimes are significantly lower compared with a UO₂ fuelled core, potentially adversely affecting core behaviour during a REA
- However, UN cores generally have reduced rod worths, more negative reactivity coefficients and lower heat capacities reducing REA severity.
- However, for the same reactivity insertion, a UN fuelled core is predicted to reach a higher terminal power due to a lower neutron lifetime.
- Fortunately, energy deposited during an REA will be lower primarily because deposition is insensitive to the lower neutron lifetime.
- UN will typically reach a lower fuel temperature resulting in lower fuel temperatures compared with a REA occurring in a UO₂ fuelled core.
- Fuel performance calculations are planned using output from this study, once UN models have been incorporated into NNL's ENIGMA code

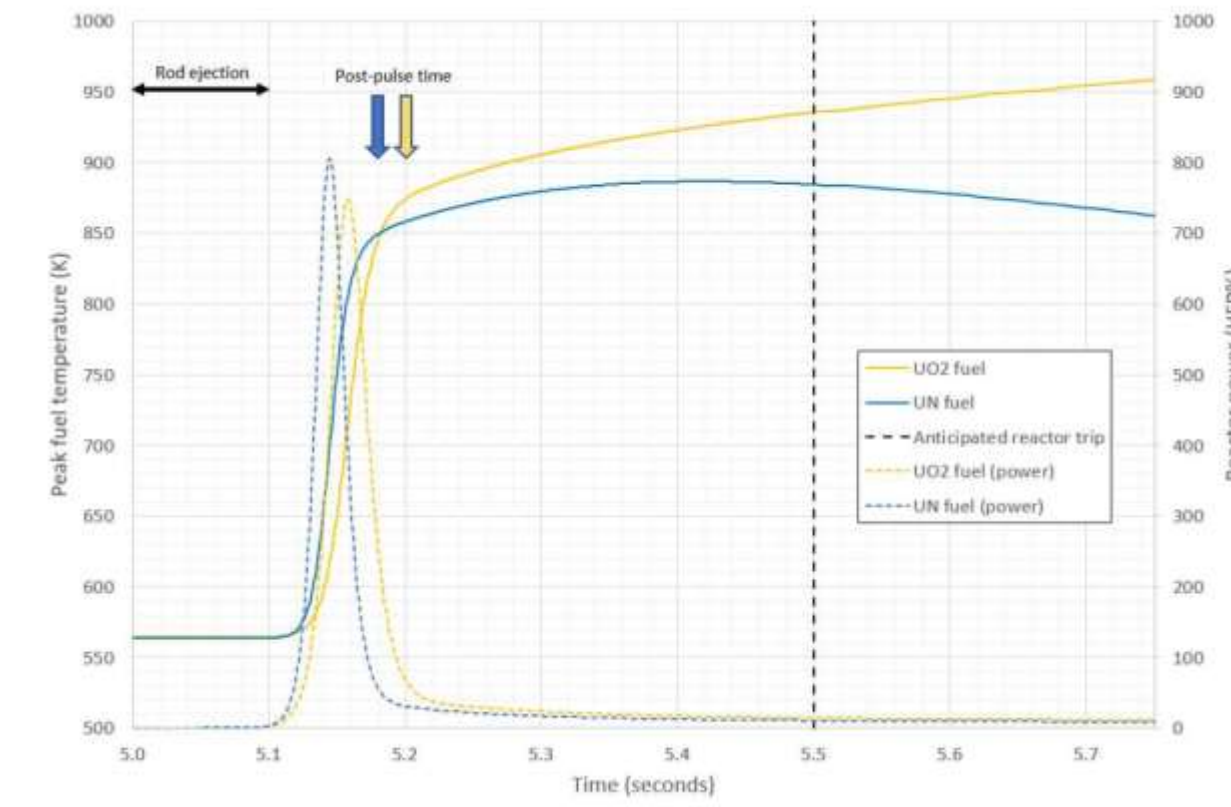
No significant issues were found that would prevent the possible use of UN fuel in a PWR. However, significant research is still required to develop a viable waterproofing technology as well as a robust fuel qualification programme involving test irradiation.



Screen capture of XIMAGE; a code available in the CMS Suite for core optimisation (Studsvik)



Power peaking vs cycle length for UO₂ and UN cores. The line plots power peaking for the UO₂ core; the uncertainty band shows the range for all UN cores considered



Core power during a limiting rod ejection accident for a UO₂ and UN fuelled core (with similar reactivity insertions of ~750 pcm)

The harder neutron spectrum in UN reduces control rod worth. Although this erodes safety margin, it also improves core behaviour during a REA.

For cases with similar reactivity insertion, higher peak powers are obtained due to shorter neutron lifetimes, but overall there is an improvement in fuel behaviour (i.e. energy deposition and peak fuel temperature) due to:

- More negative reactivity coefficient improving Doppler feedback during the initial power spike
- Lower volumetric heat capacity, enhancing Doppler feedback during the initial power spike
- Higher thermal conductivity allowing heat to dissipate at a faster rate after the initial power spike

Contact and acknowledgements

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This work was funded under the £46m Advanced Fuel Cycle Programme as part of the Department for Business, Energy and Industrial Strategy's (BEIS) £505m Energy Innovation Programme.

A REA is an infrequent fault that involves the sudden expulsion of a control rod cluster due to machinal failure. This results in a power pulse and the thermal expansion of the fuel. In severe cases this may lead to fuel clad rupture as a result of pellet clad mechanical interaction (PCMI) (jaea.go.jp)