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**The DISTINCTIVE University Consortium:
Transforming High Activity Materials Research in the UK**

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ABSTRACT

The EPSRC-supported DISTINCTIVE (Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories) consortium is a partnership of 11 research universities, working to decommission and clean up the legacy of civil nuclear energy generation. An important component of the research programme is to develop the skills and facilities to address key research questions, requiring the use of highly radioactive materials. Here we highlight the outcomes of four research projects in which access to state of the art research facilities for working with radioactive materials, supported by international partnerships, has advanced research in plutonium storage and immobilisation, and the disposal of spent nuclear fuels. First, we have developed a viable formulation and process for immobilisation of the UK plutonium stockpile, including commissioning of a radiological hot isostatic press and validation studies using plutonium-239. Second, we have further underpinned the interim storage of PuO₂, through understanding of water and chlorine sorption / desorption, pertinent to the historic practice of containment within, and degradation of PVC bags. Third, we have developed a novel methodology to investigate the *in situ* radiolysis induced dissolution of actinide oxide thin films, using synchrotron radiation, to underpin the geological disposal of spent nuclear fuel. Fourth we monitored *in situ* the oxidation and self-ignition mechanism of uranium carbide, a legacy fuel from the Dounreay Prototype Fast Reactor that is waiting for oxidation treatment prior to permanent storage and/or disposal. Through this programme of research, the DISTINCTIVE consortium is rebuilding the UK capability for research with transuranic materials, which, hitherto, was eroded over decades of disinvestment.

INTRODUCTION

The UK is engaged in a century long mission to clean up the historic legacy of civil nuclear power through a programme of decommissioning, waste management, and disposal activities, at a cost exceeding £100 Billion. Reducing the hazard, cost and timescale of this mission requires the innovation, adaptation and maturation of technologies, for insertion into site baseline plans, to address the unique challenges of this mission, underpinned by a robust evidence base of research. A pipeline of high skilled entrants to the profession is required to transfer new knowledge and propagate the next generation of subject matter experts. In the UK, a threat to delivery of the requisite evidence base and skills, has been the erosion of facilities and capability to undertake research utilising materials of high specific activity, as a result of the expense and hazard of such experimental activities. The EPSRC sponsored DISTINCTIVE consortium

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(Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories) is challenging this decline in the national capability, through a targeted programme of research, to address national waste management research needs, utilising high activity materials. In so doing, the consortium has contributed to the enhancement and creation of research infrastructure, and leveraged best-with-best international collaboration, to deliver impactful research, and upskill a cadre of research scientists in radiological materials handling.

RESEARCH HIGHLIGHTS

GLASS CERAMICS FOR DISPOSITION OF THE UK PLUTONIUM STOCKPILE

By the end of reprocessing operations, the UK will hold ca. 140 tonnes of separated plutonium. Whilst the current government policy is to fabricate Mixed Oxide (MOx) fuel, a significant fraction of the stockpile material will be unsuitable for fuel fabrication and will require an immobilisation route into passively safe wasteforms. It is possible that future immobilisation of the entire stockpile may be required, if the economic case for disposition as MOx fuel cannot be adequately demonstrated [1]. This must include the offtake of reactor operators and a rise in demand for MOx fuel. Hot isostatic pressing is a front-running technology option for immobilisation of the plutonium stockpile material, enabling batchwise manufacture of glass-ceramic wasteforms. The DISTINCTIVE project has developed a suite of hot isostatically pressed glass-ceramic wasteforms, in which, plutonium is targeted for the zirconolite ceramic phase, encapsulated within a sodium aluminosilicate glass.

Formulation and process optimisation using cerium and uranium surrogates

The first step in developing these glass-ceramic wasteforms was the optimisation of pre-treatment parameters to ensure high quality, reproducible HIP samples were achieved [2]. Investigation of the calcination and bake-out parameters during sample fabrication, highlighted the necessity for a high temperature heat treatment of the precursor materials, before sealing of the HIP canisters, to attain wasteforms of near theoretical density. The utilisation of a high temperature ex-situ calcination of the precursor materials prior to canister packing, led to a reduction of the HIP sample fabrication time by two thirds. The high temperature ex-situ calcination was coupled with a low temperature in-situ bake-out to ensure the complete removal of volatiles from inside the HIP canister and the production of high quality, high density wasteforms were reliably achieved.

Formulation studies investigated the effect of glass composition on the crystalline phase assemblage output of the glass-ceramic system [2]. Both the glass composition and glass / ceramic ratio were observed to govern the yield of the zirconolite phase, which was maximised utilising an $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$ glass composition and glass / ceramic ratio of 70 / 30. Through the use of CeO_2 as an inactive surrogate for PuO_2 , successful waste digestion into the target zirconolite phase was observed and provided positive results for progression to radioactive surrogate studies.

After establishing a potential ceramic / glass partitioning ratio through the inactive CeO_2 studies, further waste incorporation work was conducted using UO_2 . U(IV) is a more effective surrogate for Pu(IV) than Ce(IV) , due to the facile reduction of the latter to Ce(III) under HIP conditions. The UO_2 surrogate study provided an extra suite of information on the ceramic / glass partitioning behaviour of the glass-ceramic system. Near complete waste digestion was achieved with preferential actinide incorporation into the target zirconolite phase, thus in excellent agreement with the Ce samples. The crystalline phase assemblage and microstructure of these U-bearing samples were also in agreement with the inactive Ce-bearing samples and provided sufficient evidence for progression to PuO_2 verification studies.

Plutonium validation studies

In collaboration with the Australian Nuclear Science & Technology Organisation (ANSTO), and with support from the Nuclear Decommissioning Authority (NDA), PuO_2 formulation verification studies were conducted through small scale sinters and HIP samples. The formulation optimisation and surrogate studies provided evidence of the wasteform behaviour with regards to waste digestion and partitioning into the

zirconolite phase, allowing for the progression to PuO₂ verification studies. A small scale sintered sample was consolidated and characterised to verify the reactivity of the PuO₂ precursor before fabrication of the HIP samples. Dry PuO₂ powder was added to the precursors and a 0.5 g pellet was pressed from the homogenised batch. The sample was sintered at 1250 °C for 4 h in air. Results confirmed zirconolite as the major crystalline phase, with NiTiO₃ present as a direct result of Ni particles reacting in the oxidising atmosphere. The microstructure was representative of those seen in the HIP samples and successful incorporation of the Pu into the zirconolite was confirmed by SEM-EDX analysis. No residual PuO₂ was detected, thus confirmed complete waste digestion.

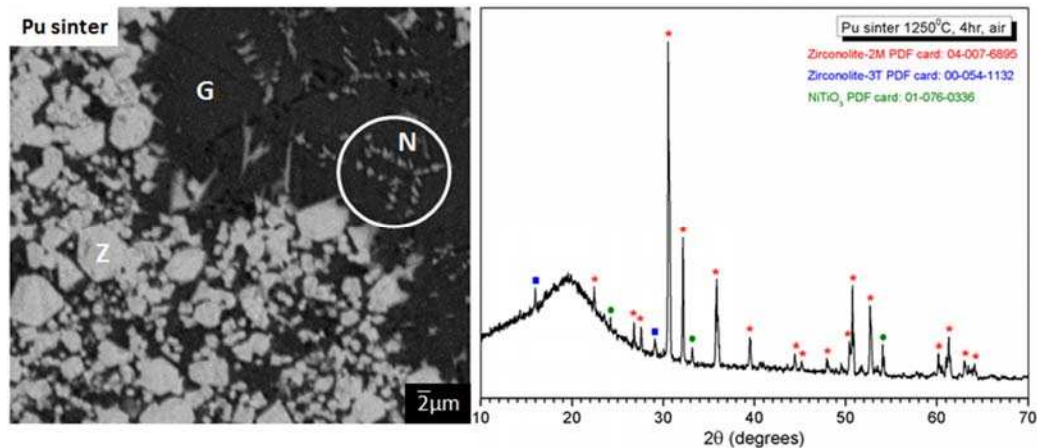


Figure 1: BSE micrograph and XRD pattern showing the microstructure and phase assemblage of a Pu-bearing sintered glass-ceramic sample. The major crystalline phase was zirconolite (Z) distributed within the glass (G) matrix. The minor phase NiTiO₃ (N) was a direct result of the oxidising atmosphere.

The first Pu-bearing HIP sample was in excellent agreement with the sintered equivalent. Full waste incorporation was achieved and zirconolite was the only crystalline phase detected by SEM and XRD. The microstructure of the HIP sample showed zirconolite crystals uniformly distributed throughout the glass matrix and confirmed no residual PuO₂ was present. This HIP sample is part of an ongoing sample matrix investigating the effective partitioning of Pu in the glass-ceramic, with respect to controlled oxygen fugacity. It has proven that the optimised glass-ceramic formulation can successfully accommodate PuO₂ for the disposition of the plutonium stockpile in the UK.

Development of a radiological Hot Isostatic pressing capability

One limitation of the HIP technology for processing radioactive material is its technology maturity level. To date, there are no operating demonstration HIP plants capable of remotely processing radioactive material above a small, research scale. Through a collaboration with American Isostatic Presses (AIP), a unique radiological containment system has been commissioned at The University of Sheffield, to enable hot isostatic pressing of glass-ceramic materials, using uranium as a plutonium surrogate. The Active Furnace Isolation Chamber (AFIC) was designed and manufactured by AIP and AMEPT, and is the first containment device that ensures complete containment of loose radioactive material during a HIP cycle in the event of a ruptured canister, with repeated operation. The innovative design of the AFIC system guarantees a secure and reliable seal of the chamber with repeated operation and has a multi-layered filter system that allows gas flow in and out, whilst impeding the free movement of radioactive particles from inside. This unique and innovative infrastructure improves the current capability of HIP for safely processing radioactive material at the research scale and it is hoped, through this collaboration, will have a strong impact on furthering the technology readiness level of this thermal treatment technology for treating the UK's Pu waste inventory.

Through development of the infrastructure, capability, collaboration, and skills, required for radiological hot isostatic pressing, this research has delivered a technically underpinned wastefrom, suitable for immobilisation of the plutonium stockpile, with an understanding of the incorporation mechanisms of cerium, uranium and plutonium in the zirconolite phase.

HEAT TREATMENT OF WATER AND CHLORIDE CONTAMINATED PuO₂

Magnox PuO₂

More than 100 tonnes of PuO₂ has been stored at Sellafield since the 1970s in metal containers with an intermediate PVC layer. 5% of this PuO₂ has become contaminated with chloride, due to thermal degradation of the PVC, and water, due to exposure to the atmosphere. Heat treatment has been proposed as a method to decontaminate the PuO₂, so that it can be safely stored before either being reused as MOx fuel or disposed of in a Geological Disposal Facility (GDF). In order to probe this, samples of the Magnox PuO₂ have been heat treated at 400, 600, 800 and 950 °C in a furnace attached to a caustic trap, with air flowing through the equipment, within an air glove box at NNL Central Laboratory. The amount of leachable chloride present on PuO₂ with a small bed depth, measured by ion chromatography, decreases as heat treatment temperature increases and has completely volatilised by 950 °C. However, less chloride is volatilised from PuO₂ with a higher bed depth of 3 cm, as less chloride is exposed to the air above and is unable to be volatilised into the caustic trap. Powder x-ray diffraction (XRD) showed that the crystal sizes increase with heat treatment temperature, almost doubling in size after 950 °C, but the lattice parameters decrease with increasing heat treatment temperature, as the defects are annealed at higher temperatures. No changes in crystal phases were detected between the untreated and heat treated PuO₂, indicating that chloride is not incorporated into the bulk of the fcc Fm $\bar{3}$ m crystal structure. PuO₂, which had previously undergone heat treatment at 700 °C, was heated to 225 °C and cooled inside a sealed (Baskerville) vessel with and without 0.05 mL water in a side chamber, to investigate the sorption mechanism of water on PuO₂. Without water, the PuO₂ produced an unidentified, ideal, non-condensable gas. With water, the PuO₂ produced a non-ideal, condensable gas. It is hypothesised that the gas produced in the dry heating cycle liberates surface sites on the PuO₂, where the water from the wet heating cycle condenses while cooling. When untreated PuO₂ is heated and cooled at 50, 100, 150, 200 and 230 °C without water, the pressure inside the sealed vessel increases with each cycle, indicating the production of a non-condensable gas each time, which is ideal above 113 °C. With 0.05 mL water, the gas produced at these temperatures is non-ideal and partially condensable, indicating that a lower number of reactive sites have been liberated on the untreated PuO₂ surface than on the PuO₂ previously heat treated at 700 °C. The amount of leachable chloride on both the PuO₂ previously heat treated at 700 °C and the untreated PuO₂ decreases after the dry cycles, but increases again on the wet cycles.

Simulant PuO₂

Simulant PuO₂ was contaminated with HCl vapour and humidified, and then heat treated at 300, 500, 700 and 950 °C at NNL Central Laboratory. The powder XRD results show a similar trend to the Magnox PuO₂, with crystal sizes increasing and lattice parameters decreasing with increasing heat treatment temperature and no change in crystal phase. The ion chromatography results also agree, as leachable chloride on the solid decreases and volatilised chloride captured in the caustic trap increases with increasing heat treatment temperature.

CeO₂ analogues

A series of chloride-contamination and heat treatment experiments have also been carried out on CeO₂ powder, as a surrogate for PuO₂. The CeO₂ was calcined at 500 and 900 °C to investigate the influence of specific surface area (SSA) on the sorption of chloride and water. It was then contaminated with HCl vapour and heat treated at 500 and 900 °C. X-Ray photoelectron (XPS) and infrared spectroscopies showed that more Cl⁻ and water adsorbed to the high SSA powder (calcined at the lower temperature) than the low SSA

powder. Heat treatment at 900 °C removed more Cl⁻ and water from the surface of the CeO₂ than heat treatment at 500 °C. These analyses showed that chloride and water appear to be linked in their sorption to the metal oxide. XRD, as in PuO₂, shows no change in crystal phase, thus no incorporation of chloride into the bulk CeO₂ crystal structure, and an increase in crystal size between synthesis, contamination and heat treatment. X-Ray absorption near edge structure (XANES) of the Ce *L_{III}* edge and extended x-ray absorption fine structure (EXAFS) analyses of the chloride-contaminated CeO₂ samples show that oxygen occupies the first co-ordination sphere around cerium ions, rather than chloride, and that cerium remains in the +4 oxidation state.

Analogue thin films

CeO₂, Ce_xO_{2-x}, ThO₂, UO₂ and U metal thin films have been synthesised, contaminated with either HCl or Cl₂ gas and heat treated via thermal program desorption coupled with mass spectrometry (TPD-MS) and analysed by XPS after each process, in order to study the surfaces of metal oxides in more detail, at ITU, Germany. Cl₂ adsorbs more easily to the metal oxides than HCl gas. Cl₂ also adsorbs more easily to reduced Ce_xO_{2-x} and U metal than to the MO₂ films. Analysis of the films as they were heated by TPD-MS reveals that no chloride was volatilised between ambient temperature and 800 °C, but the Cl⁻ intensity decreased, according to XPS. Thus, it is hypothesised that Cl⁻, which was on the thin film surface before heat treatment, diffuses beneath the surface with heat treatment to the point where it can no longer be detected by XPS, which is a surface specific analytical technique (~10 atomic layers).

RADIOLYSIS DRIVEN DISSOLUTION AT THE SURFACE OF UO₂ THIN FILMS

In this study, a series of single crystal thin films of UO₂ were exposed to an intense x-ray beam at a synchrotron source in the presence of water. These experiments were carried out at the I07 beamline, Diamond Light Source, UK and the XMaS CRG beamline, ESRF, France. We carried out, so-called source-probe experiments, simultaneously providing the radiation fields required to split water into highly oxidising radiolytic products, and probing the crystal structure, composition and morphology of the UO₂/water interface [4]. By modelling the crystallinity, electron density, surface roughness and layer thickness, we have been able to reproduce the observed reflectivity and diffraction profiles. This enables us to detect changes in oxide composition and rate of dissolution at the Ångström level, over a timescale of several minutes. These measurements could provide important corrosion rate data, dependent on

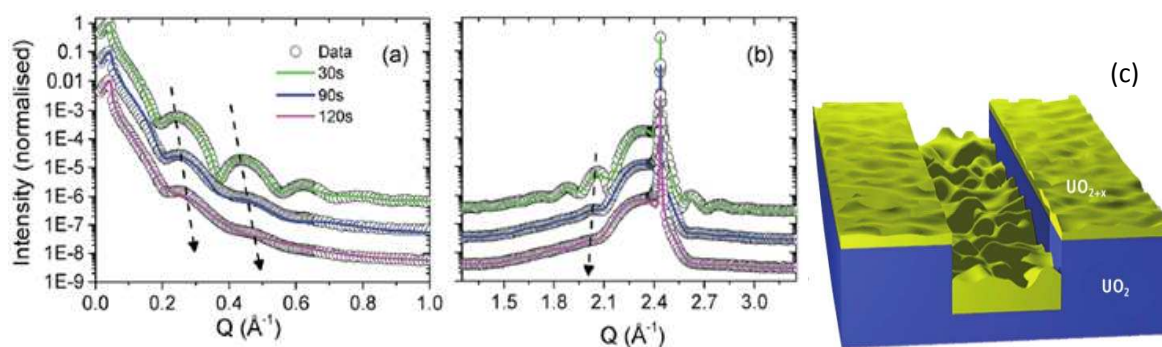


Figure 2: Panel (a) shows X-ray reflectivity data and panel (b) shows high angle diffraction data, measured at exposure times of 30 s, 90 s and 120 s; the experimental data are represented by the open black circles and the fitted calculations by the solid green, blue and magenta lines, respectively. Panel (c) shows a 3-dimensional model of the sample system, recreated from the parameters determined in (a) and (b).

crystallography, at the interface of water and UO_2 , which could impact on models of long-term storage of spent nuclear fuel.

The single-crystal thin films of UO_2 were grown at the University of Bristol in a dedicated DC magnetron sputtering facility. Samples were deposited in [001], [110] and [111] high symmetry directions. A combination of x-ray reflectivity and high-resolution diffraction allowed us to build up a full structural picture of the thin film and the substrate/film and film/air interface, see figure 2. A thin layer surface tension cell was filled with Milli-Q ultra pure type 1 water and the incident slits were set to a 200 micron square. The surface was exposed at an incident angle of $\sim 0.5^\circ$, such that the footprint was approx. 2 cm, more than covering the whole length of the sample. The water was then removed, the slits were closed down to 100 mm x 100 mm and the diffraction spectra were recorded.

In studies of this type, probing the UO_2 surface, hydrogen peroxide is commonly used as the primary radiolytic product, particularly when radiation fields are absent. We used a calibrated silicon photodiode to determine a flux at the sample position of $\sim 1 \times 10^{12}$ photons per s at an energy of 17.116 keV. The G-value, the number of molecules of reactant consumed or product formed (in our case) per unit of incident energy absorbed, is 0.6 molecules of $\text{H}_2\text{O}_2/100$ eV. The corrosion that was observed in this experiment was at a significantly higher rate than simple production of peroxide would allow. Moreover, post analysis of the samples indicated a much faster corrosion mechanism, confined to the beam footprint, suggesting that the corrosion may be predominantly due to shorter lived oxidising species, such as OH radicals.

CRACKING INDUCED OXIDATION AND IGNITION OF UC

In UK, a large legacy of exotic fuels is temporarily stored since the 1950s in the Dounreay site, Scotland. The term exotic is used to describe a miscellaneous category of fuels comprising of unirradiated mixed uranium plutonium carbides and oxides, unirradiated high enriched uranium oxides, metals, tetrafluorides, and irradiated oxides and carbides tested in the Prototype Fast Reactor (PFR). Among these exotic fuels, unirradiated uranium carbide (UC) are waiting for oxidation treatment prior to safe permanent storage and/or disposal. Oxidation is indeed considered the best option to convert a very reactive material, such as UC, to a less reactive compound such as an oxide, like UO_2 or U_3O_8 , which can be safely stored at room temperature in an environment containing air/oxygen. Contrarily to the oxide, UC is pyrophoric, hence, it can self-ignite in the presence of air/oxygen. Many attempts performed at an industrial scale to oxidise large batches of UC in furnaces showed the challenges involved during oxidation of this material. Hence, the need for a better understanding of the oxidation mechanism and sudden self-ignition is of paramount importance as it affects not only fuel decommissioning but also fuel safe handling.

This study was performed in collaboration with facilities and research centres both in UK, at NNL Preston, and in France, at the Marcoule Institute for Separation Chemistry (ICSM) thanks to a collaboration with the Atomic Energy Commission (CEA) Cadarache. UC pellets (depleted uranium with diameter of 1.9 cm, length around 2 cm, average density of 13.13 ± 0.07 g/cm³) coming from the Dounreay site were oxidised in furnace experiments in air atmosphere from 873-1173 K at NNL. UC sintered fragments (depleted uranium with a theoretical density >91% and U/C stoichiometry of 1.00 ± 0.03) were oxidised in a high-temperature environmental scanning electron microscope (HT-ESEM) at ICSM from 723 to 1173 K in an oxygen atmosphere of 2 – 100 Pa. Samples were heated in vacuum in the HT-ESEM to the desired temperature with the surface continuously monitored before and after oxygen insertion in the chamber. Thanks to the use of an image analysis technique (ImageJ) applied on SEIs taken on each sample corner every 15 seconds, it was possible to monitor the surface morphological changes of UC during oxidation treatments. Sample expansion and crack propagation during oxidation from UC to UO_2 and during ignition of UC to U_3O_8 were observed and quantified for the first time [6]. These two transformations were characterised by a non-explosive route, oxidation to UO_2 , and by an explosive event: the sudden ignition of UC to U_3O_8 (the word explosive is here used to represent a sudden and dramatic increase of sample expansion) [6]. An example for such explosive transformation triggered by UC ignition is shown in Figure 3, where the oxide product at the end of the reaction was characterised as a pulverised oxide made of $\text{U}_3\text{O}_8/\text{U}_3\text{O}_7$ in a high resolution transmission electron microscope (HRTEM).

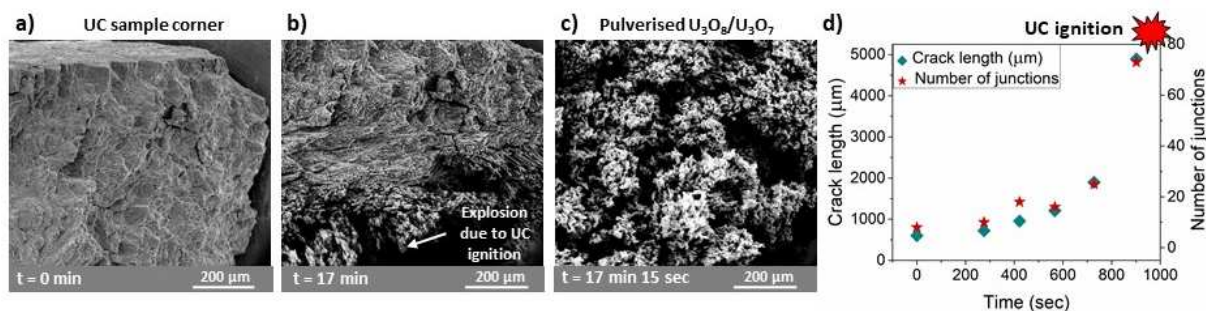


Figure 3: UC fragment oxidised at 723 K in 50 Pa O₂ atmosphere: SE images a) just after oxygen insertion, b) 17 minutes after oxygen insertion showing an explosive expansion occurring during the SEI scan time frame (a few seconds), c) 15 seconds after SEI shown in b) revealing the sample morphological changes after UC ignition, d) plot of the crack length measured throughout the experiment vs. number of crack junctions with time. Adapted from [6]

By combining the image analysis technique with *in situ* SEIs it was possible to explain both the mechanisms of oxidation to UO₂ and the self-ignition of UC. Oxidation to UO₂ was observed on samples oxidised at T = 723 K in a partial O₂ atmospheres (PO₂) ≤ 25 Pa. This reaction obeyed an exponential followed by a logarithmic trend for both crack propagation and sample expansion. Crack length, instead, stabilised completely towards the end of the experiment as no new cracks were formed, hence, the reactive surface area did not increase. UC ignition was observed on samples oxidised at T = 723 K in a PO₂ = 50 Pa, and at 773 ≤ T ≤ 848 K in a PO₂ from 10 to 100 Pa. This reaction was governed by an exponential increase of crack propagation, sample expansion, crack length and number of junctions (the crack length and number of junction exponential trend is shown in Figure 3d). UC ignition was induced by formation of a crack network which greatly increased the surface area available to react. The heat released from the ignition of the first UC fragment triggered an ignition cascade in the other fragments which resembled a self-propagating high-temperature synthesis (SHS). This reaction travelled throughout the sample with a speed between 150 – 500 ± 50 μm/s and changed dramatically the morphology of the sample surface as its size increased almost 10 times in size [6].

The oxidation and UC ignition was found to be greatly affected by temperature and oxygen partial pressure, for example, the time needed for ignition to occur decreased with increase of temperature and PO₂. A competition between cracking, producing a fragmented sample, and sintering of the oxide was key in oxidations in the range 973-1173 K both in atmospheres of 100 Pa O₂ and in atmospheric air. A thick and sintered oxide layer was observed at 1073-1173 K which was found to prevent oxidation and oxide conversion. Conversely, no sintering was observed in experiments at 873 K as the oxide directly pulverised. Oxide conversion of single UC pellets improved at 873 K when compared to 1173 K oxidation. Using a low oxidation temperature, like 873 K, could significantly benefit a large industrial scale process. The only drawback found on 873 K treatments was the presence of a larger quantity of carbon within the oxide layer.

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