

Enrichment of Chromium at Grain Boundaries in Chromia Doped UO2

Middleburgh, Simon; Dumbill, Simon; Qaisar, Adam; Vatter, Ian; Owen, Megan; Vallely, Sarah; Goddard, Dave; Eaves, David; Puide, Mattias; Limback, Magnus; Lee, Bill

Journal of Nuclear Materials

DOI: 10.1016/j.jnucmat.2023.154250

Published: 01/03/2023

Peer reviewed version

Cyswllt i'r cyhoeddiad / Link to publication

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA): Middleburgh, S., Dumbill, S., Qaisar, A., Vatter, I., Owen, M., Vallely, S., Goddard, D., Eaves, D., Puide, M., Limback, M., & Lee, B. (2023). Enrichment of Chromium at Grain Boundaries in Chromia Doped UO2. Journal of Nuclear Materials, 575, Article 154250. https://doi.org/10.1016/j.jnucmat.2023.154250

Hawliau Cyffredinol / General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
You may not further distribute the material or use it for any profit-making activity or commercial gain

- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Journal of Nuclear Materials Enrichment of Chromium at Grain Boundaries in Chromia Doped UO2 --Manuscript Draft--

Manuscript Number:	JNUMA-D-22-01327R1
Article Type:	Short Communication
Section/Category:	Nuclear fuels and materials
Keywords:	Doped fuel; Grain boundary; high resolution transmission electron microscopy; complexions
Corresponding Author:	Simon Middleburgh Bangor University UNITED KINGDOM
First Author:	Simon Middleburgh
Order of Authors:	Simon Middleburgh
	Simon Dumbill
	Adam Qaisar
	Ian Vatter
	Megan Owen
	Sarah Vallely
	Dave Goddard
	David Eaves
	Mattias Puide
	Magnus Limbäck
	William E. Lee
Abstract:	Assessment of grain boundaries in chromia (Cr2O3) doped fuels has been carried out using high resolution transmission electron microscopy to assess the structure compared to undoped fuel produced via the same process. Chemical analysis of the grain boundary was carried out using Energy Dispersive X-ray Spectroscopy (EDS). It was shown that a relatively disordered phase is formed along the grain boundaries in the doped fuel and that they were chemically enriched in chromium. This has implications for the prediction and understanding of fuel manufacture and in-reactor behaviour as many processes are highly dependent on grain boundary mechanisms.
Suggested Reviewers:	Rory Kennedy Idaho National Laboratory Rory.Kennedy@inl.gov
	Gabriel Lynch-Murphy Research Centre Jülich g.murphy@fz-juelich.de
	Erofili Kardoulaki Los Alamos National Laboratory ekardoulaki@lanl.gov
Response to Reviewers:	

Nuclear Futures Institute, Bangor University, Dean Street, Bangor, Gwynedd. LL57 1UT United Kingdom Tel.: +44 (0) 77380 828585

20th December 2022

Dear Editor,

We remain extremely excited to submit our revised manuscript entitled "Enrichment of Chromium at Grain Boundaries in Chromia Doped UO_2 " to the Journal of Nuclear Materials.

The short communication focuses on a phenomenon observed in commercial doped urania fuel, This is an exciting area of research at the moment with many institutions around the world assessing the behaviour of Cr-doped fuels for use in light water reactors. This work highlights a previously unreported phenomenon whereby the Cr additions can significantly enrich along grain boundaries in commercially manufactured fuel, thereby impacting their properties in manufacture and also during operation.

This is the first time this behaviour has been observed in this fuel type. The work was made possible by collaborating across the industry, with national laboratories, industry and universities involved.

The reviewers' comments have enriched and improved the manuscript and we are grateful for their inputs.

Accordingly, we feel that these results and the subsequent conclusions will be of substantial interest to the readership, in line with the journal's aims and would be grateful if you would consider it for publication in the Journal of Nuclear Materials.

Yours sincerely,

Prof. Simon Middleburgh

Mm-

Enrichment of Chromium at Grain Boundaries in Chromia Doped UO₂ Response to Reviewers Comments

We would like to thank both reviewers for their comments on the submitted manuscript. The following comments have been addressed below, and changes to the manuscript have been highlighted in blue.

Reviewer #1:

This work presents evidence for the segregation of Cr at the grain boundaries in Cr-doped fresh fuel UO_2 and is of interested to to the wider scientific community. The work is suitable for publication with the following minor modifications.

We thank the reviewer for their assessment of the manuscript.

1) The wording throughout the manuscript can be improved. For example, there are frequent repetitions in sentences.

The authors agree and we have gone through it with a fine-tooth comb to improve upon the quality of the writing.

2) Was the stoichiometry of the doped and un-doped pellet established? This would be important to know for a one to one comparison.

The initial stoichiometry of the AUC powders were 2.14. The final stoichiometry was 2.00. This is now noted in the manuscript and is, of course a really important factor.

3) Were the doped and un-doped pellets sintered at the same temperature? Only the sintering temperature for the doped pellet is given. Yes. This is now noted in the text.

4) Please define all acronyms used.

Apologies. This is now carried out.

5)The presentation quality of Figure 3 can be improved. Agreed. This has been fixed in line with Reviewer #2's comments too.

6) When discussing the results of the Cr segregation in the grain boundary as observed by TEM you should compare it with the results by Killeen et al. (1980) where they have also showed Cr segregation after irradiation. This work is referenced in the introduction but not in the results/discussion where it is very relevant.

This is a very good point and the work by Killeen is now expanded upon in the manuscript.

Reviewer #2:

The short communication submitted by Middleburgh et al. is of interest to the scientists in the area of nuclear fuel. Even though the question authors trying to answer is of interests, I believe that the experimental proof lacks its high-quality. Therefore, it is recommended revisiting the experimental part to acquire better proof and resubmit. Here are the main comments:

We welcome the opportunity to remedy the points raised by the reviewer and now believe that the submission is of good enough quality to meet their standards. As the reviewer notes, this is of

significant interest to the community at the moment and will hopefully spur on some more studies related to this manuscript.

1) The introductory text also needs some more focus and better flow.

Agreed. In line with Reviewer #1, we have improved the wording in the manuscript.

2) More research on Cr-doped UO₂ should be referenced.

Done. A range of extra references have been added that will improve the applicability, visibility and narrative of the manuscript.

3) I would like to see an SEM micrograph of the Cr-doped sample to confirm the grain enlargement of your sample.

This is now included.

4) Page 2, line 55: What peaks are you discussing here?

More information has been added to the text.

"...two distinct peaks are present at different dopant concentrations in the sample sintered in 1 vol.% $H_2O + H2$ at ~600 µg(Cr₂O₃)/g(UO₂) and ~2500 µg(Cr₂O₃)/g(UO₂) indicating the likelihood of multiple grain growth mechanisms."

5) Page 3, line 32: This is actually not true. A recent study carried out by Silva et al. (J Nucl Mater 552 (2021) 153003, <u>https://doi.org/10.1016/j.jnucmat.2021.153003</u>) has shown the average grain size of UO2 can increase up to 300% with TiO2 doping.

We now include some narrative on TiO_2 , a dopant that is similar to Al_2O_3 as it is not expected to be soluble in UO_2 at equilibrium to any significance but certainly has an impact on grain growth – pointing towards a grain boundary mechanism or a mechanism that is active due to the processing route accommodating Ti as a solute species.

6) Page 3, line 43: Is the hypothesis of having CrUO₄ intermediate phase is from literature? If so, what is the reference?

This has been re-worded as the communications are not referenceable. The portion of text now reads:

"The formation of $CrUO_4$ in the early stages of sintering could act as a key intermediate in the sintering behaviour of Cr-doped fuel, forming readily with UO_{2+x} [17], and the formation of the Alcontaining (Cr,Al) UO_4 may enhance the effect of this intermediate compound at some stage of the sintering process. Further work assessing the potential beneficial impact of this intermediate is required."

7) Page 4, line 10: Convert the force unit into IUPAC units.

Agreed. This has been remedied. The force is now 49 kN.

8) Fig 1. The quality of this HRTEM image is not that great. I suggest adding another image of a different area to the figure to verify the difference in the GB structure. You could also try applying some filters to clear the atomic scale resolution. I am not sure if the word 'micrograph' is suitable here since we are looking at nano-scale. Maybe use the wording 'HRTEM image".

We appreciate the guidance here. A new set of sub figures have been added and the figure title has been changed accordingly.

9) Fig 2 is not of very good quality. I suggest taking a better-quality image(s) for the undoped sample.

Again, we appreciate the guidance and have made strides to improve the quality of the undoped sample's image. We feel that the current selection highlights the necessary detail to support the discussion in the paper.

We thank the reviewers for their time and assessment of the manuscript and believe it will provide an impactful addition to the Journal of Nuclear Materials.

Enrichment of Chromium at Grain Boundaries in Chromia Doped UO₂

Simon C. Middleburgh^{1*}, Simon Dumbill², Adam Qaisar², Ian Vatter², Megan Owen^{1,3}, Sarah Vallely¹, Dave Goddard⁴, David Eaves⁵, Mattias Puide⁶, Magnus Limbäck⁶, William E. Lee¹

¹Nuclear Futures Institute, Bangor University, Bangor LL57 1UT, United Kingdom

²National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG, United Kingdom

³Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom

⁴National Nuclear Laboratory, Preston Laboratory, Springfields, Preston, Lancashire, PR4 OXJ, United Kingdom

⁵Westinghouse Springfields Fuels Ltd, Station Rd, Lea Town, Preston PR4 OXJ, United Kingdom ⁶Westinghouse Electric Sweden AB, Utvecklingsgränd 33, 722 26 Västerås, Sweden

Abstract

Assessment of grain boundaries in chromia (Cr_2O_3) doped fuels has been carried out using high resolution transmission electron microscopy to assess the structure compared to undoped fuel produced via the same process. Chemical analysis of the grain boundary was carried out using Energy Dispersive X-ray Spectroscopy (EDS). It was shown that a relatively disordered phase is formed along the grain boundaries in the doped fuel and that they were chemically enriched in chromium. This has implications for the prediction and understanding of fuel manufacture and inreactor behaviour as many processes are highly dependent on grain boundary mechanisms.

Key words:

Doped fuel; grain boundary; high resolution transmission electron microscopy; complexions

Chromia doped fuels are being considered as an evolutionary accident tolerant fuel (ATF) candidate [1] due to their reported changes in mechanical properties [2], altered fission gas release [3] [4] and improved washout behaviour [5]. These properties are expected to vary as a result of the deviations that occur in the post-sintered microstructure. Originally, these dopants were used to improve the sinterability of UO₂, particularly from conversion routes such as the AUC (ammonium uranyl carbonate) conversion process [3] [5] [6], however efforts to understand further operational benefits are being assessed by the international nuclear fuel community.

The mechanism by which the dopants produce the larger grains is not fully understood. A range of investigations, both experimental and theoretical, have tended towards two, not necessarily competing, mechanisms: (1) an increase in bulk diffusivity that therefore increases the grain size during sintering [4] and (2) an increase in grain boundary diffusivity, again increasing the grain size. As noted, multiple mechanisms may be occurring simultaneously or dependent on dopant concentration and sintering atmosphere. For example, in the work of Bourgeois et al. [7], two distinct peaks in grain size are present at different dopant concentrations in the sample sintered in 1 vol.% $H_2O + H_2$ at ~600 µg (Cr_2O_3)/g(UO₂) and ~2500 µg (Cr_2O_3)/g(UO₂) indicating the likelihood of multiple grain growth mechanisms.

Mechanism (1) requires some bulk solubility in the UO_2 matrix, and then a large enough impact to cause quite a marked microstructural change, whilst Mechanism (2) requires low solubility species existing at grain boundaries and surfaces of UO_2 rather than in solid solution in order to maximise the concentration and impact on the grain boundary, but not too much to cause grain boundary pinning or a seizure in sintering. The presence of grain boundary phases may also alter the defect chemistry of the bulk system. Recent theoretical work has shown that the formation of disordered or amorphous grain boundary phases have much higher thermodynamic drives to deviate their stoichiometry compared to the crystalline bulk UO_2 [8], and therefore may alter the bulk material's stoichiometry. This will alter the sintering behaviour of the fuel and also will change subtle properties such as bulk material lattice parameters [9].

The solubility of Cr in UO₂ has been assessed on a number of occasions. Experimentally, the solubility has been estimated as 0.07 wt.% (700 wppm) by Bourgeois et al. [7] and a thorough evaluation was provided by Riglet-Martial et al. [10] to ranging from 500 wppm to 1000 wppm (for Cr_2O_3). It is regularly noted in literature that once the solubility limit of Cr_2O_3 in UO₂ is exceeded, grain growth is reduced. Some emphasis was placed onto the oxidation state of Cr entering the UO₂ matrix. It was noted that at high temperatures and low oxygen partial pressures, the Cr may reduce to a 2+ charge state, thus altering the solution route [4] with conflicting experimental observations that may be made clearer with the use of single crystal data in the future. A solubility model was put forward by Riglet-Martial [10] highlighting the potential reduction of Cr to a 2+ charge-state at high sintering temperatures and intermediate to high oxygen partial pressures (avoiding the formation of Cr metal) and the formation of CrO_(l). The solubility model did not consider alterations to chemistry that could be present at grain boundaries and the impact of grain boundaries as defect sinks.

Killeen [3] performed some of the seminal work on Cr-doped UO₂ and highlighted, amongst other things, the segregation of Cr to grain boundaries during operation and therefore highlighting the instability of solute Cr at the dopant levels tested (0.5 wt.% in this study) as well as possible co-migration mechanisms with fission gases from the bulk to the grain boundaries.

The solubility of Al in UO_2 is reported to be negligible according to Kashibe and Une [12] and Lang [13]. This very low solution energy agrees with theoretical results performed using empirical potentials [14]. Solubility values are low and the mechanism for grain growth observed, for example by Kashibe [12] from 15 μ m in the undoped sample to 30 μ m in the 760 wppm Al₂O₃ sample, is presently not clear (especially as the redox behaviour of Al_2O_3 is markedly less varied compared to Cr_2O_3). Similarly, grain growth is observed in MgO doped UO₂ [12] and TiO₂ doped UO₂ [15], both known to have very low solubilities in UO₂ that are unlikely to impact intrinsic processes to produce changes in grain sizes observed experimentally. Specifically on TiO_2 as a dopant, Silva et al. [16] performed a study that assessed the dopant's impact when added through a sol-gel process where the resulting grain size was >300% than that of the un-doped fuel. Secondary Ti-rich phases were observed at grain boundaries and a reduction in grain size was also observed that was attributed to some solute Ti within the bulk, possibly as a result of the low-temperature gelation method. Indeed, it should be noted that the synthesis route chosen will significantly alter the distribution and behaviour of the additions to UO2, and mix-milling of powders (as is generally the production route for commercial fuels) [17] can only be compared to sol-gel and wet synthesis methods [9] [18] with care.

Other work has considered the formation of a ternary or mixed U-Cr oxide and its implications. CrUO₄ was first reported by Brisi [19] and then Hoekstra [20]. Subsequently, experimental work has highlighted the assumed charge states of both Cr and U in this compound to be 3+ and 5+, respectively [21]. Solubility of Al into this structure was both theoretically predicted and

 experimentally verified, potentially providing some answers as to the changing behaviour when codoping Al_2O_3 with Cr_2O_3 into the UO_2 system that may be pointing towards other mechanisms that dictate grain growth in Cr_2O_3/Al_2O_3 doped fuels. The formation of $CrUO_4$ in the early stages of sintering could act as a key intermediate in the sintering behaviour of Cr-doped fuel, forming readily with UO_{2+x} [21], and the formation of the Al-containing (Cr,Al) UO_4 may enhance the effect of this intermediate compound at some stage of the sintering process. Further work assessing the potential beneficial impact of this intermediate is required.

Grain boundary complexion and structure is known to impact many synthesis and in-operation mechanisms of ceramics. First and foremost, the changing structures of grain boundaries have been strongly linked to changing in grain boundary mobility and diffusion mechanisms [22] [23]. Grain boundaries can be considered in groups depending on the order at the grain boundary, and if there is a distinct film or phase between the two crystallites. Complexion IV noted to be "a true wetting film because it has a thickness that depends only on the amount of available liquid phase (i.e. the thickness would diverge in a glass melt)" [24].

This work uses pellets produced via a commercial route to investigate the grain boundary structure and composition produced as a result of doping. The doped pellet's structure is compared to an undoped fuel. The aim is to assess whether Cr is observed to segregate to grain boundaries, to assess the resulting grain boundary structures and to add to the body of work investigating the role of Cr_2O_3 and other relatively insoluble additives to UO_2 .

Production of Cr_2O_3 and Al_2O_3 doped UO_2 pellets was carried out at Westinghouse Electric Sweden's Västerås facility. AUC converted UO_2 powder (with O/U stoichiometry of 2.14) was mixed with 500 wppm of Cr_2O_3 and 150 wppm Al_2O_3 for approximately one hour to obtain full homogeneity. It is important to note that according to the existing literature, the Cr_2O_3 concentration is expected to be below the solubility limit.

The doped powder was pressed to green pellets with a force of approximately 49 kN. The green pellets were sintered in a H_2/CO_2 atmosphere at a maximum temperature of 1770 °C. Previous work by Arborelius et al. has reported expected properties and parameters of the pellets produced by this method (equivalent to pellet D3 in that work) [5].

A standard undoped UO₂ pellet was produced using similar sintering conditions (1730-1750°C in a H_2/N_2 atmosphere) to compare to the doped pellet. This was produced at the Springfields Fuels Ltd manufacturing facility using UO₂ converted through the integrated dry route. Final stoichiometries of both pellets were determined to be in the range 2.00-2.02 through X-Ray Diffraction lattice parameter measurements.

Sample examination was carried out using both Tescan XEIA3 plasma focused ion-beam and FEI Helios 600i focused ion-beam (FIB) instruments, the latter was used for transmission electron microscope (TEM) sample preparation. Figure 1 shows the back-scattered electron micrograph image of the un-doped and doped fuels highlighting the significant increase in grain size upon doping with Cr₂O₃. These images were used to identify grain boundaries that were subsequently targeted for further analysis. Lamella samples were extracted from the bulk cross-section samples and then thinned to approximately 150 nm thickness using varying ion beam energies and final stages of preparation conducted at 5 kV and a final cleaning polish at 2 kV was used.



Figure 1 - Back-scattered electron micrograph images of undoped (left) and Cr-doped UO_2 analysed in this study. Grain size enlargement is clearly shown in the doped fuel.

Samples were then examined in a JEOL 2100 TEM with a LaB₆ electron source operated at 200 kV and equipped with an Oxford Instruments Ultimax X-ray detector and AZtec software. Overview images were taken in bright-field TEM mode and high resolution TEM (HR-TEM) was used to examine the grain boundary structures. Scanning transmission (STEM) mode was used to obtain compositional maps and line profiles across grain boundaries using energy-dispersive X-ray analysis (EDX).

High resolution transmission electron microscopy (HR-TEM) was undertaken on both the Cr-doped and undoped UO₂ samples after sample preparation. The sections prepared were specifically targeted to assess the grain boundary nature of the ceramics. Figure 2 provides a micrograph of a grain boundary in the Cr-doped UO₂. The atomic ordering in the grains either side of the boundary is distinct, highlighting that the grain boundaries themselves are somewhat disordered although there appears to be evidence of some diffusive ordering, similar to the theoretical predictions proposed by Rushton et al. [25] related to glass-crystal interfaces.



Figure 2 – **Top:** High resolution transmission electron microscopy (HRTEM) image from the Cr-doped UO₂ pellet including a grain boundary. Inset is a higher magnification of a portion of the grain boundary. **Below:** other examples of HRTEM images of grain boundaries in the Cr-doped pellet.

In regions of the grain boundary reported in Figure 2, the thickness of the grain boundary can be seen to be 2-3 atomic planes thick, indicating a complexion III or IV system as defined by Dillon et al. [23]. The nature of the grain boundary appears ordered in some regions and disordered in other regions, especially those that are thicker. This observation is also in line with categorising the grain boundaries in the Cr-doped samples as complexion II or IV boundaries. These bi-layers or tri-layers have been shown to impact a number of properties including atomic transport that may impact the sintering and operation of such materials.

When assessing the grain boundary structure of the undoped system, the thickness of the grain boundary film varied considerably from nearly zero thickness (Figure 3a and 3b) to similar thicknesses observed in the doped samples (Figure 3c and 3d). This variation in grain boundary type is commensurate with previous experimental work assessing grain boundaries using electron backscattered diffraction (EBSD) techniques [26] that determined that coincident site lattice (CSL) boundary fraction was of the order of 15% of the observed grain boundaries.



Figure 3 - Examples of high resolution microscopy of four grain boundaries observed in the undoped UO_2 sample. Top (a&b): grain boundaries with very little thickness/disorder observed and Bottom (c&d): grain boundaries with a thickness similar to the doped sample.

Chemical assessment of the grain boundaries was undertaken using EDX analysis. In the doped fuel system, a number of line scans were carried out across grain boundaries and are reported in Figure

4. Due to the interaction region of the EDX analysis, the resolution around the grain boundary is not sharp, however there is a clear enrichment of Cr observed at the grain boundary. This indicates that the Cr is not in complete solid solution within the bulk of the system, which provides data to aid the mechanistic understanding of not only grain growth in these large-grained doped fuels, but will also be important to consider when assessing the material's behaviour in reactor. As expected, the undoped pellet did not show any enrichment of Cr at the grain boundary.



Figure 4 - Chromium concentration as a function of distance from the grain boundary assessed by EDX spectroscopy.

The implications of the observations are important when considering the development and use of doped fuels that enhance grain boundaries. These results highlight that the solubility of Cr into the bulk, even at the low dopant levels of 500 wppm Cr₂O₃, is not complete when considering the commercial route for pellet production and that Cr will be affecting the behaviour of grain boundaries during the sintering process and during operation. Sintering atmospheres, temperatures and profiles are known to impact the solubility and behaviour of Cr in the UO₂, and in addition to affecting the bulk behaviour, the sintering atmosphere will also be altering the structure and chemistry of the grain boundary.

The possible stabilization of higher complexity grain boundaries will likely impact the character of grain boundary bubbles that form containing fission gases, and the mobility of fission products along the grain boundary. Further work should be carried out to assess the role of Cr within the grain boundary structure on the mobility of fission gases and volatile species along them, altering their transport to the rod free volume. Our findings build upon the experimental findings from Killeen [3], who reported significant grain boundary segregation of Cr in Cr-doped fuel after irradiation. Further work should assess the source of the diffuse grain boundary observations of Killeen and whether the source could be a combination of bulk Cr moving to boundaries or whether the high concentration of Cr at the grain boundaries acted as the source of the diffuse Cr regions.

Experimental work has identified that creep is higher in Cr-doped fuels and alumino-silicate doped pellets [2]. The alteration in grain boundary structure and chemistry observed in this investigation provides a basis for this observation and highlights that Coble creep mechanisms are altered in doped fuels.

Future work should also consider the implications of the findings in this investigation on phenomena such as high burnup structure formation, the impact of the grain boundaries as sinks for defects and non-stoichiometry as well as the implications of grain boundary attack by corrosive species and steam relevant to washout events where a cladding structure has failed.

In conclusion, the present investigation has undertaken a high-resolution transmission electron microscopy assessment on doped and undoped UO_2 pellets post sintering. The grain boundary structure of the doped fuel was observed to have been altered in the doped fuel system and chemical analysis highlighted the enrichment of Cr at the grain boundaries in the doped fuel system. The observation has implications to the mechanistic understanding of the production and operation of doped fuels.

Acknowledgements

Simon Middleburgh and William Lee are funded through the Sêr Cymru II programme by Welsh European Funding Office (WEFO) under the European Development Fund (ERDF). Access to the facilities at the National Nuclear Laboratory was made possible through the NNUF access scheme through the EPSRC (EP/T011351/1). Preparatory work was carried out in the Bangor University Fuel Fabrication Facility (BUFFF) – see www.bufff.online – sponsored by the EPSRC (EP/V035223/1). This work was supported by the BEIS sponsored Nuclear Innovation Programme.

References

- Y. Che, G. Pastore, J. Hales and K. Shirvan, "Modeling of Cr2O3-doped UO2 as a near-term accident tolerant fuel for LWRs using the BISON code," *Nuclear Engineering and Design*, vol. 337, pp. 271-278, 2018.
- [2] J. Wright, C. Anghel, S. Middleburgh and M. Limback, "Fuel hardware considerations for BWR PCI mitigation," in *Top Fuel 2016: LWR fuels with enhanced safety and performance*, Boise, ID (USA), 2016.
- [3] J. Killeen, "Fission gas release and swelling in UO2 doped with Cr2O3," *Journal of Nuclear Materials,* vol. 88, pp. 177-184, 1980.
- [4] M. Cooper, G. Pastore, Y. Che, C. Matthews, A. Forslund, C. Stanek, K. Shirvan, T. Tverberg, K. Gamble, B. Mays and D. Andersson, "Fission gas diffusion and release for Cr2O3-doped UO2: From the atomic to the engineering scale," *Journal of Nuclear Materials*, vol. 545, p. 152590, 2021.
- [5] J. Arborelius, K. Backman, L. Hallstadius, M. Limback, J. Nilsson, B. Rebensdorf, G. Zhou, K. Kitano, R. Lofstrom and G. Ronnberg, "Advanced Doped UO2 Pellets in LWR Applications," *Journal of Nuclear Science and Technology*, vol. 43, pp. 967-976, 2006.

- [6] I. Greenquist, M. Tonks, M. Cooper, D. Andersson and Y. Zhang, "Grand potential sintering simulations of doped UO2 accident-tolerant fuel concepts," *Journal of Nuclear Materials*, vol. 532, p. 152052, 2020.
- [7] L. Bourgeois, P. Dehaudt, C. Lemaignan and A. Hammou, "Factors governing microstructure development of Cr2O3-doped UO2 during sintering," *Journal of Nuclear Materials*, vol. 297, pp. 313-326, 2001.
- [8] S. Middleburgh, W. Lee and M. Rushton, "Structure and properties of amorphous uranium dioxide," *Acta Materialia*, vol. 202, pp. 366-375, 2021.
- [9] P. Kegler, M. Klinkenberg, A. Bukaemskiy, G. Murphy, G. Deissmann, F. Brandt and D. Bosbach, "Chromium Doped UO2-Based Ceramics: Synthesis and Characterization of Model Materials for Modern Nuclear Fuels," *Materials*, vol. 14, p. 6160, 2021.
- [10] C. Riglet-Martial, P. Martin, D. Testemale, C. Sabathier-Devals, G. Carlot, P. Matheron, X. Iltis,
 U. Pasquet, C. Valot, C. Delafoy and R. Largenton, "Thermodynamics of chromium in UO2 fuel: A solubility model," *Journal of Nuclear Materials*, vol. 447, pp. 63-72, 2014.
- [11] S. Kashibe and K. Une, "Effect of additives (Cr2O3, Al2O3, SiO2, MgO) on diffusional release of Xe from UO2 fuels," *Journal of Nuclear Materials*, vol. 254, pp. 234-242, 1998.
- [12] S. Lang, "High-temperature Reactions of Uranium Dioxide with Various Metal Oxides," National Bureau of Standards Circular 568, Washington DC (USA), 1956.
- [13] S. Middleburgh, D. Parfitt, R. Grimes, B. Dorado, M. Bertolus, P. Blair, L. Hallstadius and K. Backman, "Solution of trivalent cations into uranium dioxide," *Journal of Nuclear Materials*, vol. 420, pp. 258-261, 2012.
- [14] K. Une, S. Kashibe and K. Ito, "Fission Gas Behavior during Postirradiation Annealing of Large Grained U02 Fuels Irradiated to 23 GWd/t," *Journal of Nuclear Science and Technology*, vol. 30, pp. 221-231, 1993.
- [15] C. Silva, R. Hunt and A. Nelson, "Microstructural and crystallographic effects of sol-gel synthesized Ti-doped UO2 sintered under reducing conditions," *Journal of Nuclear Materials*, vol. 552, p. 153003, 2021.
- [16] C. Silva, R. Hunt and K. Holliday, "An evaluation of tri-valent oxide (Cr2O3) as a grain enlarging dopant for UO2 nuclear fuels fabricated under reducing environment," *Journal of Nuclear Materials*, vol. 553, p. 153053, 2021.
- [17] H. Smith, L. Townsend, R. Mohun, T. Cordara, M. Stennett, F. Mosselmans, K. Kvaahnina and C. Corkhill, "Cr2+ solid solution in UO2 evidenced by advanced spectroscopy," *Communications Chemistry*, vol. 5, p. 163, 2022.
- [18] C. Brisi, "The uranate of the MU3O10 type," Annali di Chimica, vol. 53, p. 325, 1963.
- [19] H. Hoekstra, "Some Uranium-Transition Element Double Oxides," *Advances in Chemistry*, vol. 71, pp. 211-227, 1967.

- [20] M. Cooper, D. Gregg, Y. Zhang, G. Thorogood, G. Lumpkin, R. Grimes and S. Middleburgh, "Formation of (Cr, Al)UO4 from doped UO2 and its influence on partition of soluble fission products," *Journal of Nuclear Materials*, vol. 443, pp. 236-241, 2013.
- [21] S. Dillon, M. Harmer and J. Luo, "Grain boundary complexions in ceramics and metals: An overview," *JOM*, vol. 61, pp. 38-44, 2009.
- [22] S. Dillon and M. Harmer, "Relating Grain-Boundary Complexion to Grain-Boundary Kinetics I: Calcia-Doped Alumina," *Journal of the American Ceramic Society*, vol. 91, pp. 2304-2313, 2008.
- [23] S. Dillon, M. Tang, W. Carter and M. Harmer, "Complexion: A new concept for kinetic engineering in materials science," *Acta Materialia*, vol. 55, no. 18, pp. 6208-6218, 2007.
- [24] M. Rushton, R. Grimes and S. Owens, "Partial ordering of glass networks adjacent to simulated glass–crystal interfaces," *Journal of Non-Crystalline Solids*, vol. 357, pp. 3278-3287, 2011.
- [25] P. Nerikar, K. Rudman, T. Desai, D. Byler, C. Unal, K. McClellan, S. Phillpot, S. Sinnot, P. Peralta, B. Uberuaga and S. C.R., "Grain Boundaries in Uranium Dioxide: Scanning Electron Microscopy Experiments and Atomistic Simulations," *Journal of the American Ceramic Society*, vol. 94, no. 6, pp. 1893-1900, 2011.

Enrichment of Chromium at Grain Boundaries in Chromia Doped UO₂

Simon C. Middleburgh^{1*}, Simon Dumbill², Adam Qaisar², Ian Vatter², Megan Owen^{1,3}, Sarah Vallely¹, Dave Goddard⁴, David Eaves⁵, Mattias Puide⁶, Magnus Limbäck⁶, William E. Lee¹

¹Nuclear Futures Institute, Bangor University, Bangor LL57 1UT, United Kingdom ²National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG, United Kingdom

³Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom ⁴National Nuclear Laboratory, Preston Laboratory, Springfields, Preston, Lancashire, PR4 0XJ, United Kingdom

⁵Westinghouse Springfields Fuels Ltd, Station Rd, Lea Town, Preston PR4 OXJ, United Kingdom ⁶Westinghouse Electric Sweden AB, Utvecklingsgränd 33, 722 26 Västerås, Sweden

Abstract

Assessment of grain boundaries in chromia (Cr_2O_3) doped fuels has been carried out using high resolution transmission electron microscopy to assess the structure compared to undoped fuel produced via the same process. Chemical analysis of the grain boundary was carried out using Energy Dispersive X-ray Spectroscopy (EDS). It was shown that a relatively disordered phase is formed along the grain boundaries in the doped fuel and that they were chemically enriched in chromium. This has implications for the prediction and understanding of fuel manufacture and inreactor behaviour as many processes are highly dependent on grain boundary mechanisms.

Key words:

Doped fuel; grain boundary; high resolution transmission electron microscopy; complexions

Chromia doped fuels are being considered as an evolutionary accident tolerant fuel (ATF) candidate [1] due to their reported changes in mechanical properties [2], altered fission gas release [3] [4] and improved washout behaviour [5]. These properties are expected to vary as a result of the deviations that occur in the post-sintered microstructure. Originally, these dopants were used to improve the sinterability of UO₂, particularly from conversion routes such as the AUC (ammonium uranyl carbonate) conversion process [3] [5] [6], however efforts to understand further operational benefits are being assessed by the international nuclear fuel community.

The mechanism by which the dopants produce the larger grains is not fully understood. A range of investigations, both experimental and theoretical, have tended towards two, not necessarily competing, mechanisms: (1) an increase in bulk diffusivity that therefore increases the grain size during sintering [4] and (2) an increase in grain boundary diffusivity, again increasing the grain size. As noted, multiple mechanisms may be occurring simultaneously or dependent on dopant concentration and sintering atmosphere. For example, in the work of Bourgeois et al. [7], two distinct peaks in grain size are present at different dopant concentrations in the sample sintered in 1 vol.% $H_2O + H_2$ at ~600 µg (Cr₂O₃)/g(UO₂) and ~2500 µg (Cr₂O₃)/g(UO₂) indicating the likelihood of multiple grain growth mechanisms.

Mechanism (1) requires some bulk solubility in the UO_2 matrix, and then a large enough impact to cause quite a marked microstructural change, whilst Mechanism (2) requires low solubility species existing at grain boundaries and surfaces of UO_2 rather than in solid solution in order to maximise the concentration and impact on the grain boundary, but not too much to cause grain boundary pinning or a seizure in sintering. The presence of grain boundary phases may also alter the defect chemistry of the bulk system. Recent theoretical work has shown that the formation of disordered or amorphous grain boundary phases have much higher thermodynamic drives to deviate their stoichiometry compared to the crystalline bulk UO_2 [8], and therefore may alter the bulk material's stoichiometry. This will alter the sintering behaviour of the fuel and also will change subtle properties such as bulk material lattice parameters [9].

The solubility of Cr in UO₂ has been assessed on a number of occasions. Experimentally, the solubility has been estimated as 0.07 wt.% (700 wppm) by Bourgeois et al. [7] and a thorough evaluation was provided by Riglet-Martial et al. [10] to ranging from 500 wppm to 1000 wppm (for Cr_2O_3). It is regularly noted in literature that once the solubility limit of Cr_2O_3 in UO₂ is exceeded, grain growth is reduced. Some emphasis was placed onto the oxidation state of Cr entering the UO₂ matrix. It was noted that at high temperatures and low oxygen partial pressures, the Cr may reduce to a 2+ charge state, thus altering the solution route [4] with conflicting experimental observations that may be made clearer with the use of single crystal data in the future. A solubility model was put forward by Riglet-Martial [10] highlighting the potential reduction of Cr to a 2+ charge-state at high sintering temperatures and intermediate to high oxygen partial pressures (avoiding the formation of Cr metal) and the formation of CrO₍₁₎. The solubility model did not consider alterations to chemistry that could be present at grain boundaries and the impact of grain boundaries as defect sinks.

Killeen [3] performed some of the seminal work on Cr-doped UO_2 and highlighted, amongst other things, the segregation of Cr to grain boundaries during operation and therefore highlighting the instability of solute Cr at the dopant levels tested (0.5 wt.% in this study) as well as possible co-migration mechanisms with fission gases from the bulk to the grain boundaries.

The solubility of Al in UO_2 is reported to be negligible according to Kashibe and Une [12] and Lang [13]. This very low solution energy agrees with theoretical results performed using empirical potentials [14]. Solubility values are low and the mechanism for grain growth observed, for example by Kashibe [12] from 15 μ m in the undoped sample to 30 μ m in the 760 wppm Al₂O₃ sample, is presently not clear (especially as the redox behaviour of Al_2O_3 is markedly less varied compared to Cr_2O_3). Similarly, grain growth is observed in MgO doped UO₂ [12] and TiO₂ doped UO₂ [15], both known to have very low solubilities in UO₂ that are unlikely to impact intrinsic processes to produce changes in grain sizes observed experimentally. Specifically on TiO₂ as a dopant, Silva et al. [16] performed a study that assessed the dopant's impact when added through a sol-gel process where the resulting grain size was >300% than that of the un-doped fuel. Secondary Ti-rich phases were observed at grain boundaries and a reduction in grain size was also observed that was attributed to some solute Ti within the bulk, possibly as a result of the low-temperature gelation method. Indeed, it should be noted that the synthesis route chosen will significantly alter the distribution and behaviour of the additions to UO2, and mix-milling of powders (as is generally the production route for commercial fuels) [17] can only be compared to sol-gel and wet synthesis methods [9] [18] with care.

Other work has considered the formation of a ternary or mixed U-Cr oxide and its implications. CrUO₄ was first reported by Brisi [19] and then Hoekstra [20]. Subsequently, experimental work has highlighted the assumed charge states of both Cr and U in this compound to be 3+ and 5+, respectively [21]. Solubility of Al into this structure was both theoretically predicted and experimentally verified, potentially providing some answers as to the changing behaviour when codoping Al_2O_3 with Cr_2O_3 into the UO_2 system that may be pointing towards other mechanisms that dictate grain growth in Cr_2O_3/Al_2O_3 doped fuels. The formation of $CrUO_4$ in the early stages of sintering could act as a key intermediate in the sintering behaviour of Cr-doped fuel, forming readily with UO_{2+x} [21], and the formation of the Al-containing (Cr,Al) UO_4 may enhance the effect of this intermediate compound at some stage of the sintering process. Further work assessing the potential beneficial impact of this intermediate is required.

Grain boundary complexion and structure is known to impact many synthesis and in-operation mechanisms of ceramics. First and foremost, the changing structures of grain boundaries have been strongly linked to changing in grain boundary mobility and diffusion mechanisms [22] [23]. Grain boundaries can be considered in groups depending on the order at the grain boundary, and if there is a distinct film or phase between the two crystallites. Complexion IV noted to be "a true wetting film because it has a thickness that depends only on the amount of available liquid phase (i.e. the thickness would diverge in a glass melt)" [24].

This work uses pellets produced via a commercial route to investigate the grain boundary structure and composition produced as a result of doping. The doped pellet's structure is compared to an undoped fuel. The aim is to assess whether Cr is observed to segregate to grain boundaries, to assess the resulting grain boundary structures and to add to the body of work investigating the role of Cr_2O_3 and other relatively insoluble additives to UO_2 .

Production of Cr_2O_3 and Al_2O_3 doped UO_2 pellets was carried out at Westinghouse Electric Sweden's Västerås facility. AUC converted UO_2 powder (with O/U stoichiometry of 2.14) was mixed with 500 wppm of Cr_2O_3 and 150 wppm Al_2O_3 for approximately one hour to obtain full homogeneity. It is important to note that according to the existing literature, the Cr_2O_3 concentration is expected to be below the solubility limit.

The doped powder was pressed to green pellets with a force of approximately 49 kN. The green pellets were sintered in a H_2/CO_2 atmosphere at a maximum temperature of 1770 °C. Previous work by Arborelius et al. has reported expected properties and parameters of the pellets produced by this method (equivalent to pellet D3 in that work) [5].

A standard undoped UO₂ pellet was produced using similar sintering conditions (1730-1750°C in a H_2/N_2 atmosphere) to compare to the doped pellet. This was produced at the Springfields Fuels Ltd manufacturing facility using UO₂ converted through the integrated dry route. Final stoichiometries of both pellets were determined to be in the range 2.00-2.02 through X-Ray Diffraction lattice parameter measurements.

Sample examination was carried out using both Tescan XEIA3 plasma focused ion-beam and FEI Helios 600i focused ion-beam (FIB) instruments, the latter was used for transmission electron microscope (TEM) sample preparation. Figure 1 shows the back-scattered electron micrograph image of the un-doped and doped fuels highlighting the significant increase in grain size upon doping with Cr₂O₃. These images were used to identify grain boundaries that were subsequently targeted for further analysis. Lamella samples were extracted from the bulk cross-section samples and then thinned to approximately 150 nm thickness using varying ion beam energies and final stages of preparation conducted at 5 kV and a final cleaning polish at 2 kV was used.



Figure 1 - Back-scattered electron micrograph images of undoped (left) and Cr-doped UO_2 analysed in this study. Grain size enlargement is clearly shown in the doped fuel.

Samples were then examined in a JEOL 2100 TEM with a LaB₆ electron source operated at 200 kV and equipped with an Oxford Instruments Ultimax X-ray detector and AZtec software. Overview images were taken in bright-field TEM mode and high resolution TEM (HR-TEM) was used to examine the grain boundary structures. Scanning transmission (STEM) mode was used to obtain compositional maps and line profiles across grain boundaries using energy-dispersive X-ray analysis (EDX).

High resolution transmission electron microscopy (HR-TEM) was undertaken on both the Cr-doped and undoped UO₂ samples after sample preparation. The sections prepared were specifically targeted to assess the grain boundary nature of the ceramics. Figure 2 provides a micrograph of a grain boundary in the Cr-doped UO₂. The atomic ordering in the grains either side of the boundary is distinct, highlighting that the grain boundaries themselves are somewhat disordered although there appears to be evidence of some diffusive ordering, similar to the theoretical predictions proposed by Rushton et al. [25] related to glass-crystal interfaces.



Figure 2 – **Top:** High resolution transmission electron microscopy (HRTEM) image from the Cr-doped UO₂ pellet including a grain boundary. Inset is a higher magnification of a portion of the grain boundary. **Below:** other examples of HRTEM images of grain boundaries in the Cr-doped pellet.

In regions of the grain boundary reported in Figure 2, the thickness of the grain boundary can be seen to be 2-3 atomic planes thick, indicating a complexion III or IV system as defined by Dillon et al. [23]. The nature of the grain boundary appears ordered in some regions and disordered in other regions, especially those that are thicker. This observation is also in line with categorising the grain boundaries in the Cr-doped samples as complexion II or IV boundaries. These bi-layers or tri-layers have been shown to impact a number of properties including atomic transport that may impact the sintering and operation of such materials.

When assessing the grain boundary structure of the undoped system, the thickness of the grain boundary film varied considerably from nearly zero thickness (Figure 3a and 3b) to similar thicknesses observed in the doped samples (Figure 3c and 3d). This variation in grain boundary type is commensurate with previous experimental work assessing grain boundaries using electron back-scattered diffraction (EBSD) techniques [26] that determined that coincident site lattice (CSL) boundary fraction was of the order of 15% of the observed grain boundaries.



Figure 3 - Examples of high resolution microscopy of four grain boundaries observed in the undoped UO₂ sample. Top (a&b): grain boundaries with very little thickness/disorder observed and Bottom (c&d): grain boundaries with a thickness similar to the doped sample.

Chemical assessment of the grain boundaries was undertaken using EDX analysis. In the doped fuel system, a number of line scans were carried out across grain boundaries and are reported in Figure

4. Due to the interaction region of the EDX analysis, the resolution around the grain boundary is not sharp, however there is a clear enrichment of Cr observed at the grain boundary. This indicates that the Cr is not in complete solid solution within the bulk of the system, which provides data to aid the mechanistic understanding of not only grain growth in these large-grained doped fuels, but will also be important to consider when assessing the material's behaviour in reactor. As expected, the undoped pellet did not show any enrichment of Cr at the grain boundary.



Figure 4 - Chromium concentration as a function of distance from the grain boundary assessed by EDX spectroscopy.

The implications of the observations are important when considering the development and use of doped fuels that enhance grain boundaries. These results highlight that the solubility of Cr into the bulk, even at the low dopant levels of 500 wppm Cr₂O₃, is not complete when considering the commercial route for pellet production and that Cr will be affecting the behaviour of grain boundaries during the sintering process and during operation. Sintering atmospheres, temperatures and profiles are known to impact the solubility and behaviour of Cr in the UO₂, and in addition to affecting the bulk behaviour, the sintering atmosphere will also be altering the structure and chemistry of the grain boundary.

The possible stabilization of higher complexity grain boundaries will likely impact the character of grain boundary bubbles that form containing fission gases, and the mobility of fission products along the grain boundary. Further work should be carried out to assess the role of Cr within the grain boundary structure on the mobility of fission gases and volatile species along them, altering their transport to the rod free volume. Our findings build upon the experimental findings from Killeen [3], who reported significant grain boundary segregation of Cr in Cr-doped fuel after irradiation. Further work should assess the source of the diffuse grain boundary observations of Killeen and whether the source could be a combination of bulk Cr moving to boundaries or whether the high concentration of Cr at the grain boundaries acted as the source of the diffuse Cr regions.

Experimental work has identified that creep is higher in Cr-doped fuels and alumino-silicate doped pellets [2]. The alteration in grain boundary structure and chemistry observed in this investigation provides a basis for this observation and highlights that Coble creep mechanisms are altered in doped fuels.

Future work should also consider the implications of the findings in this investigation on phenomena such as high burnup structure formation, the impact of the grain boundaries as sinks for defects and non-stoichiometry as well as the implications of grain boundary attack by corrosive species and steam relevant to washout events where a cladding structure has failed.

In conclusion, the present investigation has undertaken a high-resolution transmission electron microscopy assessment on doped and undoped UO_2 pellets post sintering. The grain boundary structure of the doped fuel was observed to have been altered in the doped fuel system and chemical analysis highlighted the enrichment of Cr at the grain boundaries in the doped fuel system. The observation has implications to the mechanistic understanding of the production and operation of doped fuels.

Acknowledgements

Simon Middleburgh and William Lee are funded through the Sêr Cymru II programme by Welsh European Funding Office (WEFO) under the European Development Fund (ERDF). Access to the facilities at the National Nuclear Laboratory was made possible through the NNUF access scheme through the EPSRC (EP/T011351/1). Preparatory work was carried out in the Bangor University Fuel Fabrication Facility (BUFFF) – see www.bufff.online – sponsored by the EPSRC (EP/V035223/1). This work was supported by the BEIS sponsored Nuclear Innovation Programme.

References

- Y. Che, G. Pastore, J. Hales and K. Shirvan, "Modeling of Cr2O3-doped UO2 as a near-term accident tolerant fuel for LWRs using the BISON code," *Nuclear Engineering and Design*, vol. 337, pp. 271-278, 2018.
- [2] J. Wright, C. Anghel, S. Middleburgh and M. Limback, "Fuel hardware considerations for BWR PCI mitigation," in *Top Fuel 2016: LWR fuels with enhanced safety and performance*, Boise, ID (USA), 2016.
- [3] J. Killeen, "Fission gas release and swelling in UO2 doped with Cr2O3," *Journal of Nuclear Materials,* vol. 88, pp. 177-184, 1980.
- [4] M. Cooper, G. Pastore, Y. Che, C. Matthews, A. Forslund, C. Stanek, K. Shirvan, T. Tverberg, K. Gamble, B. Mays and D. Andersson, "Fission gas diffusion and release for Cr2O3-doped UO2: From the atomic to the engineering scale," *Journal of Nuclear Materials*, vol. 545, p. 152590, 2021.
- [5] J. Arborelius, K. Backman, L. Hallstadius, M. Limback, J. Nilsson, B. Rebensdorf, G. Zhou, K. Kitano, R. Lofstrom and G. Ronnberg, "Advanced Doped UO2 Pellets in LWR Applications," *Journal of Nuclear Science and Technology*, vol. 43, pp. 967-976, 2006.

- [6] I. Greenquist, M. Tonks, M. Cooper, D. Andersson and Y. Zhang, "Grand potential sintering simulations of doped UO2 accident-tolerant fuel concepts," *Journal of Nuclear Materials*, vol. 532, p. 152052, 2020.
- [7] L. Bourgeois, P. Dehaudt, C. Lemaignan and A. Hammou, "Factors governing microstructure development of Cr2O3-doped UO2 during sintering," *Journal of Nuclear Materials*, vol. 297, pp. 313-326, 2001.
- [8] S. Middleburgh, W. Lee and M. Rushton, "Structure and properties of amorphous uranium dioxide," *Acta Materialia*, vol. 202, pp. 366-375, 2021.
- [9] P. Kegler, M. Klinkenberg, A. Bukaemskiy, G. Murphy, G. Deissmann, F. Brandt and D. Bosbach, "Chromium Doped UO2-Based Ceramics: Synthesis and Characterization of Model Materials for Modern Nuclear Fuels," *Materials*, vol. 14, p. 6160, 2021.
- [10] C. Riglet-Martial, P. Martin, D. Testemale, C. Sabathier-Devals, G. Carlot, P. Matheron, X. Iltis,
 U. Pasquet, C. Valot, C. Delafoy and R. Largenton, "Thermodynamics of chromium in UO2 fuel: A solubility model," *Journal of Nuclear Materials*, vol. 447, pp. 63-72, 2014.
- [11] S. Kashibe and K. Une, "Effect of additives (Cr2O3, Al2O3, SiO2, MgO) on diffusional release of Xe from UO2 fuels," *Journal of Nuclear Materials*, vol. 254, pp. 234-242, 1998.
- [12] S. Lang, "High-temperature Reactions of Uranium Dioxide with Various Metal Oxides," National Bureau of Standards Circular 568, Washington DC (USA), 1956.
- [13] S. Middleburgh, D. Parfitt, R. Grimes, B. Dorado, M. Bertolus, P. Blair, L. Hallstadius and K. Backman, "Solution of trivalent cations into uranium dioxide," *Journal of Nuclear Materials*, vol. 420, pp. 258-261, 2012.
- [14] K. Une, S. Kashibe and K. Ito, "Fission Gas Behavior during Postirradiation Annealing of Large Grained U02 Fuels Irradiated to 23 GWd/t," *Journal of Nuclear Science and Technology*, vol. 30, pp. 221-231, 1993.
- [15] C. Silva, R. Hunt and A. Nelson, "Microstructural and crystallographic effects of sol-gel synthesized Ti-doped UO2 sintered under reducing conditions," *Journal of Nuclear Materials*, vol. 552, p. 153003, 2021.
- [16] C. Silva, R. Hunt and K. Holliday, "An evaluation of tri-valent oxide (Cr2O3) as a grain enlarging dopant for UO2 nuclear fuels fabricated under reducing environment," *Journal of Nuclear Materials*, vol. 553, p. 153053, 2021.
- [17] H. Smith, L. Townsend, R. Mohun, T. Cordara, M. Stennett, F. Mosselmans, K. Kvaahnina and C. Corkhill, "Cr2+ solid solution in UO2 evidenced by advanced spectroscopy," *Communications Chemistry*, vol. 5, p. 163, 2022.
- [18] C. Brisi, "The uranate of the MU3O10 type," Annali di Chimica, vol. 53, p. 325, 1963.
- [19] H. Hoekstra, "Some Uranium-Transition Element Double Oxides," *Advances in Chemistry*, vol. 71, pp. 211-227, 1967.

- [20] M. Cooper, D. Gregg, Y. Zhang, G. Thorogood, G. Lumpkin, R. Grimes and S. Middleburgh, "Formation of (Cr, Al)UO4 from doped UO2 and its influence on partition of soluble fission products," *Journal of Nuclear Materials*, vol. 443, pp. 236-241, 2013.
- [21] S. Dillon, M. Harmer and J. Luo, "Grain boundary complexions in ceramics and metals: An overview," *JOM*, vol. 61, pp. 38-44, 2009.
- [22] S. Dillon and M. Harmer, "Relating Grain-Boundary Complexion to Grain-Boundary Kinetics I: Calcia-Doped Alumina," *Journal of the American Ceramic Society*, vol. 91, pp. 2304-2313, 2008.
- [23] S. Dillon, M. Tang, W. Carter and M. Harmer, "Complexion: A new concept for kinetic engineering in materials science," *Acta Materialia*, vol. 55, no. 18, pp. 6208-6218, 2007.
- [24] M. Rushton, R. Grimes and S. Owens, "Partial ordering of glass networks adjacent to simulated glass–crystal interfaces," *Journal of Non-Crystalline Solids*, vol. 357, pp. 3278-3287, 2011.
- [25] P. Nerikar, K. Rudman, T. Desai, D. Byler, C. Unal, K. McClellan, S. Phillpot, S. Sinnot, P. Peralta, B. Uberuaga and S. C.R., "Grain Boundaries in Uranium Dioxide: Scanning Electron Microscopy Experiments and Atomistic Simulations," *Journal of the American Ceramic Society*, vol. 94, no. 6, pp. 1893-1900, 2011.

Credit Statement

Simon C. Middleburgh: Conceptualization, Formal analysis, Writing -original draft, review & editing, Supervision.

Simon Dumbill: Conceptualization, Methodology, Formal analysis, Writing -original draft, review & editing, Data curation, Investigation.

Adam Qaisar: Conceptualization, Methodology, Formal analysis, Writing -original draft, review & editing, Data curation, Investigation.

Ian Vatter: Methodology, Formal analysis, Data curation, Investigation.

Megan Owen: Formal analysis, Writing -original draft.

Sarah Vallely: Methodology, Formal analysis, Writing -original draft, Investigation.

Dave Goddard: Conceptualization, Methodology, Formal analysis, Writing -original draft, Resources, review & editing.

David Eaves: Conceptualization, review & editing, Resources

Mattias Puide: Conceptualization, review & editing.

Magnus Limbäck: Funding acquisition, Resources

William E. Lee: Writing -original draft, review & editing, Funding acquisition

Declaration of interests

□The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

⊠The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Megan Owen reports financial support was provided by Westinghouse Electric Simon Middleburgh reports financial support was provided by Westinghouse Electric.