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Oxidation of UN/U₂N₃- UO₂ composites: an evaluation of UO₂ as an oxidation barrier for the nitride phases

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A B S T R A C T

Composite fuels such as UN-UO₂ are being considered to address the lower oxidation resistance of the UN fuel from a safety perspective for use in light water reactors, whilst improving the in-reactor behaviour of the more ubiquitous UO₂ fuel. An innovative UN-UO₂ accident tolerant fuel has recently been fabricated and studied: UN microspheres embedded in UO₂ matrix. In the present study, detailed oxidative thermogravimetric investigations (TGA/DSC) of high-density UN/U₂N₃-UO₂ composite fuels (91-97 wt%), as well as post oxidised microstructures obtained by SEM, are reported and analysed. Triplicate TGA measurements of each specimen were carried out at 5 K/min up to 973 K in a synthetic air atmosphere to assess their oxidation kinetics. The mass variation due to the oxidation reactions (~%), the oxidation onset temperatures (OOTs), and the maximum reaction temperatures (MRTs) are also presented and discussed. The results show that all composites have similar post oxidised microstructures with mostly intergranular cracking and spalling. The oxidation resistance of the pellet with initially 10 wt% of UN microspheres is surprisingly better than the UO₂ reference. Moreover, there is no significant difference in the OOT (~557 K) and MRT (~615 K) when 30 wt% or 50 wt% of embedded UN microspheres are used. Therefore, the findings in this article demonstrate that the UO₂ matrix acts as a barrier to improve the oxidation resistance of the nitride phases at the beginning of life conditions.

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1. Introduction

After the Fukushima Daiichi disaster in 2011, the nuclear community has strived to engineer a successor to the standard uranium dioxide (UO₂)-Zr fuel-cladding system within light water reactors (LWRs). This severe accident scenario demonstrated that the standard fuel system degrades rapidly in such extreme conditions [1]. From that point on, many studies have been carried out focusing on fabricating accident tolerant fuel (ATF) materials that can withstand accident conditions for a longer time. These new ATF materials have to maintain or enhance the fuel performance under normal and transient operating conditions, as well as during a potential design basis accident (DBA) and beyond-design basis accident (BDBA) [2].

Uranium nitride (UN) has been considered a promising ATF candidate to substitute UO₂ in LWRs mainly because of its higher uranium density, thermal conductivity, and similar melting point in comparison with UO₂ [3]. These improved properties would allow operating the reactor with a lower fuel centreline temperature, which provides the benefit of a higher margin for melting. Additionally, an improved fission density would enable higher burnup, larger power uprates, and longer fuel resident time [4–6] that are often labelled as advanced technology fuel attributes. However, the UN fuel has low oxidation resistance when in contact with the coolant water in the LWR system [7]. In such a situation, the nitride fuel readily reacts with the coolant and loses its structural integrity, resulting in fuel pellet oxidation, pulverisation, washout and relocation.

Composite fuel designs are considered to overcome the lower oxidation resistance of the UN fuel. The main idea of such composites is to combine the UN with a material that has a better oxidation resistance. This material would form a protective barrier...
around the UN and, therefore, prevent its oxidation. Several materials such as CrN and AlN [8], ZrN [9], U2Si2 [10,11], and UO2 [12–14] have been studied. Among these options, UO2 shows great advantages since it is already used as a fuel in LWR, as well as it has a good oxidation resistance when in contact with the coolant water.

Many studies on UN degradation/oxidation have been performed since the 1960s [7,15–26]. Nevertheless, there are few studies in the literature related to the degradation/oxidation of UN-UO2 composite fuels [25,27], but none of them is related to UN microspheres embedded in UO2 matrix. Both previous studies used mixtures of UO2 and UN powders to fabricate the composites. Watkins et al. [25] investigated the degradation behaviour of UN-UO2 (5–10 wt%) sintered pellets (> 90 %TD) in high-pressure water. The samples were subjected to hydrothermal oxidation in a static autoclave filled with water at high temperatures (523-623 K) and pressures (up to 16.5 MPa), which are relevant to LWR operating conditions for a short duration. The authors concluded that grain boundary attack and spallation are the primary degradation mechanism in hydrothermal oxidation conditions. Shrivpasra et al. [27] reported thermogravimetric analyses of UN-UO2 (5–30 v%) in steam (62–83 %) during heating to 1273 K, and isothermal data for such composites at 623 K under 82 % steam during 12 h. In both thermogravimetric experiments, the addition of UO2 delayed the oxidation onset temperature when compared to pure UN. So, the autoclave experiments have permitted the reproduction of an LWR-type environment, but have not provided useful information such as the oxidation onset temperature and the maximum reaction rate, as thermogravimetry has provided. Thus, both autoclave and thermogravimetric investigations are relevant and complementary.

An innovative UN-UO2 accident tolerant fuel has recently been fabricated and studied by the authors of this work [28]: UN microspheres embedded in UO2 matrix. Since this composite fuel is a new concept, there is no data regarding its oxidation resistance neither using thermogravimetric examination nor autoclave test. As a first approach, thermogravimetric investigations are essential to understand the material parameters which govern the oxidation reactions of this fuel.

In the present study, detailed thermogravimetric (TG) and differential scanning calorimetry (DSC) investigations of the oxidation reactions in a synthetic air atmosphere up to 973 K are reported and discussed. High-density UN-UO2 (91–97 %TD) composites, within the limits for LWR application [29,30], were selected from our previous study [28] and are investigated here. This work also describes the influence of the amount (wt%) of each phase present in the sintered pellet, i.e. UO2, UN and α-U2N3, on the oxidation kinetics. Additionally, pure UO2, powder and UN microspheres, as well as UO2 and UN sintered samples are evaluated and used as references (UO2 pellet and UN microspheres). As a result of introducing triplicates in the TGA experiments, uncertainties related to the total weight variation (%), oxidation onset temperatures (OOTs), maximum reaction temperatures (MRTs), as well as the reliability of the TG results were obtained and demonstrated. Therefore, from the findings present in this study, future works are encouraged to perform additional investigations to assess the oxidation resistance of this fuel concept in TGA steam oxidation and/or autoclave test in an LWR-type environment.

2. Methods

2.1. UN-UO2 composite fuel fabrication

Uranium nitride (UN) microspheres were fabricated by the internal sol-gel process at Chalmers University of Technology [31,32]. The reported amounts of nitrogen, carbon and oxygen, as well as the associated errors in the triplicate measurements (given as one standard deviation), were 5.72 ± 0.07 wt%, 833 ± 550 ppm and 1010 ±150 ppm, respectively, which give a chemical formula U(N0.13C0.32O0.55). N and O analyses were performed by the inert fusion method, using a LECO TC436DR equipment inside a nitrogen-filled glovebox (< 500 ppm O2) to minimise oxygen incorporation during sample preparation and analyses. The equipment was calibrated before the analyses by running blank samples for the zero calibration and D-lab standard (provided by Degenerors laboratory) containing 9.71 wt% N and 3 wt% O. The calibration standard was run three times and the furnace constants for N and O, respectively of the instrument, were adjusted if the measurement average deviated from the target value by more than 2 %. A C analysis was performed by the combustion method using a LECO CS744 instrument. Prior to carbon measurement, triplicate measurements of blank samples and a calibration standard were performed. The blank samples contained the crucible and combustion accelerator (Lecocell-II, to ensure proper heating of every sample), and the results were used for correcting the measurement baseline to zero. The calibration standard used is a drift standard for calibrating the instrument on top of the multipoint baseline calibration of the instrument. The drift calibration standard used was a carbon-containing steel pin standard from LECO containing 0.799 ± 0.011 wt% C. The as-fabricated UN microspheres were kept under argon for the duration of the investigations (< 1 ppm O2).

Uranium dioxide (UO2) powder was provided by Westinghouse Electric Sweden AB, which had the following properties: O/U ratio of 2.13, fill density of 2.19 g/cm3, specific surface area (B.E.T.) of 5.33 m2/g, mean particle size of 20.20 μm, and 990 ppm of H2O.

Mixtures of 10, 30 and 50 wt% of as-fabricated UN microspheres (52 %TD) and UO2, powder, as well as pure UO2, powder and UN microspheres, were sintered by the spark plasma sintering (SPS) method at the National SPS Facility in Stockholm/Sweden. This method is a field-assisted sintering technology, which uses low voltage and high current combined with an applied pressure to consolidate powders [33,34]. The mixtures of UO2, powder and as-fabricated UN microspheres (~ 4 g in total) were prepared inside a glovebox (< 0.1 ppm O2) connected to the SPS machine. The mixtures were manually homogenised in a small beaker (25 mL) for 1 min with a spatula, poured out in an assembled graphite die (with graphite punches), and transferred to the SPS chamber (more details can be found in our previous article [28]). The SPS equipment used in this study is a modified Dr Sinter machine inside a glovebox, under argon atmosphere (< 0.1 ppm O2), to minimise sample oxidation during preparation and sintering. The SPS chamber was depressurised to about 2 Pa to sinter the samples at 1773 K and 80 MPa, using the following thermal profile: heating at 100 K/min until 1573 K and then 50 K/min until 1773 K, held at this plateau for 3 min, and cooled to room temperature using two different cooling rates. First, a slow cooling (SC) profile: 10 K/min (1773–1573 K), 20 K/min (1573–1373 K) and 50 K/min (1373–973 K). Second, a fast cooling (FC) profile: 50 K/min (1773–1173 K). In both cases, from 973 K (SC) and 1173 K (FC) on, the cooling held naturally, i.e. no control over the cooling rate was applied. Additional details about the SPS equipment and sample preparation, as well as the sintering procedures, can be found in our previous article [28].

The samples are identified in this paper as UN(X)-UO2 (SC/FC), where X is the initial weight fraction (wt%) of UN microspheres in the composite, and SC/FC specifies which cooling rate was applied. Table 1 reports the sample identifications and the SPS parameters used in this study.

2.2. Oxidation experiments

The oxidation kinetics of the samples were assessed by thermogravimetric analyses (TGA) in a synthetic air flow of 20 mL/min, using a TGA Discovery equipment (TA Instruments) with a weight
sensitivity of 0.1 μg. The samples were placed in a platinum pan without cover and heated up to 973 K at 5 K/min, held at this plateau for 10 min, and then cooled to room temperature. Each sintered pellet (~3.5 g, ~6 mm x 5 mm diameter x height) was cracked in small pieces, and about 45 mg were used in the TG experiments. The weight variation (%) was defined as the percentage due to the weight gain during the oxidation reactions. Also, oxidation onset temperature (OOT) was defined as the temperature at which 5% of the total weight variation was observed [20], while the maximum reaction temperatures (MRTs) were obtained by analyses of the first derivatives of the weight variation curves (%/min). These considerations are suitable to adopt a consistent basis of comparison between each sample.

Three TG replicate measurements were performed for each sample to assess the standard deviations of all mean values of total weight variation (%), OOTs, MRTs, as well as the repeatability and reliability of the TG results. The standard deviations of the mean values were calculated by dividing the standard deviation of each variable (i.e. total weight variation (%), OOTs, MRTs) by the square root of the number of repeated measurements made [35], which is equal to three in our study. As-fabricated UO$_{2.13}$ powder and uncrushed UN microspheres were also oxidised to provide insights about their oxidation behaviours and data for comparison with UO$_2$ (SC) and UN (SC) samples.

Additionally, differential scanning calorimetry (DSC) analysis was performed in a Netzsch STA 449 F3 Jupiter equipment under a synthetic air flow of 40 mL/min. Approximately 90 mg of UN(50)-UO$_2$ (FC) composite fuel was characterised by DSC to evaluate the thermodynamics involved during the oxidation of the three phases present in the sintered material, i.e. UO$_2$, UN and α-U$_2$N$_3$. The material was also heated at 5 K/min up to 973 K, kept at this temperature for 10 min, and cooled to room temperature.

2.3. Characterisation

UN microspheres and UO$_{2.13}$ powder were characterised by scanning electron microscopy (SEM) and X-ray diffraction (XRD) to evaluate their morphologies and crystalline structures, respectively. The SEM used in all analyses was an SEM FEI XL30 with the INCA software. The external surfaces of both compounds were examined using the secondary electrons (SE) detector. Bulk morphologies of sintered UN microspheres and UO$_{2.13}$ powder, UN (SC) and UO$_2$ (SC) samples, respectively, were examined after standard metallographic preparation (grinding and polishing) of pellets that were hot mounted in a phenolic resin with carbon filler. Colloidal silica suspension (OP-U, 0.04 μm, Struers) was used to perform a final polishing (2 min) to enhance the contrast between the grains of UO$_2$ (SC).

The XRD scans of the raw materials were carried out in a Siemens D5000 diffractometer with Cu$Kα$ radiation (Ni filter), 2θ ranging between 20° and 120°, with 2θ step of 0.02° and acquisition time of 9 s for each step. The UN microspheres were milled inside a glovebox filled with argon (< 250 ppm O$_2$) using a mortar and pestle, and then encapsulated in an air-tight XRD specimen holder (Bruker model A100B138-B141) to avoid any oxidation during the analysis.

After sintering, the external surfaces of the samples were ground to remove the residual graphite foil from the SPS experiments. XRD and elemental analyses had been performed before in sintered pellets and the results showed that the C contents were consistent with the initial materials [36]. Therefore, grinding the sintered pellet surface is enough to remove the bounded graphite paper from SPS.

A modified Archimedean method, with chloroform as the immersion medium, was used to measure the sintered densities of all samples [36]. Afterwards, the sintered pellets were cut longitudinally and milled to powder using a mortar and pestle in an argon-filled glovebox (< 250 ppm O$_2$) for XRD analyses, using the same equipment, special holder, and parameters. The theoretical densities (TD) were computed based on the weight fractions of each phase after SPS using the Rietveld method and the software MAUD [37]. Before all XRD measurements, the software MAUD were configured with the information from the Siemens D5000 diffractometer (e.g. wavelengths, goniometer radius). Additionally, an instrumental broadening determination (with yttrium oxide) was performed after calculating the lattice parameters and the weight fractions after sintering [38]. The considered TD reference values [39] for UO$_2$, UN and α-U$_2$N$_3$ were 10.96 g/cm$^3$, 14.32 g/cm$^3$ and 11.24 g/cm$^3$, respectively. SEM examinations were performed in the polished longitudinal cross sections, coated with carbon, using both secondary and backscattered electron (BSE) detectors.

SEM-BSE images were used to estimate the average grain sizes of the UO$_2$ phase in the composites using the software ImageJ [40,41]. The averages were computed based on 5 measurements per grain, considering 20 grains per image and 3 images per sample. Brightness and contrast were adjusted to enhance the grain orientation contrasts. In total, 100 measurements per sample were collected and the average grain sizes, with 95 % confident intervals [35], were obtained from these values.

Post oxidised samples were examined using the same SEM equipment to analyse their surface morphologies. Energy-dispersive X-ray spectroscopy (EDS) was also used to identify the chemical elements present in the oxidised samples.

3. Results and discussion

3.1. Phase and morphology of the raw materials and non-oxidised samples

Fig. 1 (a) and Fig. 1 (b) report the morphologies of the UO$_{2.13}$ powder and UN microsphere, respectively. UO$_{2.13}$ powder’s morphology was characteristic of the industrial ammonium uranium carbonate (AUC) wet route [42], with internal porosity that mainly contributes to the surface area of the material. UN microspheres were porous, with some cracks on the surface from the fabrication process, and had a density of about 52 %TD [28].

The XRD patterns of the UO$_{2.13}$ powder and UO$_2$ (SC) sample, as well as the UN microspheres and UN (SC) sample, are presented

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>UN microsphere (wt%)</th>
<th>Cooling rate (K/min)</th>
<th>Sample identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_{2.13}$ powder</td>
<td>0</td>
<td>10 (1773-1573 K), 20 (1573-1373 K) and 50 (1373-973 K)</td>
<td>UO$_2$ (SC)</td>
</tr>
<tr>
<td>UN microsphere</td>
<td>100</td>
<td>10 (1773-1573 K), 20 (1573-1373 K) and 50 (1373-973 K)</td>
<td>UN (SC)</td>
</tr>
<tr>
<td>UN-UO$_2$</td>
<td>10</td>
<td>50 (1773-1173 K)</td>
<td>UN(10)-UO$_2$ (FC)</td>
</tr>
<tr>
<td>UN-UO$_2$</td>
<td>30</td>
<td>10 (1773-1573 K), 20 (1573-1373 K) and 50 (1373-973 K)</td>
<td>UN(30)-UO$_2$ (SC)</td>
</tr>
<tr>
<td>UN-UO$_2$</td>
<td>50</td>
<td>50 (1773-1173 K)</td>
<td>UN(50)-UO$_2$ (SC)</td>
</tr>
</tbody>
</table>

All samples were sintered at 1773 K and 80 MPa for 3 min. SC = slow cooling, FC = fast cooling.
The UN-UO₂ composite fuel microstructures described in Fig. 4 (a-d) show that a third phase, α-U₂N₃ (sesquinitride), was formed during fabrication as a result of the interaction between UO₂ and UN [28]. Similar microstructural features were observed in a previous study of the reaction of UO₂ with carbon in the presence of N₂ at 1973 K [51]. Moreover, based on our previous article [28] and published data [12–14], the interaction between the UN and UO₂ does not depend on the sintering atmosphere and density/morphology/type of the UN phase. Yet, the interaction between the UN and UO₂ does not depend on the O/U ratio either. As demonstrated by [14], sintering UO₂ powder with dense UN pieces (125–1000 μm, 95.7–97.2 %TD) resulted in a second nitride phase. This behaviour may be due to the equilibrium phase of UO₂, which describes that the oxide can be present as a hypo-stoichiometric phase (UO₂⁻) at the sintering temperature and low oxygen potential [52]. The amount of each phase in the sintered materials affected the oxidation kinetics of the samples (details are described in the upcoming sections).

Our previous study [28] showed that sintering the UN-UO₂ composites at low temperatures (< 1173 K) and pressures (< 40 MPa), combined with a fast cooling profile, may minimise the amount of the α-U₂N₃ phase. Previous studies on the U-O, U-N, and quaternary system U-C-O-N [53–56] provide important information regarding the UO₂, UN₂, UN₂O₃, and UN₂N₃-UO₂ systems, as well as propose that the formation of the UN₂N₃ phase during sintering may be minimised by either lowering the sintering temperature or changing the sintering atmosphere to argon.

Table 2 reports the average grain sizes of the UO₂ (SC) and UN (SC) samples, as well as of the UO₂ phase in the composites. The computed average grain size for UO₂ (SC) was 3.2 ± 0.2 μm, slightly different from a previous study (5.6 ± 1.6 μm) that used similar SPS parameters (1623 K, 40 MPa, 5 min) [47]. This difference may be due to an extra 2 min in the sintering time, since the authors found that the average grain size increases with the sintering time. UN (SC) sample’s value was 3.1 ± 0.4 μm, lower than the result obtained by Johnson and Lopes [50]. The authors sintered UN powder by SPS at 1723 K (90 MPa, 3 min) and obtained an average grain size of 7.3 ± 0.2 μm. Since the expected sinterability of micro-sized powder is higher than coarse microspheres [49], this may be the reason why the authors found a larger average grain size. Regarding the composites, as a general rule, the higher the amount of nitride phases in the sample, the higher the average grain size of the UO₂ matrix. Since N forms a solid solution with the UO₂ matrix, such as UO₂-N, the grain growth was enhanced with the increase of the UN initial amount [49]. On the other hand, by only changing the cooling rate, the average grain size did not differ significantly when the uncertainties are considered.

Fig. 5 presents the powder XRD diffractograms of the sintered samples. In all composite fuels, a sesquinitride phase (α-U₂N₃) was
Fig. 2. X-ray diffraction patterns of the (a) UO$_{2.13}$ powder and UO$_2$ (SC) sample, and (b) UN microspheres and UN (SC) sample. UO$_{2.13}$ broadening peaks can be attributed to peak overlap owing to the presence of secondary phases such as U$_3$O$_7$ and U$_4$O$_9$ [25], as well as U$_3$O$_8$ [43,44]. Low intensity peaks (•) are present in the nitrides at (about) 28° (111) and 33° (200), which correspond to the UO$_2$ phase originated from oxygen impurity.

Fig. 3. Micrographs of non-oxidised (a) UO$_2$ (SC) and (b) UN (SC) samples. Higher magnification images better show the pores and grains morphologies. UO$_2$ (SC) had a dense microstructure with small and rounded pores (< 2 μm) on the grain corners, characteristic of closed porosity [49]. Conversely, UN (SC) had a porous structure with large, irregular and interconnected open pores (< 14 μm).

present, together with the UO$_2$ and UN initial phases. The amount of each phase, as well as the sintered and theoretical densities of all samples, are described in Table 3. The weight fractions of UN microspheres decreased in the composite fuels as a result of the interaction between the UN and UO$_2$ during fabrication, as demonstrated in our previous article [28]. The amounts of UN microspheres consumed/reacted during fabrication were then 87%, 87%, 63% and 30% for samples UN (10)-UO$_2$, UN (30)-UO$_2$ (SC), UN (30)-UO$_2$ (FC) and UN (50)-UO$_2$ (FC), respectively. Composite fuels with sintered densities of 91-96%TD were obtained using SPS in just 3 min of sintering time.

From Table 3, the final α-U$_3$N$_2$/UO$_2$ wt% ratios for the samples UN(30)-UO$_2$ (SC), UN(30)-UO$_2$ (FC) and UN(50)-UO$_2$ (FC) were approximately 0.20, 0.21, and 0.21, respectively. Conversely, the ratio for the sample with (initially) 10 wt% of UN microspheres was ~0.04, which was the lowest value among the composites mainly due to the highest wt% of UO$_2$. Thus, for a higher initial amount of UN microspheres (30 wt%, 50 wt%), the final α-U$_3$N$_2$/UO$_2$ wt% ratios showed a similar trend in the final composites (~0.20). Furthermore, the sintered/original molar ratios of nitrogen for the UN(10)-UO$_2$ (SC), UN(30)-UO$_2$ (SC), UN(30)-UO$_2$ (FC) and UN(50)-UO$_2$ (FC) specimens were 0.66, 0.93, 1.13, and 1.03, respectively. These results indicate that most of the initial N was retained in the sintered composites, as experimentally observed during the sintering of pure UN microspheres and a UN-UO$_2$ composite; no significant variation in the vacuum pressure at high temperatures (~ 773 K) [28].

3.2. Oxidation behaviour of the raw materials and ATF composites

TGA measurements were carried out in triplicate to assess the uncertainties and reliability related to the weight variations (%), OOTs and MRTs. However, for the sake of better visualisation, only one result per sample is presented in the following figures in the text. All measurements are available in Appendix A, which shows good repeatability and reliability of the experiments. Therefore, the results obtained from the microanalyses using TGA can be used as a starting point to understand the macro behaviour of the samples.
Fig. 4. SEM-BSE images of composite fuels showing (left) low magnification images, as well as samples (a) UN(10)-UO$_2$ (SC), (b) UN(30)-UO$_2$ (SC), (c) UN(30)-UO$_2$ (FC), and (d) UN(50)-UO$_2$ (FC). The composite microstructures were obtained from longitudinal cross-sections of the pellets at ~3 mm from the edge. The same microstructural features were observed near the pellet edges. A third phase indicated by the arrows, $\alpha$-U$_2$N$_3$ (sesquinitride), was formed in all UN-UO$_2$ composite fuels. The amount of UN microspheres and the cooling rates affected the amount and/or shape of the sesquinitride phase (more details can be found in [28]).

Fig. 5. X-ray diffraction patterns of the UO$_2$ (SC) and UN microspheres samples (references), as well as the UN-UO$_2$ composite fuels. Peaks related to the phase $\alpha$-U$_2$N$_3$ (ICSD PDF 00-015-0426) are present in all sintered composites.
Table 3
Amount of phases and sample densities after sintering.

<table>
<thead>
<tr>
<th>Sample identification</th>
<th>Amount of phases after sintering (wt%)</th>
<th>Theoretical density (TD) (g/cm³)</th>
<th>Sintered density (g/cm³) (% TD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂ (SC)</td>
<td>100 0 0</td>
<td>10.96 [39]</td>
<td>10.69 97.5</td>
</tr>
<tr>
<td>UN (SC)</td>
<td>0 100 0</td>
<td>14.32 [39]</td>
<td>12.00 83.8</td>
</tr>
<tr>
<td>UN(10)-UO₂ (FC)</td>
<td>95.0 ± 0.8 1.3 ± 0.2 3.7 ± 0.3</td>
<td>11.02</td>
<td>10.47 95.1</td>
</tr>
<tr>
<td>UN(30)-UO₂ (SC)</td>
<td>79.8 ± 0.7 3.9 ± 0.2 16.3 ± 0.6</td>
<td>11.14</td>
<td>10.65 95.6</td>
</tr>
<tr>
<td>UN(30)-UO₂ (FC)</td>
<td>73.4 ± 0.5 11.1 ± 0.2 15.5 ± 0.4</td>
<td>11.38</td>
<td>10.78 94.8</td>
</tr>
<tr>
<td>UN(50)-UO₂ (FC)</td>
<td>53.8 ± 0.4 34.9 ± 0.3 11.3 ± 0.4</td>
<td>12.16</td>
<td>11.11 91.3</td>
</tr>
</tbody>
</table>

* Calculated from the XRD data using the Rietveld refinement method and the software MAUD [37].
† Computed based on the weight fractions and individual theoretical densities of UO₂ (10.96 g/cm³), UN (14.32 g/cm³), and U₂N₃ (11.24 g/cm³) [39].

Fig. 6. Weight variations of all samples as a result of the oxidation reactions. Mass decreases at high temperatures (> 800 K) in the nitrides samples, as well as in the composites with 30 wt% and 50 wt% of UN microspheres, can be interpreted as nitrogen release from an intermediate oxynitride that is formed during the oxidation of the nitride phases [20,48].

Table 4
Theoretical oxidation reactions occurred in the oxidation thermogravimetric experiments, considering that the U₃O₈ phase was the ultimate product in all experiments [7,17,20,57].

<table>
<thead>
<tr>
<th>Oxidation reaction</th>
<th>Equation</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 UO₂ + O₂ → U₃O₈</td>
<td>(1)</td>
<td>UO₂ (SC) pellet oxidation reaction.</td>
</tr>
<tr>
<td>6 UN + 8 O₂ → 2 U₃O₈ + 3 N₂</td>
<td>(2)</td>
<td>UN (SC) pellet oxidation reaction.</td>
</tr>
<tr>
<td>3 U₂N₃ + 4 O₂ → 2 U₃O₈ + 4.5 N₂</td>
<td>(3)</td>
<td>Oxidation of α-U₂N₃ present in the sintered samples.</td>
</tr>
<tr>
<td>x UN₂O₃ + y UN + z U₂N₃ + D₁ → U₃O₈ + N₂</td>
<td>(4)*</td>
<td>Overall oxidation reaction of the sintered samples.</td>
</tr>
</tbody>
</table>

* x, y and z are related to the amounts of UO₂, UN and α-U₂N₃, respectively, present in the sintered pellets (Table 3).

Weight variation (%) measurements of the specimens oxidised in a synthetic air atmosphere up to 973 K are shown in Fig. 6, which indicates the differences between the nitride, composites, and UO₂ behaviours. The mass decreases observed at high temperatures (> 800 K), in both the nitrides and composites with 30 wt% and 50 wt% of UN microspheres, are also observed in previous studies [24,48]. According to these previous studies, the mass decreases can be interpreted as the release of nitrogen (as N₂ gas) from an intermediate oxynitride product that is formed during the oxidation of the nitride phases. We have not detected nitrogen in the SEM-EDS examinations; only oxygen and uranium as chemical elements were present in all the oxidised samples.

Theoretical weight variations were obtained using the reactions described in Table 4, considering that the ultimate product in all experiments was U₃O₈ and that the nitrogen exits the samples as N₂ gas [7,17,20,57]. These theoretical values were compared to the ones obtained from the TG results, with their deviations described in Table 5 as a percentage change (% change). The errors associated to the real values were obtained by considering the maximum and minimum values from the TG results. The percentage change was defined as the difference between the theoretical and real values divided by the theoretical one. All samples showed small weight variation uncertainties (≤ ± 0.17%) and percentage changes (≤ 4.5 %), indicating that the equations in Table 4 can describe the oxidation of the specimens, as well as showing good repeatability of the experiments. The weight variation of UO₂ (SC) (3.94 %) was only 0.3 % different from the stoichiometric UO₂ pellet. When the errors in both real and theoretical values are considered, the weight gain (real) of the samples UN (SC), UN (30)-UO₂, and UN (50)-UO₂ can be considered equivalent to the respective theoretical values. Sample UN (10)-UO₂ was the only one that presented a real
value slightly inferior to the theoretical one (the highest percentage change, 4.5%).

The weight variation of the UO₂ (SC) sample (3.94 %) in Table 4, when compared to the theoretical value (3.95 %), indicates that the UO₂,₁₃ powder reduced to stoichiometric UO₂ during sintering. Previous studies using spark plasma sintering [47] and conventional sintering [58–60] in vacuum atmospheres demonstrated that the UO₂,₁ₓ powder was reduced to UO₂,₀ during the sintering process. Ge et al. [47] justified the powder reduction as a result of the interaction between the graphite foil (from the SPS die) and UO₂,₁ₓ to form UC on the pellet surface (XRD result). After grinding the pellet to remove the graphite foil, only the UO₂ phase was present in the XRD diffractogram. Kuttty et al. [58] studied the sintering behaviour (dilatometry) of UO₂,₁₅ up to 1673 K in vacuum, demonstrating that the shrinkage curves for vacuum exactly coincided with that for Ar and Ar-8 % H₂. Therefore, the reduction of UO₂,₁ₓ to UO₂,₀ can happen independent of the sintering process (SPS or conventional sintering) and sintering atmosphere (Ar, vacuum, H₂).

The oxidation onset and maximum reaction temperatures, extracted from the weight variation curves (Fig. 7, Fig. 8, Fig. 9), are summarised in Table 5. The uncertainties related to both OOTs and MRTs are also described, showing a minimum variation of ± 1 K and a maximum of ± 9 K.

Fig. 7 portrays the weight variation curves for the raw materials, UO₂ (SC) and UN (SC) samples. The first derivatives of each curve, here named as reaction rates, are also plotted in the figure. The oxidation of the UO₂,₁₃ powder (Fig. 7 (a)) showed two oxidation steps: the first one is associated to a parabolic oxidation curve, while the second one is related to a sigmoid weight variation curve. The first step corresponded to the formation of U₃O₇/U₃O₈ on UO₂ powders, following a diffusion-controlled mechanism [61]. The results showed an OOT and MRT of 440 ± 3 K and 458 ± 2 K, respectively, and a weight gain of 0.86 % up to 523 K, which is in agreement with the formation of the U₃O₇/U₃O₈ phases [57]. The second step, associated with a sigmoid curve, is interpreted as the oxidation of the U₃O₇/U₃O₈ phases into U₃O₈ by a nucleation and growth mechanism [62]. OOT and MRT of this step were 623 ± 3 K and 631 ± 3 K, respectively, with a total weight variation of 2.47 ± 1 %, which is in agreement with a previous TG analysis [63].

Fig. 7 (b) shows the complete oxidation of UO₂ (SC) into U₃O₈, with a total weight variation of 3.94 ± 0.00 %; quite similar to the nominal value of 3.95 % (Table 5). In the UO₂ (SC) case, the oxidation followed a sigmoid curve in one major step: from UO₂...
to $\text{U}_2\text{O}_8$. The oxidation started with incubation time, at which a fine layer of $\text{U}_2\text{O}_7$ was formed on the external surface, followed by a parabolic kinetic ($-623 - 680$ K), and then a linear kinetic ($-680 - 750$ K) until the complete oxidation into $\text{U}_3\text{O}_8$ [57,61]. The OOT (570 ± 5 K) and MRT (704 ± 2 K) for $\text{UO}_2$ (SC) were higher than the $\text{UO}_2\text{N}_3$ powder, since the oxygen chemisorption and the diffusion-controlled formation of $\text{U}_3\text{O}_8$ are both proportional to the surface area [57,64,65]. Thus, the higher the surface area, or the smaller the particle size, the faster the oxidation process.

UN microspheres and UN (SC) weight variation curves are presented in Fig. 7 (c) and Fig. 7 (d), respectively. The oxidation behaviours of both samples are similar, with sigmoid curves and total weight variation close to the nominal value of 11.37 %. The OOT for the UN microspheres (549 ± 1 K) was slightly higher than the UN (SC) (533 ± 2 K). As previously demonstrated [20], the oxidation resistance of the UN samples can be improved by eliminating open porosity. In our case, however, open porosity was not the only parameter that affected the oxidations. Yet, since the densities of the UN samples were different, the surface areas of both samples were also different and impacted the oxidation behaviour. Thus, a combination of higher open porosity and surface area of the UN microspheres (52 %TD), compared to UN (SC) (83.8 %TD), resulted in an OOT increment of about 16 K. Regarding the MRTs, the microspheres showed a lower temperature and higher rate, indicating that the formation of $\text{U}_3\text{O}_8$ was faster after the formation of an oxide layer during the incubation time. These results were expected since the UN microspheres were porous, which provides more surface area to be attacked during oxidation. Our ongoing work is focused on optimising the UN-$\text{UO}_2$ composite by using denser (80-95 wt%, based on previous studies [66-68]) and coated UN microspheres to avoid the interaction between UN and $\text{UO}_2$, as well as to delay the oxidation onset temperature of the UN microspheres.

The amount of UN microspheres affected the oxidation kinetics of the composite fuels, as reported in Fig. 8. For the same cooling rate, e.g. fast cooling (FC), the higher the UN content in the sintered composites, the higher the total weight variation. Additionally, there was a sesquinitride phase in the sintered composites, $\alpha$-$\text{U}_2\text{N}_3$, that formed during fabrication as a result of the interaction between UN and $\text{UO}_2$ (Fig. 4, Fig. 5, [28]). The oxidation of this sesquinitride also contributes to increasing the total weight varia-

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Fig. 8. Influence of the initial amount of UN microspheres (wt%) on the (a) weight variations and (b) reaction rates. The oxidation behaviour of UN(10)-$\text{UO}_2$ (SC) was similar to the $\text{UO}_2$ (SC) reference. The composite showed a higher OOT and MRT, as well as slower reaction rate at the maximum point. No changes in OOT was observed when the initial amount of UN microspheres changed from 30 wt% to 50 wt%. These results seemed to demonstrate that the $\text{UO}_2$ matrix provided a barrier against oxidation of the nitride phases.
tions. As reported in Table 3, the total amount of UN + α-U₃N₄ in UN(10)-UO₂ (FC), UN(30)-UO₂ (FC) and UN(50)-UO₂ (FC) were 5.0 wt% 26.6 wt% and 46.2 wt%, respectively. Regarding the grain sizes of the UO₂ phase of the composites (Table 2), the higher the initial weight fraction of UN microspheres, the larger the average oxide grain sizes in the final pellets. The initial oxidation rates, up to (about) 50 % yield, were faster when the matrix grain sizes increased. Quémand et al. [69] found that the oxidation rate up to ~ 50 % yield increased when the grain sizes diminished. This different behaviour might be because they were analysing pure UO₂ sample, as well as owing to additional complexity of the UN-UO₂ system: sesquinitride precipitates along and inside the UO₂ grain and UN embedded microspheres. Therefore, the initial oxidation rates in Fig. 8 depended not only on the average oxide grain sizes, but also on the nitride amounts in the sintered samples, which seemed to impact much more the rates than the grain sizes themselves.

Fig. 8 also reports the influence of the initial amount of microspheres on the OOTs and MRTs. The OOT of UN(10)-UO₂ (SC) (593 ± 6 K) was surprisingly 23 K higher than the reference UO₂ (SC). Additionally, the composite showed a slightly higher MRT and lower oxidation rate at the maximum point, indicating that the oxidation reaction was more moderate in the composite than in the UO₂ (SC) reference. A previous study [23] proposed that the formation of U-N-O compounds on the surface of nitried uranium can resist the diffusion of oxygen ions into the inner layer. Also, Lu et al. [19] showed that the corrosion resistance of the U₃N₄ phase is better than the U or UN phase structure films. Thus, the complexity related to the U-O-N system seems to retard the oxygen diffusion through the sample in some cases. Increasing the initial amount of UN microspheres from 10 wt% to 30 wt% and 50 wt% have not affected the OOTs. Also, these composites had similar OOTs when compared with the UO₂ (SC) reference. These results seemed to demonstrate that the UO₂ matrix provided a barrier against oxidation of the nitride phases. However, the reaction occurred approximately three times faster in UN(50)-UO₂ (FC) (0.84 ± 0.14 %/min) than in UN(30)-UO₂ (FC) (0.29 ± 0.01 %/min) at the maximum rates, since the amount of nitrides was the highest in UN(50)-UO₂ (FC).

The influence of the cooling rates on the oxidation kinetics is reported in Fig. 9. The faster the cooling, the higher the nitride amounts in the sintered composite and, consequently, the greater
the total weight variation. Samples UN(30)-UO$_2$ (SC) and UN(30)-
UO$_2$ (FC) had a total amount of nitrates of 20.2 wt% and 26.6 wt%,
respectively (Table 3). Concerning the OOTs reported in Fig. 9 (a),
the cooling rate affected neither the chemisorption of oxygen onto
the composites, nor the diffusion-controlled formation of U$_3$O$_8$
during the early oxidation stage (< 523 K) [57,64,65]. Thus, the
OOTs for the composites were quite similar to the UO$_2$ (SC) ref-
erence, when the uncertainties are considered, demonstrating that
the UO$_2$ matrix retard the oxidation of the nitride phases. Never-
theless, the MRTs were affected by the cooling rate (Fig. 9 (b)). In
the case of UN(30)-UO$_2$ (FC), the oxidation reaction reached a max-
imum of 0.29 ± 0.01 %/min at 618 ± 3 K, while the slowly cooled
sample showed a slightly lower reaction rate (0.26 ± 0.01 %/min)
at a higher temperature (641 ± 4 K). Therefore, the cooling rate
affected directly the amount of UN + α-U$_2$N$_3$ in the composites
and, consequently, the oxidation kinetics: the faster the cooling,
the higher the amount of nitrides and the reaction rate, and the
lower the MRT.

From the DSC data plotted in Fig. 10, two linear kinetic regions
associated with exothermic peaks are observed: first, be-
tween 573 K and 650 K; and second, between 660 K and 685 K. At
these regions, a proposed mechanism for the composite oxidation
is that the reaction occurred via UO$_2$ grain boundary attack at fresh
UO$_2$ surfaces that formed during cracking and nucleation/growth
of U$_3$O$_8$ after an incubation time [57,65,69,70]. Simultaneously to
the grain boundary attack, the α-U$_2$N$_3$ phase oxidised since it was
present along and inside the UO$_2$ grains (Fig. 4). With the extent
of reaction, the embedded UN microspheres were also reached by
oxygen and resulted in a strong exothermic DSC peak at 673 K, which
is characteristic of a highly exothermic nitride phase oxidation
[15]. Therefore, the UO$_2$ addition was beneficial to retard and
smooth the oxidation of the nitride phases.

3.3. Post oxidation morphology

Fig. 11 shows the micrographs of the as-fabricated and oxidised
UO$_{2.13}$ powder, UO$_2$ (SC), UN microspheres, and UN (SC) samples.
UO$_{2.13}$ powder’s overall morphology has not changed after its ox-
idation, which is known to have a complex kinetic above 473 K
owing to a simultaneous formation of U$_3$O$_7$ and U$_3$O$_8$ [71]. Since
the powder had an initial surface area of 5.33 m$^2$/g, with most of
it coming from internal porosity (Fig. 1 (a)), a net increase of ~36 %
in volume due to its oxidation to U$_3$O$_8$ [70] might have been com-
pensated by porosity and, then, avoided macro-cracking. Con-
versely, the oxidised UO$_2$ (SC) sample showed a general surface
roughening and spalling after oxidation, as illustrated by SEM–SE
images of a fragment in Fig. 11. As previously presented in [57,61]
and discussed in section 3.2, the U$_3$O$_8$ formation on the UO$_2$ (SC)
pellet occurred after the formation of a U$_3$O$_7$ layer at the begin-
ing of the reaction. This layer increased until reaching a critical
thickness and then spalled from the UO$_2$ as powder, generating
cracks at the pellet surface. These cracks can be associated with
a stress state created by the U$_3$O$_7$ on UO$_2$, since the U$_3$O$_7$ phase
has a smaller lattice parameter than the UO$_2$ phase [69]. After-
wards, the oxidation reaction continued via grain boundary attack,
with simultaneous cracking and nucleation/growth of U$_3$O$_8$ at the
freshly created surfaces via linear kinetics until consuming all UO$_2$
[57,65,69,70]. Fig. 11 shows that macro-cracks were mostly formed
at the UO$_2$ grain boundaries, with some micro-cracks inside the
grains as well. Additionally, there are small fragments in the image
that could have been generated during transportation, since the co-
hesive forces in the oxidised UO$_2$ samples are weak and may crack
into powder when weak stress is applied [69].

UN microspheres and UN (SC) samples showed similar oxida-
tion kinetics (Fig. 7 (c,d)) and post oxidised microstructures
(Fig. 11). As a general behaviour, the growth mechanism of the
U$_3$O$_8$ phase might have followed a succession of steps, such as ads-
orption of oxygen on the external surface, including inside the mi-
crospheres’ open pores, and external interface reaction followed by
diffusion through the U$_3$O$_7$ towards the freshly UN internal phase.
The cracks observed in the UN samples seemed to occur at the be-
inning of the sigmoid curves, after reaching a critical oxide layer
(similar to the UO$_2$ pellet) [57,61], and then inducing a rapid in-
crease of the oxidation rates (Fig. 7 (c,d)) due to new reactive and
fresh surfaces of UN. Furthermore, oxidation along grain bound-
daries introduced large stresses that the brittle nitride samples were
unable to withstand. Similar intergranular cracking and spalling
behaviours have been observed during hydrothermal oxidation of
UN at 523–623 K and pressures up to 16.5 MPa [25], as well as
during steam oxidation at 573 K and 9 MPa [21].
Fig. 11. Micrographs of as-fabricated and oxidised UO$_{2.13}$ powder, UO$_2$ (SC) UN microspheres, and UN (SC) samples. UO$_{2.13}$ powder’s morphology did not change significantly after oxidation. Similar post oxidised microstructures with mostly intergranular cracking and spalling were observed in the UO$_2$ (SC) and nitrates samples.

Fig. 12 reports the micrographs of the as-fabricated and oxidised UN-UO$_2$ composite fuels. In general, the oxidised morphologies showed a corroded surface with intergranular cracking and spalling, and some intragranular cracks as well. As discussed in section 3.2, the formation of a critical oxide layer generated cracks at the surfaces, which enhanced the reaction rates by nucleation and growth of U$_3$O$_8$ on a freshly surface. Ex-situ SEM examinations did not allow a complete visualisation on how the oxidation reactions evolved. A previous article reports in-situ oxidation of UO$_2$ fuel pellet at 603 K and P$_{O_2}$ = 265 Pa up to 5.5 h [69]. The authors demonstrated that two types of cracks occurred during oxidation: first, macro-cracks occurred at the grain boundaries after 30 min of isothermal oxidation, followed by micro-cracking at the cracked surfaces that enhanced spallation. They also showed that the sample was still oxidising when the pellet was completely cracked with a constant weight variation, i.e. no more reactive surfaces was created. At this final stage, nucleation and growth of U$_3$O$_8$ proceeded until the total consumption of the UO$_2$ phase.

4. Conclusions

This article is presenting, for the first time, thermogravimetric experiments in triplicates concerning the oxidation resistance of high-density (91-97 %TD) UN/U$_2$N$_3$-UO$_2$ composite fuels in a synthetic air atmosphere below 973 K. The results show that the oxidation resistance of the composite with initially 10 wt% of UN microspheres is surprisingly better than the UO$_2$ reference. The OOT of UN(10)-UO$_2$ (SC) (593 ± 6 K) is about 23 K higher than the references UO$_2$ (SC). Additionally, this composite shows a slightly higher MRT and lower reaction rate at the maximum rate, indicating that the oxidation reaction is smoother in the composite than in the UO$_2$ (SC). Additionally, there is no significant difference in the OOTs (~560 K) and MRTs (~613 K) when using 30 wt% or 50 wt% of embedded UN microspheres. These behaviours are a direct result of the improved oxidation resistance provided by the UO$_2$ phase, which acts as a protective barrier for the nitride phases. Nevertheless, the oxidation reaction occurs approximately three times faster in UN(50)-UO$_2$ (FC) (0.84 ± 0.14 %/min) than in UN(30)-UO$_2$ (FC) (0.29 ± 0.01 %/min) at the maximum rates, since the total amount of nitrates (UN + α-U$_2$N$_3$) is the highest in UN(50)-UO$_2$ (FC) (46.2 wt%). Regarding the cooling rates, the faster cooling process during fabrication, the higher the total nitride contents in the sintered composites. This behaviour results in an expected higher total weight variation in UN(30)-UO$_2$ (FC) (5.37 ± 5 %) than in UN(30)-UO$_2$ (SC) (5.02 ± 2 %).

DSC analysis of UN(50)-UO$_2$ (FC) demonstrates more clearly that the oxidation of the composite fuels seems to follow two linear kinetics regions at 573-650 K and 660-685 K. At these regions,
a proposed mechanism is that the oxidation occurs via UO$_2$ grain boundary attack at freshly exposed UO$_2$ surfaces that are formed during cracking and nucleation/growth of the U$_3$O$_8$ phase. During the grain boundary attacks, it is suggested that the $\alpha$-U$_2$N$_3$ phase oxidise since it is present along and inside the UO$_2$ grains. With the extent of reaction, the UN phase is also reached by oxygen and results in a strong exothermic DSC peak at 673 K. The oxidised composites have similar morphologies, showing a corroded surface with mostly intergranular cracking and spalling as a result of the oxidation reactions. Furthermore, the nitrides and UO$_2$ (SC) microstructures have a general roughening and spalling with intragranular and some intergranular cracks. Conversely, the overall morphology of the UO$_{2\times11}$ powder does not change after its oxidation.

The findings in this study demonstrate that the UO$_2$ matrix acts as a barrier to improve the oxidation resistance of the nitride phases as they would exist at the beginning of life conditions. Therefore, the use of the UO$_2$ fuel to protect the UN microspheres is promising and requires future developments/tests to be used as an accident tolerant fuel in LWR.

**Declaration of Competing Interest**

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.

**CRediT authorship contribution statement**

Diogo Ribeiro Costa: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. Marcus Hedberg: Investigation, Writing - review & editing. Simon C. Middleburgh: Writing - review & editing, Funding acquisition. Janne Wallenius: Funding acquisition. Pär Olsson: Resources, Supervision, Project administration, Funding acquisition. Denise Adorno Lopes: Conceptualization, Validation, Writing - review & editing, Supervision.

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**Appendix**

All TGA experiments were performed in triplicate. The results for the raw materials, as well as for the UO$_2$ (SC) and UN (SC) samples, are plotted in Fig. A1. The coloured/bolded graphs are the data used in the article, and the grey curves indicate the replicates. Fig. A2.
Fig. A1. Triplicate measurements of (a) UO$_{2.13}$ powder, (b) UO$_2$ (SC), (c) UN microspheres, and (d) UN (SC). The coloured/bolded curves are the ones used in the article. The results show good repeatability and reliability of the TGA experiments, with the largest discrepancy occurring in UN (SC) between 550-650 K.

Fig. A2. Triplicate measurements of (a) UN(10)-UO$_2$ (FC), (b) UN(30)-UO$_2$ (SC), (c) UN(30)-UO$_2$ (FC), and (d) UN(50)-UO$_2$ (FC). The coloured/bolded curves are the ones used in the article. The results show good repeatability and reliability of the TGA experiments.

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