Low-Temperature Oxidation of Fine UO₂ Powders: A Process of Nanosized Domain Development

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Supporting Information

ABSTRACT: The nanostructure and phase evolution in low-temperature oxidized (40–250 °C), fine UO₂ powders (<200 nm) have been investigated by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM). The extent of oxidation was also measured via in situ thermogravimetric analysis. The oxidation of fine powders was found to proceed differently as compared to oxidation of coarse-grained UO₂. No discrete surface oxide layer was observed and no U₃O₈ was formed, despite the high degree of oxidation (up to O/U = 2.45). Instead, nanosized (5–15 nm) amorphous nuclei (interpreted as amorphous UO₃), unmodulated and modulated U₃O₈, and a continuous range of U₄O₉–₂ phases with varying tetragonal distortion (c/a > 1) were observed. Oxidation involves formation of higher uranium oxides in nanodomains near the grain surface which, initially, have a disordered defect structure (“disordered U₃O₈”). As oxidation progresses, domain growth increases and the long-period modulated structure of U₃O₈ develops (“ordered U₃O₈”). A similar mechanism is understood to happen also in U₃O₇–₂.

1. INTRODUCTION

Oxidation of uranium(IV) oxide (UO₂) has been the subject of research for more than 70 years. Most of the previous studies have been focused on the behavior at moderate temperatures (100–400 °C), a region of interest in both the front end and back end of the UO₂ nuclear fuel cycle. Control of the oxygen intake is of importance for nuclear fuel production, more precisely for the UO₂ powder processing stages. Powder context of spent fuel stability under medium- and long-term conversion of UO₂ to the more thermodynamically stable powders, which react pyrophorically when exposed to air, has been studied. Additionally, oxidation of UO₂ single crystals has been investigated. A significant portion of work has been devoted to the oxidation behavior of both non-irradiated and irradiated UO₂ fuel pellets in the context of spent fuel stability under medium- and long-term storage conditions. The focus has mainly been on the conversion of UO₂ to the more thermodynamically stable oxide U₃O₈. The formation of U₃O₈ leads to about 36% volume expansion, which may be detrimental for the integrity of the fuel cladding. Also, oxide compounds having U⁴⁺ and U⁶⁺ oxidation states show an increased solubility in aqueous environments, which is of concern in the repository of spent nuclear fuel.

Upon oxidation, the fluorite (Fm3m) crystal structure of UO₂, (a₀ ≈ 547.127(8) pm) contracts linearly while still retaining its cubic symmetry. Excess oxygen is incorporated onto positions which are slightly displaced from the interstitial sites. Additionally, vacancies appear at some of the regular oxygen sites. The resulting effect is a local, but random, reorganization of the anion sublattice. A wide phase domain of hyperstoichiometric UO₂ₓ (x ≤ 0.25) exists at temperatures between 250 and 2850 °C. At lower temperatures the oxygen solubility limit is considered to be quite small (x ≤ 0.03). Oxidation in excess of this limit results in a two-phase domain of UO₂ₓ and U₃O₇ (0.06 ≤ x ≤ 0.02). The crystal structure of U₃O₇ is commonly described as a superstructure, based on a fluorite-like parent cell multiplied by four in all directions (i.e., 4a₀ × 4a₀ × 4a₀; a₀ = 543.9 pm). The defect structure has been described by an ordering of cuboctahedral oxygen clusters, and, lately, by split di- and quad-interstitial clusters.

As oxidation proceeds beyond U₃O₇ the structure deforms anisotropically from cubic to tetragonal symmetry, but the exact formation mechanism is still under debate. The compound formed is usually classified as U₃O₇−₂ although U₃O₇−₃ is probably a more appropriate designation. The nonstoichiometric character of U₃O₇−₂ is recognized in its variable tetragonal unit cell parameters (c/a ≠ 1). The variability of the ratio c/a has, however, also been related to the strain produced by topotactic growth (i.e., formation of a new crystalline phase within a reactant) of U₃O₇ within U₃O₈. The solid solubility limit is expected to be close to O/U = 2.33, and the associated lattice parameters are reported in the range a₀ = 536.3–539.8 pm and c₀ = 553.1–556.5 pm. A generally accepted crystalline structure has not been formulated for the phase or phases commonly referred to as U₃O₇.

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described it as fluorite-based and having a defect structure based on the formation of cuboctahedral oxygen clusters. 1,4,4,5

Recent ab initio studies confirmed the formation of oxygen clusters, but failed to reproduce the experimentally observed tetragonal distortion, 41 or to prove the cuboctahedral arrangement due to limitations in the simulation cell. 37 Electron diffraction (Thomas and Taylor, unpublished but cited in other works, 5,54,55 and Leinders et al. 5,56) and neutron diffraction 5 experiments evidence the presence of superstructure reflections indicating an ordered arrangement of the defect clusters. The electron diffraction investigations showed that the modulation is different from that of U₃O₇, but a precise description of the superstructure has not been formulated.

The most stable UO₂ oxidation product formed in dry air is orthorhombic α-UO₂. 4,5 U₃O₈ formation is usually associated with a process of nucleation and growth from U₃O₈ in nonirradiated powder and pellets. 2,3,50,51 Theoretically, oxidation of UO₂ completes at the composition UO₉, a pure UO₈ compound. In contrast, all previously discussed oxidation products are mixed-valence compounds. 31,52,53 The U₃O₇ polymorphs (7 known modifications) are moderately stable in air and dissociate into U₂O₅ and O₂ at temperatures between 450 and 700 °C. 54 UO₂ is typically obtained as a decomposition product of uranium compounds prepared via solution chemistry (e.g., uranyl nitrate hexahydrate and ammonium diuranate), 55,56 but amorphous UO₃ and schoepite (UO₃·2H₂O) were also reported to form in air-oxidized UO₂ powders and pellets. 2,4,21,57,58

The consensus has been that oxidation of UO₂ proceeds, at least initially, as a diffusion-driven surface reaction involving formation of a product layer. 36,59 The sequence of crystalline compounds formed upon increasing the oxygen content is UO₂ → U₂O₅ → U₃O₇ → U₃O₈, here disregarding the non-stoichiometric regions in the U–O system. 58 Formation of an oxide layer on the grain boundaries of irradiated UO₂ pellets has been readily observed by electron microscopy. Similar results have not been reproduced for fine powders and single crystals. 2,10 High-resolution transmission electron microscopy (HR-TEM) with a subnanometer-scale spatial resolution can be a powerful tool for studying the complex oxidation behavior of UO₂.

In this work, the mechanisms of surface oxidation of freshly reduced UO₂ powders are investigated in the low-temperature range from 40 to 250 °C. Samples were prepared by solid state synthesis under isothermal and isobaric conditions (dry, 450 and 700 °C) and subsequent thermal analysis. 47,48 Small quantities of U₃O₈ were present in both the U₄O₉ and U₃O₇ samples. From an XRD Rietveld refinement, the amount of U₃O₈ was found to be 1.5 wt % in our U₄O₉ and 3.8 wt % in our U₃O₇ samples. These amounts are taken into account in the presented stoichiometry values for U₄O₉ and U₃O₇. The presence of U₃O₈ did not interfere with the reference compound reflections in XRD.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Samples were prepared from two depleted UO₂₃₈+ batches (average O/U ≈ 2.1) produced via the integrated dry route (IDR process) and supplied by FBFC International (Dessel, Belgium). The impurity content of the as-received powder was evaluated using inductively coupled plasma mass spectrometry (ICP-MS, ThermoFisher XSeries2). In total, the presence of 50 elements was probed. The combined metallic impurity fraction was 136 µg g⁻¹ and 47 µg g⁻¹ in the two batches. In order to obtain samples with different surface areas, a wet route dissolution process was used. The as-received powders were first dissolved in HNO₃ (4 M aqueous solution) and subsequently titrated with an excess of a 4 M NH₄OH aqueous solution. The precipitate so formed was vacuum filtered and dried at 80 °C for several hours to obtain clear yellow (NH₄)₂U₂O₇ (ammonium diuranate or ADU) powder.

Three uranium oxide precursor powders, having low (L), medium (M), and high (H) specific surface areas, were prepared from the produced ADU powder via dry-route processing. Surface areas were measured by nitrogen gas adsorption (BET analysis using a Micromeritics TriStar II 3200), see Table 1. The corresponding theoretical spherical particle size (d_BET), calculated from the surface area values, is added to this table. Further processing of the powders was performed in a Carbolite TZF1800 tube furnace with continuous flows of dry active gases (dew point < −80 °C). Powder H was obtained by calcination of the ADU powder in synthetic air (N₂/21 vol % O₂) at 550 °C for 30 min. X-ray analysis showed that the compound thus formed was β-UO₃. Powders M and L were obtained by calcination in synthetic air at 650 °C for 30 min and 4 h, respectively. The compounds thus formed were identified as α-UO₃. Small amounts of the precursor powders were subsequently sampled, reduced to stoichiometric UO₂, and oxidized under specific conditions (see section 2.2).

Three powders of uranium oxide with varying stoichiometry in a reference crystalline state (UO₂LH₄, U₃O₇, U₄O₉) were additionally produced using the above-described thermal equipment. The as-received UO₂₃₈+ (2 m² g⁻¹) was first reduced to stoichiometric UO₂ at 700 °C in a flow of Ar/5 vol % H₂. After cooling to room temperature and purging with pure Ar, the flushing gas was switched to Ar/0.01 vol % O₂ for several hours. This procedure passivates the powdered material from uncontrollable oxidation upon retrieval from the furnace and exposure to the normal atmosphere. 11 The average stoichiometry O/U of the powder thus obtained was 2.05 as measured by gravimetry. U₃O₇ (O/U = 2.24) was produced by heating the as-received powder at 200 °C in Ar/0.01 vol % O₂ for 24 h. U₄O₉ (O/U = 2.14) was obtained by heating the as-received powder at 250 °C in synthetic air for 7 h. Small quantities of U₃O₇ were present in both the U₃O₇ and U₄O₉ powders. From an XRD Rietveld refinement, the stoichiometry of U₃O₇ was found to be 1.5 wt % in our U₄O₉ and 3.8 wt % in our U₃O₇ samples. These amounts are taken into account in the presented stoichiometry values for U₄O₉ and U₃O₇. The presence of U₃O₇ did not interfere with the reference compound reflections in XRD.

2.2. Thermogravimetric Analysis (TGA). Thermogravimetric analysis on various samples of the three precursor powders was performed with a Netsch STA 449 FI Jupiter thermogravimeter, coupled to a quadrupole mass spectrometer (403 D Atolos) to analyze the evolved gases. The oxygen and water contents of the exiting gas were monitored with an oxygen analyzer (Setag OXYBOX AIR) and dew point analyzer (Alpha Moisture Systems ADHT-BL), respectively. All gases were of high purity (99.9999%) with no measurable water content (dew point < −80 °C). A constant flow of argon gas (20 mL min⁻¹) was maintained through the balance compartment and leading into the furnace chamber, here referred to as the protective gas flow, resulting in increased balance stability. The flushing (active) gas entered the furnace chamber directly through a secondary inlet with a flow of 80 mL min⁻¹. The total exiting gas flow was therefore equal to 100 mL min⁻¹. The gas supply was controlled via various mass flow controllers (Bronkhorst EL-FLOW), individually calibrated to the type of gas used.

| Table 1. Specific Surface Area (SSA), Theoretical Spherical Particle Size (d_BET), and Precursor Oxides (Precursor) |
|--------------------------------------------------|-------|-------|
| SSA (m² g⁻¹) | L | M | H |
| d_BET (nm) | 179 | 77 | 34 |
| Precursor | UO₂ | U₃O₇ | U₄O₉ |

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Sample powders (30–35 mg each) were loaded in a small Pt/Rh crucible with lid and placed on the sample carrier, foreseen with a type S thermocouple (Pt–10% Rh/Pt). Thereafter the furnace was closed, degassed to 10⁻⁴ mbar, and refilled with dry argon. This purging process was repeated three times, thus allowing the dew point of the exiting gas to reach ~74 °C or less before the start of any measurement. In a constant flow of 100 mL min⁻¹ of argon, a concentration of about 10 ppm of O₂ was measured to leak into the system.

The thermal analysis profile consisted of three stages. A graphical presentation of the temperature profile and gas atmosphere conditions applied in the furnace is given in Figure 1. During the first stage the sample material is reduced to stoichiometric UO₂ by heating to 700 °C in a flow of argon with 4 vol % H₂. Then, after cooling to the target temperature T₀x (≈ 40, 70, 100, 130, 160, 190, or 250 °C), the furnace chamber is flushed for 3 h with argon (stage two). In the final stage, while maintaining the sample at an isothermal temperature, the flushing gas is changed to dry, synthetic air thus allowing oxidation of the freshly reduced samples.

Mass change was continuously recorded with an accuracy of ±14 μg (1σ). All TGA runs were corrected for drift and buoyancy by subtracting an empty crucible with lid and placed on the sample carrier, foreseen with a type K thermocouple (Pt13%Rh/Pt 2% Rh). This allowed retrieving the powder after analysis. During sample preparation, transfer, and measurement, the specimens were exposed to the normal lab environment (room temperature, relative humidity ~50%). The lattice parameters presented throughout the text are recalculated to their value at 20 °C, using the linear thermal expansion coefficient for UO₂ of 9.739 × 10⁻⁶ °C⁻¹ near room temperature. For U₃O₇, the same coefficient was assumed, as was also proposed for the case of UO₂ by Martin. Rietveld analysis of the X-ray diffractograms was performed with PANalytical HighScore Plus (v4.1). Details on the methodology can be found in the Supporting Information.

### 2.4. Electron Microscopy

Transmission electron microscopy (TEM) was performed with a 300 kV JEOL 3010 microscope equipped with an in-column Gatan 794 MSC CCD camera and a side-entry double tilt specimen holder. A small amount of powder (<1 mg) was randomly sampled and dispersed by isopropanol in a beaker. Short intervals (~10 s) of ultrasonic degglomeration were applied to break up the soft agglomerates into individual grains. The suspension was then pipetted onto a holey carbon grid, and the isopropanol was left to evaporate. Data analysis was performed with Gatan Microscopy Suite (GMS) 2.

The structural information contained within HR-TEM images was analyzed by application of noise filtering over selected areas of the images. The method applied throughout this work consisted of a fast Fourier transform (FFT) procedure to convert the crystalline contribution in a real space image into lattice reflections of a reciprocal space image. A set of lattice planes was then selected by masking the corresponding reflections, excluding the central beam. The masked area was slightly smoothed at the edges (by 3–5 pixels) and subsequently recomputed into a real space image (inverse FFT), thus showing a filtered image of selected lattice planes.

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**Figure 1.** Schematic of the temperature profile applied in TGA. The oxidation temperature (T₀x) was chosen between 40 and 250 °C, as indicated on the graph. Colored dashed lines delimit the associated conditions in the furnace: reducing, inert, and oxidizing.

### 3. RESULTS

A systematic set of oxidized UO₂ powders differing in specific surface area was prepared by solid state synthesis and measured via in situ thermogravimetric analysis. A consistent treatment was applied, in which a sample of precursor powder was always first reduced to stoichiometric UO₂ and subsequently oxidized at a selected temperature, ranging between 40 and 250 °C. All prepared powders were analyzed via XRD, and a considerately chosen selection of samples was further analyzed using HR-TEM.

#### 3.1. Thermogravimetric Analysis

Mass increase curves showing the effect of oxidation on freshly reduced UO₂ powders are shown in Figure 2 (L, M, H), for all three precursor powders. The mass gain is expressed as an increase in average stoichiometry (O/U), here considered as homogenous oxygen absorption. The oxidation experiments on precursor powders M at 190 °C and H at 160 and 190 °C were performed in two stages to avoid flash heating of the sample material. During these TGA runs the reduced powders were first allowed to oxidize at a temperature of 130 °C before heating to higher temperatures.

The effect of surface area on oxidation rate is readily observed when comparing the curves of the individual samples. At any given time and temperature, the extent of oxidation is larger with higher specimen surface area, and the difference is most significant at temperatures between 40 and 100 °C. The total mass gain at the end point of each TGA run is listed in Table 2. During the flushing stage, following the reduction step, already a slight mass increase was measured due to uptake of oxygen impurities that enter the system. These amounts are included in the presented values.

At all but the highest temperatures investigated the TGA data shows a decreasing rate of mass increase as the reaction progresses. Quite notably, the curves level off as the mass increase exceeds about 2.2 wt % (O/U ≈ 2.37). The temperature at which this intermediate state is reached depends

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on the powder surface area: $T_{\text{ox}} = 190 \degree C$ for samples L, $130 \degree C \leq T_{\text{ox}} \leq 160 \degree C$ for samples M, and $100 \degree C \leq T_{\text{ox}} \leq 160 \degree C$ for samples H. The corresponding average stoichiometry lies in the range $2.38 \leq \text{O/U} \leq 2.42$ for all three sample types, the exact value increasing slightly with higher sample surface area. At 250 $\degree C$, sample L shows an accelerated rate as compared to the behavior at lower temperatures. A similar behavior is observed for samples M and H already at 190 $\degree C$. At 40 $\degree C$ a stable mass value was obtained only for sample L, illustrating limited extent of oxidation at low temperature and with larger surface area.

Thermal analysis was repeated with an extended isothermal dwell time (+10 h) on two different samples. At 160 $\degree C$ precursor powder L oxidized to O/U = 2.35. At 100 $\degree C$ precursor powder M reached an O/U = 2.37. Oxidation was still ongoing at the end point of the measurement, albeit with a low reaction rate. Likely, with an unlimited dwell time at the chosen temperatures, mass increase will reach a limiting value at or just below the above-mentioned range $2.38 \leq \text{O/U} \leq 2.42$.

3.2. X-ray Diffraction. The crystallographic changes that occur during the oxidation of UO$_2$ are assessed with respect to three reference states: UO$_{2.03}$, U$_4$O$_9$, U$_3$O$_7$. Therefore, X-ray diffractograms of these reference oxides were evaluated using the Rietveld method. Figure 3 shows a selected region for the three diffractograms, all corrected for specimen displacement and normalized to the $(111)_p$ reflected intensity. The subscript “p” refers to parent structure indexing, i.e., the presented data relates to the average structure of the U$_4$O$_9$ and U$_3$O$_7$ superstructures.

For all reference samples a fluorite-type parent structure is assumed, with additional occupation of octahedral interstitial sites by oxygen. The space groups are $Fm\bar{3}m$, $F43m$, and $P4_2/nmm$ (origin choice 2) for UO$_{2.03}$, U$_4$O$_9$, and U$_3$O$_7$, respectively. The composition of the unit cells is summarized in Table 3. These structural models present the ideal, undistorted state for fluorite-type uranium oxides. In reality, the incorporation of additional oxygen atoms induces

![Figure 2. Experimental mass increase curves showing a decreasing rate of reaction up to an average stoichiometry close to 2.40. At the highest temperatures applied, the reaction appears to accelerate again. Oxidation of precursor powders M at 190 °C and H at 160 and 190 °C was performed in two stages to avoid flash heating.](image)

![Figure 3. X-ray diffractograms showing the (200)$_p$ reflections of UO$_{2.03}$ and U$_4$O$_9$ and the (200)$_p + (002)$_p$ reflections of U$_3$O$_7$ (Cu K$_{\alpha1,2}$).](image)

**Table 2. Average Stoichiometry at End Point of Each TGA Run**

<table>
<thead>
<tr>
<th>$T_{\text{ox}}$ (°C)</th>
<th>L</th>
<th>M</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>2.06</td>
<td>2.13</td>
<td>2.22</td>
</tr>
<tr>
<td>70</td>
<td>2.08</td>
<td>2.19</td>
<td>2.32</td>
</tr>
<tr>
<td>100</td>
<td>2.15</td>
<td>2.32</td>
<td>2.40</td>
</tr>
<tr>
<td>130</td>
<td>2.26</td>
<td>2.39</td>
<td>2.41</td>
</tr>
<tr>
<td>160</td>
<td>2.33</td>
<td>2.39</td>
<td>2.42</td>
</tr>
<tr>
<td>190</td>
<td>2.38</td>
<td>2.42</td>
<td>2.45</td>
</tr>
<tr>
<td>250</td>
<td>2.45</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.** X-ray diffractograms showing the $(200)_p$ reflections of UO$_{2.03}$ and U$_4$O$_9$ and the $(200)_p + (002)_p$ reflections of U$_3$O$_7$ (Cu K$_{\alpha1,2}$).
distortions which mainly affect the oxygen sublattice. Such information is, however, ineffectively probed with XRD, allowing assessment of the diffraction data using the undistorted parent structures. An overview of the parameters evaluated using Rietveld refinement is given in Table 4. The \( \text{U}_2\text{O}_3 \) lattice parameter corresponds to values found by other researchers, when recalculated to 20 °C. Excellent agreement was obtained between experimental data and the fitted profile. Bragg R-factors were equal to 0.021, 0.032, and 0.036 for the used \( \text{U}_2\text{O}_3 \), \( \text{U}_4\text{O}_9 \), and \( \text{U}_3\text{O}_7 \) models, respectively. Diffractograms displaying the fitted Rietveld pattern and difference profile over the complete angular range are available (Figures S1–S3).

All samples produced during TGA and discussed above were subsequently analyzed via X-ray diffraction. Due to the small quantities, specimens for X-ray analysis could not be prepared via the usually preferred back-loading technique. Instead, the sample powders were dispersed onto a zero-background holder, i.e., a silicon crystal cut such that no diffracting conditions are met. By tuning the detector acquisition settings and optimizing the optics, high-quality diffractograms were recorded over the range 20–145° 2\( \theta \). Figure 4 (L, M, H) shows extracts of the (200) reflection for each of the samples produced under the various conditions. The presented region is chosen for the purpose of illustration as it presents a better peak-to-noise ratio than the higher angular region. Complete diffractograms are provided (Figures S4–S6). The data presented here are corrected for specimen displacement and normalized to the (111)\(_p\) diffraction peak intensity. Asymmetric peak broadening and peak shifts toward higher angles can be readily observed upon comparing the different diffractograms. Also, the appearance of the tetragonal (002)\(_p\) reflection near 32.2° 2\( \theta \) can be distinguished. The onset of tetragonal deformation appears to occur at lower temperatures for samples with higher surface area.

The zero-background setup did not decrease the detection limit of crystalline impurities in the X-ray diffractograms. This was verified by preparing a powder mixed with \( \text{U}_3\text{O}_8 \) and measured under identical conditions. Impurity concentrations above 1 wt % were readily detectable in the current XRD setup. Nevertheless, no traces of \( \text{U}_3\text{O}_8 \) were detected in the diffractograms of the oxidized samples, which were measured

### Table 3. Composition of the Parent Structure Cells Used as Input in the Rietveld Refinement

<table>
<thead>
<tr>
<th>atoms</th>
<th>( \text{U}_2\text{O}_3 )</th>
<th>( \text{U}_4\text{O}_9 )</th>
<th>( \text{U}_3\text{O}_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>4 a 1</td>
<td>4 a 1</td>
<td>4 f 1</td>
</tr>
<tr>
<td>O</td>
<td>8 c 1</td>
<td>4 c 1</td>
<td>2 a 1</td>
</tr>
<tr>
<td></td>
<td>4 b 0.03</td>
<td>4 d 1</td>
<td>2 b 1</td>
</tr>
<tr>
<td></td>
<td>4 b 0.24</td>
<td></td>
<td>4 c 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 e 0.34</td>
</tr>
<tr>
<td>av O/U</td>
<td>2.03</td>
<td>2.24</td>
<td>2.34</td>
</tr>
</tbody>
</table>

### Table 4. Parameters Obtained after Parent Structure Rietveld Refinement of the \( \text{U}_2\text{O}_3 \), \( \text{U}_4\text{O}_9 \), and \( \text{U}_3\text{O}_7 \) X-ray Diffractograms

<table>
<thead>
<tr>
<th>lattice parameters (pm)</th>
<th>temp ( R_{\text{wp}} )</th>
<th>all O (Å)</th>
<th>agreement factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{U}_2\text{O}_3 )</td>
<td>546.79</td>
<td>0.401 ± 0.004</td>
<td>0.50 ± 0.04</td>
</tr>
<tr>
<td>( \text{U}_4\text{O}_9 )</td>
<td>543.62</td>
<td>0.387 ± 0.008</td>
<td>0.60 ± 0.07</td>
</tr>
<tr>
<td>( \text{U}_3\text{O}_7 )</td>
<td>537.99</td>
<td>0.535 ± 0.006</td>
<td>0.51 ± 0.05</td>
</tr>
</tbody>
</table>
in a 2θ range to include the α-U₃O₈ (001) reflection specifically for this reason.

The presence of other crystalline uranium oxides was evaluated via full pattern fitting (Rietveld method). Three possible phases were considered: UO₂₋₀.⁰₃, U₄O₉, and U₃O₇, each with input parameters equal to those obtained for the reference compounds (see Table 4). As a starting point, scale factors of the three phases were successively refined for each of the oxidized samples. This showed that asymmetric peak broadening and subsequent peak shift could be adequately modeled by the introduction of U₄O₉ in the fitted profile. With increasing oxidation temperature the U₄O₉ content increases while the contribution of remaining UO₂₋₀.⁰₃ diminishes and eventually disappears. A significant further increase in weighted-profile agreement factors was obtained by the introduction of the U₃O₇ phase, which refined to an appreciable content only in samples oxidized at temperatures of 100 °C (samples H), 130 °C (samples M), 160 °C (samples L), and higher.

The prior evaluation was used to identify possible phases present in each of the oxidized samples; the chosen criterion was a contribution larger than 1 wt % in the fitted profile. Phases with a smaller contribution were discarded. Thereafter, the fit was improved by individually refining Cagliotti and line profile parameters of the selected phases. This procedure is justified both for the type of sample (L, M, H), as their crystallite size differs significantly from those of the reference powders, and for the phases themselves (UO₂₋₀.⁰₃, U₄O₉, U₃O₇), as the latter two are associated with nanosized domain formation (see following HR-TEM results and recent studies⁶,⁶³). An overview of the expected and weighted-profile agreement factors obtained after the first Rietveld analysis is reported in Table S1.

Ample data is available on the variability of the tetragonal distortion in U₃O₇ (see Table 4). Generally attributed to a non-stoichiometric character (U₃O₇₋ₓ),³ therefore, the tetragonal unit cell parameters (a, c) of the previously introduced U₃O₇ phases were additionally refined, hereafter referred to as U₃O₇₋ₓ. A considerable improvement of the fit (between 14% and 40% reduction in Rwp factors) was obtained (see Table S1). An overview of the crystalline phases and their associated weight fraction in each of the samples is presented in Figure 5. Powders oxidized at equal temperatures contain an increased content of U₄O₉ and/or U₃O₇₋ₓ for powders with higher specific surface area. If one assumes that the stoichiometry of the individual compounds is equal to those of the reference powders (O/U = 2.03, 2.24, and 2.34, respectively), an average stoichiometry can be readily calculated (Figure 5, white dots).

The average stoichiometry derived from the weight fractions determined by XRD shows a similar trend to what is observed in TGA (Figure 5, white squares), but the values of the average stoichiometry derived from the XRD observations are systematically lower than the values obtained by TGA. Since in the XRD analysis only the crystalline compounds are accounted for, any contribution from amorphous phases might go unnoticed, as will be discussed below.

The lattice parameter evolution of the U₃O₇₋ₓ phase is presented in Figure 6, together with parent cell lattice parameter values of the U₃O₈ reference sample. A clear trend is visible: with increasing oxidation temperature the tetragonal distortion, i.e., the ratio c/a increases. This feature is here more clearly illustrated by the dashed lines, which represent parabolic fits to the data grouped per lattice parameter value (84.3% ≤ R² ≤ 86.0%). At the intersection of both fitted curves, which presents the condition c/a = 1, the lattice parameter is found equal to 544 (2) pm (1σ). This value lies within the range of reported U₃O₇ lattice parameters at room temperature.¹,³⁸ Another important observation is that the measured lattice parameters for U₃O₇₋ₓ are still appreciably different from those of the reference U₃O₇, notwithstanding the fact that most of these samples are already severely oxidized (up to O/U = 2.45).

3.3. Transmission Electron Microscopy (TEM). A selection of samples for HR-TEM analysis was considerably chosen to cover a wide range of oxidation extent. Based on the XRD Rietveld assessment, powders were selected containing either mostly UO₂₋₀.⁰₃ (sample L, 40 °C), U₃O₉ (sample H, 40 °C), or U₃O₇₋ₓ (sample H, 100 °C). The effect of oxidation temperature on the crystallinity of the oxidation products was evaluated by investigating powders with an equal...
U₄O₉ or U₃O₇−z concentration to those previously selected, but obtained at higher temperatures (samples H, 70 and 160 °C, respectively). Figure 7 shows bright field (BF) images of samples L (40 °C) and H (70 °C). Two sharply defined features are observed for each of the samples, indicated by the arrows. These features, hereafter referred to as nucleation sites, were recurring throughout all samples and appeared with larger dimensions in samples oxidized at a higher temperature (ranging between 5 and 15 nm in diameter). HR-TEM analysis focused on these areas, and the edges of the grains.

The analyzed samples did not show any structure defects close to the surface of the grains, nor in the proximity of the nucleation sites. Figures 8–11b show fast Fourier transformed (FFT) patterns and noise filtered images of the {111}ₚ-equivalent planes corresponding to the selected large area, for samples H oxidized at different temperatures. The apparent mismatch in lattice planes near some of the edges in the images are artifacts due to Fourier transformation of part of the delimited area outside of the grain. Here, the discussion focuses on {111}ₚ-equivalent planes as there have been reports of lattice defects along these planes in both stoichiometric and hyperstoichiometric UO₂. Occasionally, faint satellite reflections are observed, resulting from crystal superstructures. The precision with which reciprocal lattice spacings (d*) can be determined from Fourier transforms does not allow to distinguish between the d*-values associated with the different intermediate compounds (they differ only about 1% for the low order reflections). The appearance of satellite reflections, however, can be used to distinguish between these compounds. Along a [110]ₚ-zone oriented pattern U₄O₉ will show superlattice reflections corresponding to 1/4 [112]ₚ, whereas U₃O₇ will show satellites along 1/3 ⟨002⟩ₚ-type directions.

Figure 6. Evolution of the U₃O₇−z lattice parameters, as measured by XRD Rietveld refinement in samples oxidized at the given temperature. For comparison, also the parent structure parameters of the U₂O₅ reference powder have been added to the graph. Dashed lines represent a parabolic fit to the data, grouped per lattice parameter value a or c.

Figure 7. (a) BF image of sample L oxidized at 40 °C. (b) BF image with lattice resolution of sample H oxidized at 70 °C. Both grains show two distinct features at the surface. The slightly blurred-out region at the grain surface of panel a results from amorphous scatter of the holey carbon grid.

Figure 8. (a) HR-TEM image of sample H oxidized at 40 °C, with a small nucleation site indicated by the arrow. (b) FFT pattern of the delimited area and filtered image showing the corresponding {111} lattice planes. No superstructure reflections are observed via FFT, and no lattice defects are present near the grain surface or in the proximity of the nucleation site.

Figure 9. (a) HR-TEM image of sample H oxidized at 70 °C, showing a large nucleation site. (b) FFT pattern of the indicated area and filtered image showing the corresponding {111} lattice planes with no lattice defects. (c–e) FFT patterns of the small areas, showing superstructure reflections corresponding to 1/4 [112]ₚ and 1/4 [112̅]ₚ in a pattern taken at the grain surface.
Sample L oxidized at 40 °C did not show the presence of a superstructure in the analyzed grains (Figure S7). This observation is as expected since, according to XRD analysis, this powder contains mostly UO$_2$O$_{0.5}$. Sample H, on the other hand, likely contains over 75 wt % of U$_4$O$_9$ phase (Figure S5). Nevertheless, no superstructure reflections were recognized in FFT patterns of the HR-TEM images (see Figure 8).

The local crystal structure is further evaluated on the basis of small area FFT analysis. FFT patterns of sample H oxidized at 70 °C show satellites corresponding to 1/4 {112}$_p$ in a very limited region, close to the surface of the grain. Similar intensities are no longer observed in patterns taken more toward the bulk, see Figure 9c–e. This observation is again surprising in the context of the prior XRD analysis, where the crystal structure of this sample was attributed mostly to the U$_4$O$_9$ phase, similar to the H sample oxidized at 40 °C. As already mentioned, no crystallographic difference was observed between the area corresponding to a nucleation site and its surroundings.

Most of the grains of sample H oxidized at 100 °C did not contain modulated structures, according to the analysis of HR-TEM images. Occasionally modulation was observed in the bulk of the grain and sometimes extending out to the surface, visible by contrast modulations in real-space images (Figure 10a and Figure S8a). FFT patterns of these areas showed the typical U$_4$O$_9$ satellites. Small domains clearly absent of modulation were found near the grain surface (areas delimited by the dashed lines). The fact that modulation was only occasionally observed can be seen to correspond to an increased extent of unmodulated domains in most of the grains. Considering the XRD Rietveld assessment for this sample, i.e., 75 wt % attributed to the U$_4$O$_9$ phase, these domains likely consist of U$_4$O$_9$−$_{0.5}$ having a disordered defect structure.

Due to instability of the material, resulting from charging effects, the quality of TEM analysis on sample H oxidized at a temperature of 160 °C was less than optimal. Such difficulties were already encountered, but to a much lower extent, in sample H oxidized at 100 °C. This observation indicates that an increasingly larger fraction of badly conducting material is present in the samples oxidized at higher temperatures. In BF imaging mode nucleation sites were again observed, scattered over the surface of the grains and having diameters up to 15 nm. The few grains for which HR-TEM analysis was possible showed practically no type of modulation; very faint satellites according to the U$_4$O$_9$ superstructure were only occasionally encountered. A protrusion on the surface of an oxidized grain is observed (Figure 11a), understood to be a nucleation site seen from a side projection. The protruding matter is clearly amorphous: the lattice interference pattern of the bulk grain ends at the boundary between grain surface and nucleation site (Figure 11a,b), and no crystalline contribution is measured in a Fourier transformed pattern of an area corresponding to the protrusion (Figure 11c).

### 4. DISCUSSION

The current investigation aimed to better understand the mechanism of oxidation in fine UO$_2$ powders. Various powders with either low (L, 4.0 m$^2$ g$^{-1}$), medium (M, 9.3 m$^2$ g$^{-1}$), or high (H, 21.1 m$^2$ g$^{-1}$) specific surface area were first reduced to stoichiometric UO$_2$ and subsequently oxidized at temperatures between 40 and 250 °C. The oxidation progress was measured by in situ TGA, and structural analysis was performed by XRD and HR-TEM.

TGA data shows that an intermediate state of oxidation is reached as the average stoichiometry approaches 2.40; the exact value varies slightly with surface area. This is considerably higher than the value of 2.33, which is often reported. Usually, the intermediate state is attributed to complete oxidation of UO$_2$ into U$_4$O$_9$ without subsequent U$_3$O$_7$ formation: UO$_2$ → U$_4$O$_9$ → U$_3$O$_7$. During low-temperature oxidation in air, as the composition exceeds 2.33, one may...
expect that hyperstoichiometric phases of $U_{1-x}O_{2-x}$, $U_{1-x}O_{4}$, or $UO_3$ are formed.

The oxidized powders were further analyzed via XRD (Rietveld method) and HR-TEM. The purpose of Rietveld refinement was to quantify the crystalline constituents formed within each sample. The structural information on three well-characterized reference uranium oxide compounds ($UO_2$, $U_4O_9$, $U_3O_7$) was used for the phase quantification of the oxidized samples. The X-ray data are interpreted on the basis of the unit cell parameters of the fluorite-based parent structure. In the current XRD setup no superlattice reflections were detected for $UO_2$, and $U_4O_9$, but the structural differences between $UO_1.9$, $U_4O_9$, and $U_3O_7$ reference compounds were readily distinguished in the parent structure reflections.

X-ray diffractograms of the oxidized powders show the evolution of asymmetrical peak broadening and eventually a peak shift toward larger Bragg angles. In powders which were oxidized at temperatures up to 130 °C (samples L), 100 °C (samples M), or 70 °C (samples H) this was adequately modeled via the introduction of a $UO_2$ phase in the Rietveld refinement. Some early works report that, at low oxidation temperatures ($T < 160$ °C), instead of cubic $U_3O_7$, a pseudocubic, tetragonal phase is formed with unit cell parameters almost identical to those of $UO_2$ and with $c/a$ ratio smaller than 1 ($\approx 0.98$). This phase was sometimes called a-$UO_2$ to distinguish it from “regular” $U_3O_7$ (or β-$U_3O_7$), which has a $c/a$ ratio larger than one. The existence of the a-$UO_2$ phase has become doubtful in recent years, as it has not been observed with modern techniques such as synchrotron X-ray diffraction. Similarly, we found no evidence for a tetragonal phase with $c/a$ ratio smaller than 1 in any of the samples, and also the HR-TEM investigations confirmed that the typical $U_3O_7$ modulation sets in for the samples oxidized at temperatures as low as 70 °C.

We use the notation $U_3O_7\cdot z$ to refer to the range of tetragonal phases with continuously varying $c/a$ ratio ($1.009 < c/a < 1.024$, see Figure 6). According to Rietveld analysis, the $U_3O_7\cdot z$ phase is observed only in powders oxidized above 100 °C for powder with high surface area (samples H), above 130 °C for powder with medium surface area (samples M), and above 160 °C for powder with low surface area (samples L). Refinement of the $U_3O_7\cdot z$ lattice parameters significantly improved the fit for the XRD data (see Table S1). The tetragonal distortion ($c/a$ ratio) was found to increase with increasing oxidation temperature (see Figure 6), and this is interpreted as a change in stoichiometry of the $U_3O_7\cdot z$ phase, as $z$ approaches zero.

The reference $U_3O_7$ powder had a larger $c/a$ ratio ($c/a = 1.029$) than the end value reached on the oxidized samples. The reference $U_3O_7$ sample was prepared by oxidation of as-received $UO_2$ powder which had a low specific surface area ($\sim 2$ m$^2$ g$^{-1}$). Oxidation was performed at 250 °C in dry air for 7 h. During the heat treatment some $UO_2$ was formed, about 3.8 wt % as quantified via Rietveld refinement, and no $U_3O_9$ was observed. One of the L samples (4 m$^2$ g$^{-1}$) was similarly oxidized at the same temperature, for an extended time of 15 h. Rietveld assessment of the X-ray data for this sample attributed about 25 wt % to $UO_2$, the remaining part being $U_3O_7\cdot z$, and no $UO_2$ was detected. Clearly, the powder particle size affects the oxidation process.

In a recent study by Quémard et al. it was also found that fine $UO_2$ powders ($200$ nm $\approx 2.7$ m$^2$ g$^{-1}$) showed a significantly decreased $U_3O_7$ formation rate, as compared to coarse-grained powders and pellets. After a prolonged oxidation time (100 h) at 250 °C, a conversion equivalent to O/U = 2.44 was reached, similarly to the oxidation behavior of our powders. It was proposed that oxidation of $UO_2$ at temperatures between 200 and 330 °C occurs by formation of a $U_3O_7$ layer and that this layer cracks upon reaching a critical depth ($10^3$–$10^4$ nm), thus providing fresh surfaces of underlying $UO_2$ for continuation of the reaction. In fine powders the critical layer depth cannot be reached and $U_3O_9$ formation is restricted to initiate at the surface of the particles, whereas a cracked layer would otherwise induce more available surface area. Despite the substantial oxidation determined from the mass increase analysis (up to O/U = 2.45), neither XRD nor TEM could detect $UO_2$ in any of the nano领略tic powders ($<200$ nm).

Average stoichiometry values measured via TGA were considerably higher than values calculated from the weight fractions associated with the crystalline components derived from XRD Rietveld refinement (see Figure 5). The latter values assume stoichiometry for the intermediate oxides equal to O/U = 2.03, 2.24, and 2.34 for the $UO_2$,$_{0,03}$, $U_4O_9$, and $U_3O_7$ phases, respectively. Hyperstoichiometry has not been reported for $U_3O_9$, but a small hypostoichiometry field exists. The stoichiometry of the tetragonal $U_3O_7$ phases does not seem to significantly exceed O/U = 2.33, and a likely a broad hypostoichiometric $U_3O_{7-x}$ domain exists in which the axial ratio $c/a$ increases with increasing oxygen content.

The difference between the TGA derived O/U values and the values derived from the XRD analysis (Figure 5) becomes negligible only if the stoichiometry of the tetragonal phase in the oxidized samples would be in the range 2.40 < O/U < 2.55. Considering, however, that the $c/a$ ratio of the tetragonal phase in these samples was consistently smaller than that of the reference powder (for which O/U = 2.34), this seems unlikely. In addition, the structural changes that might be expected for a compound with O/U up to 2.5, i.e., further distortion of the tetragonal lattice to lower symmetry, are not observed in the diffraction data. Even if such changes would be unrecognizable within the experimental uncertainty, the discrepancy would still remain for samples in which only cubic phases are identified. Alternatively, since no crystalline phases of higher oxides (e.g., $U_4O_9$) are observed, the difference can also be attributed to the presence of an amorphous phase, which remains undetected by XRD analysis.

In the TEM analysis circular-shaped nucleation sites were observed, consistently located on the surface of the oxidized grains. Their size was larger in samples oxidized at higher temperatures (see, e.g., Figure 7). No lattice defects were found in the vicinity of these features, the electron diffraction patterns did not show additional reflections, and the real space images did not show diffraction contrast effects near or in these areas and the rest of the grain. Figure 11 shows a well-delimited amorphous phase extending outward from the sample surface which is interpreted as a nucleation site growing on the surface of the grain. The systematic absence of Moiré fringes related with other nucleation sites is a further indication that they also consist of an amorphous phase.

Our hypothesis is that for fine powders below a certain size limit ($<200$ nm) oxidation occurs with formation of amorphous $UO_2$, which nucleates on the surface of the grains. This interpretation is consistent with the findings of Hoekstra et al. on room temperature oxidation of $UO_2$ powder with high surface area ($\sim 30$ m$^2$ g$^{-1}$). For coarser powders (e.g., the prepared reference powders) oxidation favors formation of
The discrepancies observed between TGA and XRD that of the reference U3O7 powder) for all oxidized powders. As (UO2+) of the two phases was undistinguishable. In the current work on is also evidenced by the absence of Moiré superlattice reconnections in selected area diffraction patterns, since the small di

The evidence suggests that these areas, already identified as consisting of amorphous matter, could be amorphous UO3. The presence of amorphous UO3 effectively explains the discrepancies observed between TGA and XRD results.

Amorphous UO3 has a significantly lower density (6.8 g cm−3) as compared to that of the fluorite-type uranium oxides (≈11 g cm−3). Conversion of a volume within a grain of dense material into UO3 would result in a significant amount of lattice strain. However, this was not readily observed during TEM analysis. Given that the nucleation sites appear to grow on the surface of the oxidized grains, it may be expected that some strain is only induced at the interface between crystalline matrix and amorphous phase. Noise-filtered images of the {111} equivalent planes (Figures 8, 9, and 11) indeed show limited deformation in the vicinity of the nucleation sites.

Thomas et al. investigated oxidized, spent UO3 fuel pellets. They found distinct, large U3O8 domains (~500 nm thick) at the grain boundaries and a slight mismatch between the phase interfaces. In their analysis, U3O8 was identified on the basis of superlattice reflections in selected area diffraction patterns, since the small difference in parent structure lattice parameter of the two phases was undistinguishable. In the current work on fine powders, no discrete surface oxide layer was observed. This is also evidenced by the absence of Moiré patterns throughout the analyzed grains. The intermediate oxides (UO2.03, U4O9, U3O8) have very similar parent structure lattice spacings, e.g., 3.14 ≤ d(111) ≤ 3.16 Å. Superposition of discrete domains containing one of these compounds, unless considerably misoriented toward each other, is expected to produce Moiré fringes in HR-TEM images. One such example would be a surface coating of U3O8 or UO3 on a bulk U3O7 grain. Regions containing U3O8 have been identified, and these regions are not misoriented toward their surroundings, as evidenced by the analysis of FFT patterns.

Phase identification via TEM was based on the observation of domains showing long-period modulation in the HR-TEM images. As previously mentioned, the precision with which reciprocal lattice spacings are measured in FFT patterns of these domains does not allow to distinguish between the fluorite-based parent structures of the intermediate compounds UO2.03, U4O9 and U3O8. Rietveld refinement of the X-ray diffraction data attributed more than 75 wt % of the crystalline matter in samples H oxidized at 40 and 70 °C to the U3O7 phase (the remainder being UO2.01), see Figure 5. At 100 °C and above, a nearly constant fraction of about 25 wt % U3O7 is observed, the remaining being UO2.03−x. Surprisingly, the TEM analysis of the modulated domains gave partly conflicting results. The samples oxidized at 40 °C did not show any modulated phase at all (Figure 8 and Figure S7). Oxidation at 70 °C showed the typical U4O9 modulation in small domains located near the grain surface (Figure 9). Modulation was mainly absent after oxidation at 100 °C, however, in one grain the modulated U4O9 structure was readily observed (Figure 10 and Figure S8). Here, the U4O9 domains were located in the bulk of the grain, with unmodulated zones near the grain surface.

The HR-TEM observations at 40 and 70 °C indicate that in the early stage of oxidation a fluorite-type phase is formed with disordered oxygen defects, referred to as disordered UO3. Long-range ordering of the defects with the formation of a modulated structure (ordered UO3), but without changing the parent structure dimensions, occurs in the next stage. Belbeoch et al. introduced the notation UO2.25 to refer to the phase without long-range ordering, while they used the notation UO3 to refer to the modulated state. They observed a phase transition around 65 °C between a low-temperature pseudo-cubic (rhombohedral, α = 90.078°) phase showing weak superstructure reflections and a cubic phase showing stronger reflections. The decrease in satellite intensity was more significant in fine grain-sized powders (<1 μm).

Later observations by Naito confirmed the phase transformation first described by Belbeoch et al., but he reported that the modulation is only affected in hypostoichiometric U4O9-x stoichiometric U4O9 would not show different modulation intensities below or above the transition temperature. Allen et al., in their TEM work on oxidized, polycrystalline UO2 samples (O/U = 2.24), observed islands showing U3O8 modulation in electron diffraction patterns, surrounded by an apparently unmodulated matrix. They distinguished between UO3 and the matrix, having a disordered defect structure, for which they used the more general notation UO2.25 (but consistent with the notation UO2.25 by Belbeoch et al.).

The phase which is generally referred to as U3O8 contains a small number of oxygen defects and exists in a narrow stoichiometry domain 2.235 ≤ O/U ≤ 2.245, but does not include the exact 2.25 stoichiometry. Since the deviation is so small, the exact composition is usually disregarded. Cooper and Willis reassessed the refinement of the U3O8 crystal structure.

![Figure 12. Estimated amorphous UO3 (A-UO3) content in the powder samples which were oxidized for 15 h, from the discrepancy between TGA and XRD average stoichiometry values. Vertical lines present the propagated error (1σ), taking into account the uncertainty on TGA and Rietveld refined values.](image-url)
above the phase transition temperature, based on long-range ordering of cuboctahedral oxygen clusters and applying slightly more strict local symmetry restraints. Theoretical composition of U₄O₈.₉₄₄ (O/U ≈ 2.24) for the average cell, which is in agreement with Willis’s earlier findings. The theoretical cell composition was subsequently used as a starting point in the assessment of the defect structure in the low-temperature phase.

The present observations of long-range ordering can thus be interpreted in terms of deviations from the optimal stoichiometry which is required for the long-range ordering of the defect clusters (U₄O₉.₉₄₄ or O/U ≈ 2.24). When one deviates from this optimal stoichiometry, the intensity of the superstructure reflections decreases and eventually the ordering disappears. In the remainder, the term “disordered U₁O₉” or in short “U₁O₉ (dis)” is used to identify the state without superstructure reflections (previously called UO₂₂₅) in the notation of Belbeoch et al.) and “ordered U₁O₉” or “U₁O₉ (ord)” identifies the long-range ordered structure. The notation U₁O₉ is maintained when distinction between the modulated and unmodulated phases is not relevant.

In the oxidation experiments at 40 and 70 °C, both UO₂₋₀.₀₃₂ and disordered U₁O₉ coexist and one can thus expect that the U₁O₉ phase may not yet have reached the stoichiometry required for the development of long-range ordering. For the sample oxidized at 100 °C, the U₁O₉ phase is in equilibrium with tetragonal U₂O₇₋₀₀₉ and it may be expected that it has reached the appropriate stoichiometry, and hence, the ordered phase U₁O₉ (ord) forms.

Well-crystallized U₁O₉ develops long-range ordering but with a different modulation wave vector than for U₂O₇₋₀₀₉ (ord). In sample H oxidized at 100 °C, for which Rietveld refinement attributes over 75 wt % of the crystalline matter to the U₁O₇₋₀₂₉ phase and slightly less than 25 wt % to U₂O₇₋₀₀₉, the TEM analysis could not reveal any zones with the modulation typical for U₂O₇₋₀₂₉. In one particular grain, domains showing long-period modulation were observed, but the superstructures were typical for U₁O₇₋₀₂₉ (ord). Whenever present, the modulated phases were observed in the bulk of the grain, with smaller domains of unmodulated structures near the grain surface. Although it is not possible to determine the slight tetragonal deformation from the HR-TEM observations, one might expect that further oxidation starts at the grain surface and that the unmodulated domains near the grain surface are U₂O₇₋₀₂₉. The fact that no modulation was observed in other grains of this sample then conforms with XRD results (75 wt % U₂O₇₋₀₂₉). An evaluation of the local stoichiometry in the unmodulated structures may provide more insight, for example performed via scanning TEM electron energy loss spectroscopy (EELS) analysis. In summary, our interpretation is illustrated in the schematic of Figure 13.

Similar as for U₁O₇₋₀₀₉ it might be so that the long-range ordered modulation of U₂O₇ only develops within a narrow stoichiometry domain and that, outside of this domain, the tetragonal distortion of the parent structure sets in, but long-range ordering of the oxygen defects does not occur. It remains unclear whether in the fine powders studied here the U₁O₇₋₀₂₉ phase will eventually develop into long-range ordered U₁O₉. As already mentioned, none of the U₁O₇₋₀₂₉ phases found in the fine powders displayed a tetragonal distortion (c/a ratio) equal to that of the coarse-grained U₁O₉ reference powder.

5. CONCLUSIONS

The oxidation mechanisms in fine U₁O₃ powders (<200 nm) have been investigated. A variety of samples from three precursor powders having low (L, 4.0 m² g⁻¹), medium (M, 9.3 m² g⁻¹), and high (H, 21.1 m² g⁻¹) specific surface area were first reduced to stoichiometric UO₂ and subsequently oxidized under isothermal (40–250 °C) and isobaric conditions. The extent of oxidation was followed by in situ TGA, and postanalyzer of the powder samples was performed using XRD and HR-TEM.

According to TGA, the average stoichiometry of the samples reached values between O/U = 2.06 and 2.45. At oxidation temperatures up to 190 °C (samples L and 160 °C (samples M and H), the reaction rate was decreasing, eventually leveling off at O/U values close to 2.40. At higher oxidation temperatures the reaction progressed beyond this intermediate state. The crystalline constituents in the oxidized powder samples were quantified via Rietveld refinement of the X-ray diffraction data. Formation of increasing amounts of U₁O₉ in the early stage of oxidation explains the observed asymmetrical peak broadening and peak shift toward higher Bragg angles in the diffractograms. Tetragonal peak splitting occurring with extended oxidation is attributed to formation of a hypo-stoichiometric U₃O₇₋₀₂₉ phase with variable tetragonal distortion (c/a > 1). For the fine powders used in this study, the U₃O₇₋₀₂₉ phase remains considerably different from the reference U₁O₇ structure observed in coarser powder.

Even with high degree of oxidation no U₃O₈ was formed as evidenced by XRD analysis. A discrepancy exists between average stoichiometry values measured by TGA and those calculated from weight fractions attributed to the crystalline phases via XRD Rietveld refinement. The difference can be explained by the presence of significant amounts of amorphous UO₂ which remained undetected by XRD. HR-TEM analysis confirms that an amorphous phase nucleates on the surface of oxidized grains, and the nucleation sites appear to grow (from a few nm up to about 15 nm) with higher oxidation temperature.
The low-temperature UO₂ oxidation mechanism appears to be remarkably different for fine powders (<200 nm) as compared to coarser materials. Fully developed, long-range ordered U₄O₉ was not obtained, no U₃O₇ formation, and distinct surface layers were not observed. Oxidation above the solubility limit of UO₂⁺⁺ proceeds via formation of higher oxides (U₄O₉ and U₃O₇) in nanodomains. Both modulated and unmodulated U₃O₇ appear to occur, which can be understood given the fact that long-range ordering of oxygen defects in U₄O₉ only takes place in a narrow stoichiometry domain around O/U = 2.24. No modulation has been observed in the U₃O₇ phase, which might be attributed to a similar effect: given the fact that the tetragonal distortion (c/a ratio) always remained different in fine powders from that in coarser powders, the optical stochiometry for development of long-range order in U₃O₇ might not have been observed. To what extent the possible formation of amorphous UO₃ plays a role in this, remains to be investigated.

ASSOCIATED CONTENT

- Supporting Information
  - Rietveld refinement methodology, X-ray diffractograms, and HR-TEM images (PDF)

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REFERENCES

(64) Martin, D. G. J. Nucl. Mater. 1988, 152, 94.