In situ Synthesis and Characterization of Uranium Carbide Using High Temperature Neutron Diffraction

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We investigated the formation of UC_x from UO_{2+x} and graphite in situ using neutron diffraction at high temperatures with particular focus on resolving the conflicting reports on the crystal structure of non-quenchable cubic UC₂. The agents were UO₂ nanopowder, which closely imitates nano grains observed in spent reactor fuels, and graphite powder. In situ neutron diffraction revealed the onset of the $\text{UO}_2 + 2\text{C} \rightarrow \text{UC} + \text{CO}_2$ reaction at 1440°C, with its completion at 1500°C. Upon further heating, carbon diffuses into the uranium carbide forming C₂ groups at the octahedral sites. This resulting high temperature cubic UC₂ phase is similar to the NaCl-type structure as proposed by Bowman et al. Our novel experimental data provide insights into the mechanism and kinetics of formation of UC as well as characteristics of the high

temperature cubic UC_2 phase which agree with proposed rotational rehybridization found from simulations by Wen et al.

Introduction

Thermodynamic properties of uranium carbides are of special interest for a deeper understanding and prediction of in-reactor fuel performance as well as reactor safety calculations for Generation IV nuclear reactors. The interest in uranium carbides for nuclear fuel applications is based on their high melting points, lack of phase transformations at normal operating temperatures and dimensional stability under irradiation (all of which apply also to UO_2) coupled with a considerably higher thermal conductivity (Figure 1) and higher fissile density than UO_2 [1]. As a direct result of the higher thermal conductivity age induced thermal expansion known as ‘bambooing’ which has been observed in UO_2 fuel pellets [2] is expected to be greatly reduced in UC_x . A potential drawback to UC_x fuels is a required atmosphere control during manufacturing [3] as well as overall scarce understanding and experience when compared to UO_2 . Additionally UC_2 can further be employed as a reduction agent when mixed with UO_2 to maintain its stoichiometry as proposed for Very High Temperature Reactor[2].

Figure 1: Thermal conductivity of stoichiometric UC and UO_{2.0} (fully dense) as a function of temperature [4] [5].

In situ high temperature diffraction data for uranium carbides are sparse and the reliability of crystal structures is therefore limited. The Inorganic Crystal Structure Database (ICSD) [6] lists 51 entries of uranium carbide structures. Merely three of these entries address the non-quenchable [7] cubic UC₂ δ -phase which is reported to be stable between 1769°C and 2560°C[8]. This phase is labeled non-quenchable as attempts to preserve its structure via sudden temperature drops for characterization at ambient conditions have been unsuccessful [7]. Remarkably, these three experiments by Bowman et al. [9] (investigated using neutrons), Wilson [10] (X-ray diffraction, XRD) and Bredig [7] (XRD) originating in the early 1960's reveal conflicting results which have not been clearly resolved with modern diffraction techniques. Despite the UC₂ crystal structure being the basis for nuclear reactor-relevant thermodynamics calculations [11], [12] there has not been, to the best of our knowledge, a more recent study to unambiguously determine the crystal structure of the cubic UC₂ δ -phase. Only sporadic data of conversion

reactions are published with broad temperature and time ranges [13][14]. Thus in situ studies with controlled grain-sizes and defined stoichiometry are needed.

Neutron diffraction is the characterization tool of choice to examine crystallographic changes of compounds consisting of light elements, such as oxygen, nitrogen or carbon, and heavy elements, such as uranium, as their scattering powers are typically of the same order of magnitude. In particular, the coherent scattering cross sections for thermal neutrons for uranium ($\sigma_U = 8.9$ b), carbon ($\sigma_C = 5.5$ b), and oxygen ($\sigma_O = 4.2$ b) are within a factor of two. In contrast, these differences in scattering power for X-rays are factors of 15.3 ($Z_U/Z_C=92/6$) and 11.5 ($Z_U/Z_O=92/8$), which results in a diffraction signal dominated by the heavier uranium sublattice. Thus, details of the carbon or oxygen sublattices become vanishingly small, which are the decisive difference between the three crystal structures to be resolved in this work (see [15] for a comparison of simulated neutron and X-ray diffraction patterns for these structures).

Continuing a series of in situ investigations of the synthesis of refractory carbide[16][17][18][19], we investigated the synthesis of uraniumcarbide. We chose to start our experiment with the carbothermic reduction of UO_2 as the synthesis from the elements would have created pyrophoric hazards during the experiment.

Avoiding structural changes of the fuel during its lifetime is beneficial as internal stresses, cracks, etc. are reduced. Within a 100 to 200 μm thick outer layer of reactor fuel pellets, originally 10 to 20 μm large UO_2 grains subdivide into ~ 1000 grains of less than 1 μm size after about $2 \cdot 10^{21} \frac{fissions}{cm^3}$ (about 8.5% burnup) at low temperatures [20]. Here, we studied the reaction of such nanoparticle UO_2 fuel with graphite powder. Because the physical and chemical properties of UO_2 powders are expected to be particle size dependent [21], we expect a slightly lower reaction temperature compared to 2000°C reported in the literature[22]. This demonstrates

how in situ high temperature neutron diffraction can be used to study chemical reactions in nuclear fuel materials[23].

Our novel approach of using uranyl acetate to synthesize UO_2 powder without the use of irradiation [24], [25] or nitrates [26] is also different from the reaction by Wang et al. [27] in that we used calcium instead of ethylenediamine as the reducing agent. Benefits are a highly stoichiometric result of the synthesis in combination with the ability to produce larger quantities.

Experimental Setup

Neutron Diffraction

Two neutron diffraction experiments have been conducted with the High Pressure-Preferred Orientation (HIPPO) [28][29] diffractometer at the Los Alamos Neutron Science Center (LANSCE) [30][31]. The instrument is described in detail in the aforementioned references and we provide just a brief overview here. HIPPO views a high-flux/medium resolution moderator emitting neutron pulses at a frequency of 20 Hz. The comparably short flight path between moderator and sample of ~ 8.89 m combined with 1200 ^3He detector tubes arranged on five rings around the incident beam direction allow for short integration times, enabling the kinetic studies reported here. The detectors are mounted on 45 panels which are arranged on rings with nominal diffraction angles of 40° , 60° , 90° , 120° , and 144° . For data analysis, time-of-flight histograms of each detector tube are integrated either per panel, resulting in 45 histograms suitable for texture analysis, or per ring, suitable for diffraction data analysis assuming no preferred orientation. The sample chamber has a volume of ~ 2 m³ and accommodates various sample environments. Despite great efforts for beam collimation, spurious peaks originating from the furnace and not the sample were observed. With HIPPO's many detectors, these can be easily discriminated

against the sample diffraction signal since spurious peaks occur at different d-spacings in different detectors and are not present in all detectors due to the employed shielding and collimation. We manually excluded individual detector tubes with substantial signal from such spurious peaks to determine optimal collection parameters. For both experiments reported here we utilized a high temperature furnace with a graphite resistive tube heater to achieve steady-state temperatures in excess of 2200°C [32]. The carbothermic reduction of UO_2 as well as the high temperature UC_2 δ -phase were observed in situ during our first experiment while the second focused on an in depth examination of the δ -phase.

We collected isothermal neutron diffraction data for 30 minutes every 250°C between 250°C and 2000°C. The 30 minutes were collected as six data sets of five minutes each to enable the study of kinetics. During heating with 10°C/min, data in 2 min intervals were collected. The actual experiment, excluding setup and alignment, was completed in ~11 h. The pressed sample pellet was sandwiched between graphite papers and stood on its side inserted into a graphite stand with openings for incident and transmitted beam as depicted in Figure 2.

In a second experiment we collected diffraction data for 30 minutes every 250°C between 1250°C and 2000°C, as well as for 6 h at 2100°C and 2200°C. Heating and cooling rates were 50°C/min. Here, the pressed sample pellet was presintered rendering any containment superfluous.

Figure 2: Left: Photograph (right inset) and CAD model cutaway of hot-zone showing sample (center, purple), suspended by sample stick (red) inside graphite tube (brown), surrounded by water-cooled aluminum shells (grey). Incident neutrons (red dashed arrow) are either diffracted to the detector banks (yellow cones) or transmitted (orange dashed arrow). Right: Sample holder for first experiment showing sample disc standing on its side sandwiched between graphite paper and clamped by a graphite stand.

Sample Preparation

We pressed 12.5 mmol UO_2 powder (3.375 g) and 37.5 mmol graphite powder (0.45 g) into a 16 mm in diameter and 4 mm high pellet. Thus, a mixture of UO_2 and 75 at.% C with a molar ratio of $\text{C}:\text{UO}_2 = 3:1$ was achieved. This ratio is ideal for our investigation, allowing up to a third of the carbon atoms to escape the sample in form of CO_2 , while the remaining two carbon atoms per uranium are available to produce UC_2 at high temperatures. To increase structural integrity we added 60 mg of Naphthalene (C_{10}H_8) to the sample. The 99.999 % pure graphite powder with grain size $< 7 \mu\text{m}$ was obtained from Alfa Aesar. We synthesized the UO_2 powder from an aqueous solution of uranyl acetate by dissolving 4.24 g (10 mmol) of uranyl acetate dihydrate in 100 ml of H_2O . A stoichiometric amount of calcium (4.1 g, 10 mmol) was slowly added to the uranyl acetate solution under vigorous stirring. Uranium trioxide precipitated as an orange solid

while calcium acetate remained in solution. After filtration and washing with water, the orange cake of uranium trioxide hydrate was repetitively re-suspended in a small amount of boiling water, filtered and washed until no more calcium was detected in the filtrate. The solid material was then placed in a vacuum oven at 120°C for 12 hours to produce anhydrous uranium trioxide. This material is a fluffy orange powder, which is largely amorphous to X-ray. The yield is nearly quantitative upon precipitation, but a substantial amount of material is lost during washing and filtration owing to the slight solubility of UO_3 in water. UO_3 was reduced to UO_2 by placing it into an alumina boat inside a tube furnace at 400-500°C for 6 hours under a gentle stream of 6% hydrogen in argon gas mixture. The (mostly black) powder was stirred in the boat after 2 hours. The resulting powder was extremely fine and showed only uranium dioxide under X-ray diffraction. X-ray fluorescence showed no residual calcium. The material oxidizes over time from standing in air and could end up being slightly hyperstoichiometric at the time of the experiment.

SEM and TEM of UO_2 powder

In order to determine the average crystallite size of the UO_2 powder we dispersed less than 1 mg substance on a double sided Cu tape joined to an Al SEM slab. The SEM was conducted in a model Magellan³ 400 built by FEI Company. A ‘cauliflower structure’ (Figure 3) indicating nano-scale particles is observed equivalent to UO_2 fuel with 45GWd/t burn-up [20]. Thus, engineering the fuel to commence with this structure may cause less structural evolution through the fuel life cycle which could increase fuel integrity. In order to resolve these nano structures, a second sample for a TEM investigation was prepared by suspending less than 1 mg of UO_2 in HPLC grade acetone. Sonicating the sample in a glass veil immersed in an ultrasonic bath dispersed the nano particles evenly in the liquid. A 3.05 mm in diameter Cu grid with a carbon coating on the

opposite side was wetted four times and evaporated. The TEM analysis in a model Tecnai G² F30 from FEI Company confirmed the crystallite size to be ~80 nm (Figure 4).

Figure 3: A SEM of the UO₂ powder sample prior to our high-temperature experiment shows a 'cauliflower' structure.

Figure 4: A TEM of the UO₂ powder sample prior to our high-temperature experiment confirms an average crystallite size of ~80 nm (left) and reveals cavities of ~8 nm diameter (right) containing inclusions leftover from the synthesis. As the particles are agglomerated despite sonication the particle size is undetermined.

Data Analysis

As most of the data sets have been collected during non-isothermal conditions, with a mere two-minute of neutron integration time, the statistical error was minimized in two ways. For data refined with the script software *gsaslanguage* [33], which allows automated analysis of diffraction data using the GSAS Rietveld package, we employed a moving average over five data sets prior to the refinement process as shown to be effective by [34]. Single peak fits, on the other hand, are calculated from individual, not averaged data sets, that were processed with a five-value wide median filter which smoothed the graph significantly, as proven by Vogel et al. [35].

Data were analyzed using Rietveld refinement. Individual runs at isothermal conditions were integrated to increase statistics, inspected and initially analyzed with the Materials Analysis Using Diffraction (MAUD) package. A total of 147 recorded data sets were analyzed utilizing a script-based approach in combination with either SMARTSware [36] code which utilizes the General Structure Analysis System (GSAS) to perform a single peak fit or *gsaslanguage* to refine the entire spectrum. The latter custom sequential script models up to four phases simultaneously, namely 2H graphite, 3R graphite, UO_2 and U_xC with the site occupancy x ranging between 0.5 and 1, describing UC_2 and UC respectively. The intermediate phases U_2C_3 and the tetragonal UC_2 phase were not observed during the 11 hour short experiment which is in agreement with [37]. To make the fit more robust we constrained the isotropic thermal motion parameter U_{ISO} of both graphite phases, which is reasonable to assume as they describe identical atoms in similar local environments. In order to minimize variables and encourage a proper thermal behavior where comparable masses express similar thermal motions, the thermal motion of uranium atoms in UO_2 and UC are constrained to each other, as well as their oxygen and carbon ions

respectively. Moreover, our analysis refines lattice parameter and thus, unit cell volume, phase fraction and peak width of each phase. Results of one data set initialize the refinement of the next set. To increase the credibility of the sequential analysis, an additional calculation in reverse order (data set 147 to 1) was also performed. We chose to show results of only one analysis direction because the final results are identical within statistical uncertainties, and to improve figure clarity. The most robust refinement was achieved by first varying the phase scales followed by the lattice parameters in sequence of declining weight fraction or phase scale. A third refinement step varies the peak width for each phase in an equally sequenced fashion. A fourth step refines the thermal motion parameters and lastly, the uranium site occupancy in the U_xC phase.

The high temperature data from the second experiment were fit using GSAS and gsaslanguage. This ensured that for each of the three proposed structures an identical refinement strategy was applied.

Results

Post heat treatment of First Sample

A post-experiment Rietveld refinement revealed no significant texture, as the sample was formed from powder at a uniform temperature without introducing anisotropic external stimuli during the experiment. A histogram recorded by the 150° backscattering detector panels of HIPPO, including Rietveld fit, is shown in Figure 5. The Rietveld refinement determined a sample composition of 96 wt% UC, 3 wt% UC_2 tetragonal phase with rest 2H graphite. It is likely that the observed 1 wt% 2H graphite originates not from the sample itself, but from one of the two graphite foils which sandwich the sample. One of these reacted with the sample and could not be

fully removed before the measurement in the sample changer. No cubic UC_2 phase can be detected in the sample at room temperature confirming this phase cannot be quenched as predicted [7]. Neither UO_2 nor 3R graphite is found in the sample, indicating that both fully transformed to uranium carbide.

Figure 5: MAUD refinement for post-heat data of 150° detectors. The overlaid black line represents the peak fit calculated with MAUD. The difference between data and fit is plotted on the bottom.

Carbothermic Reduction of First Sample

Figure 6 serves as a qualitative overview of the experimental results conducted in the high-temperature furnace and is described in this and the following section. Sequentially recorded histograms from the 40° detectors are normalized, diffraction intensities color coded, and plotted in individual rows. Temperature changes and equithermal holding points are indicated in the thermal profile on the left side. Dominate phases and the Miller indices of their brightest reflections are given throughout the experiment progression. The transition temperature when

graphite and UO_2 reflections exchange for emerging UC reflections is evident at $\sim 1500^\circ\text{C}$. Although the reaction temperature is within the predicted range of 1500°C - 2000°C [14], the reaction completes in less than five minutes as opposed to conservative ex situ heat treatments performed at 2000°C for several hours[13].

Figure 6: The contour plot shows observed intensity as a function of experiment progress (y-axis) and d-spacing based on data recorded from the 40° detectors. The left graph correlates experiment progress with sample temperature. The total time for this data set was ~ 11 hours.

High Temperature UC_2 δ -phase at 2200°C

Diffraction data of the second experiment collected at 2200°C for 6 hours is shown in

Figure 7. We fitted each of the three published crystal structures to the dataset without excluding

any region. The NaCl-type structure proposed by Bowman et al. accomplished the best fit with a χ^2 of 6.9. The pyrite-type structure proposed by Wilson and the fluorite-type structure by Bredig achieved a fit with a χ^2 of 7.9 and 10.1, respectively. The poor match of the pyrite model is obvious in the 40° detector banks where the necessary 210 and 210 reflections are missing in the recorded data. On the other hand, the Wilson structure largely misses to predict the main 200 reflection present in the 90° detector banks. The reason the fits are not better in quality altogether is due to diffraction from furnace components in the diffraction data, such as are visible at $\sim 2.2\text{\AA}$ in the 90° detector banks. If such sporadic peaks would occur in all banks at the same diffraction angle, they would originate from the sample. However, peaks which only occur in some detector banks are caused by diffraction from furnace components. These are not in the calibrated sample position and thus appear at different d-spacings in different detector banks or only in a few detector banks if the path for this “contamination” diffraction intensity is obstructed for some detector panels. Due to the large number of detector banks on the HIPPO diffractometer these spurious contamination peaks can be unambiguously identified.

Figure 7: Diffraction data (green) with calculated fits for the three structural candidates and difference curve of 40°, 60° and 90° detector bank (top to bottom) recorded at 2200°C.

Diffraction peaks not visible in all detector banks are considered spurious peaks from off-center furnace components rather than originating from the sample.

Discussion

Structure of the cubic UC₂ δ -phase

The CaF₂ type structure which achieved the poorest fit also seems to be improbable on chemical grounds, as it would imply a breaking of the strong C-C bonds of the C₂ ions that exist with an interatomic distance of 1.34 Å in the intermediate tetragonal phase [38]. If such breakage occurred in the formation of this CaF₂/fluorite-type structure, where the C-C distance is 2.72 Å, the fluorite high-temperature structure should be quenchable as the formation of the bond represents a major crystallographic change in the solid [7]. However, the ability to quench the high temperature phase has not been observed. The observed continuous increase of carbon concentration in UC described below ultimately led to a sudden decrease of the UC diffraction peaks at the same position indicating the formation of the cubic UC₂ phase further substantiates this argument of similitude between these phases, both of the NaCl-type structure. The C-C bond length in the pyrite structure is 1.443 Å [39] and thus compatible with the tetragonal UC₂ structure. It is worth pointing out that the C-C dumbbells in the pyrite structure are static, while those observed by Bowman et al. [9] and in this work are dynamically disordered with the center of the dumbbells located at the midpoint of each edge of the unit cells as in the NaCl structure. However, this would create a different motif which is repeated throughout the crystal and thus leads to a distinctly different diffraction signal than the dynamically disordered dumbbells.

Starting at 1800°C, the intensity of UC reflections markedly declines (Figure 6). This led us to abort the first experiment as we suspected that the sample disintegrated and fell out of the sample holder. However, upon cooling the diffraction intensity was fully recovered. Partial melting of the sample can be rejected as an explanation because no metallic uranium (melting temperature of 1135°C) was found in the post-experiment sample (Figure 5) and the sample preserved its shape. A number of order-disorder transitions in the anion sublattices have been reported resulting in an intensity loss of reflections as observed in this work. A diffuse structural transition termed ‘Bredig transition’ is marked by the anions sublattice to move freely forming a superionic conductor [40]. The erratic movement of the unbound anions (carbon ions) eliminates the periodicity in the sublattice, consisting only of periodicity originating from the uranium atoms, which will alter the diffraction pattern. The Bredig transition has been observed for many fluorite-type structures including UO_2 , generally near 0.8-0.84 [40] of the melting temperature [41]. Hayes [42] refers to this phenomenon as ‘premelting’ and includes silver halides and rare-gas solids. However, in that case a simple bcc uranium sublattice would exist, which did not match our diffraction data, indicating that there is another contribution to the periodicity generating diffraction aside from solely the uranium atoms.

ICSD used a NaCl-type defect structure with half occupied uranium cations to describe the 2:1 ratio of C to U ions. Bowman et al. actually proposed fully occupied U sites in combination with a C_2 molecule at the octahedral anion site of the NaCl-type structure.

Kracek et al. [43] first described the ‘free-rotation’ model for sodium nitrate which constricts sublattice movements to rotations around a fixed interstitial point and belongs to the mean-field (or Landau) theory. A vanishing of the superlattice reflections in calcite (CaCO_3) and sodium nitrate (NaNO_3) has been explained with the free-rotation model [44]. As the transition

temperature is approached, the nitrate and carbonate molecular ions, NO_3 and CO_3 respectively, increase in angular oscillation about the c axis, eventually leading to a continuous rotation of the whole unit. Harris [44] more recently described this phenomenon using the XY model of the universality principle, resulting in a more accurate match. Free rotation along with random orientation has been first suggested for C_2 groups in the cubic UC_2 phase by Bowman et al. [9]. The postulated free rotation model or its more recent enhanced counterpart, the XY model, are good candidates describing the thermally activated anion movements of the C_2 dumbbells necessary to attenuate the pyrite-type reflections analogous to the simulation of a premelted sublattice. Another promising model considers oscillation rather than rotation of the C_2 molecules. These simulations by Wen et al. [39] utilizing the HSE (Heyd-Scuseria-Ernzerhof) screened Coulomb hybrid density functional show good agreement with structural, optical and electronic properties of cubic UC_2 by $\sim 30^\circ$ angular oscillation of C_2 molecules with a 1.443 Å bond length. Which of the above mentioned models, the free rotation or the somewhat more constrained oscillation, describes the experimental data best needs further investigation. However, both models explain that the high temperature phase cannot be quenched as the dynamic disorder of the C_2 dumbbells cannot be sustained at ambient conditions.

Rotational dynamic disorder cannot be readily described with the Rietveld packages used in this work. Lokshin et al. [45] successfully analyzed rotational molecular dynamics in clathrate hydrate using FullProf. Alternatively, Nishimura et al. [46] evaluated dynamic disorder of Li in Li_xFePO_4 using maximum entropy methods to obtain the nuclear density distribution. Idemoto et al used the pair distribution function method to study the local structure of complex oxides [47]. While all of the aforementioned analysis methods were demonstrated with HIPPO and would be useful to further characterize the δ -phase structure, the data quality of the present setup for the

ultra-high temperature furnace precludes their application and we are limited to Rietveld analysis.

Uranium Monocarbide

Concurrently to the formation of uranium carbide, the graphite and UO_2 content in the sample start to decline at 1441°C and are completely vanished at 1650°C (Figure 6), while the UC phase appears, following the redox transformation

As shown through chemical analysis of quenched samples by Mukerjee et al. [48], the carbon content declines in agreement with this reaction equation predicting the discharge of CO_2 gas. As a reaction temperature just below 2000°C is indicated by the literature [22], we did not employ a slower temperature profile to investigate this event in more depth. The bulk portion of this transformation completed at 1500°C , as indicated in the intensity drop of the 220 UO_2 peak. For a mole ratio of $\text{C}:\text{UO}_2 = 3:1$, similar to our material, Mukerjee et al. [48] determined a transformation onset at 1300°C with completion at 1500°C with ex situ measurements. Onset and completion are both $\sim 150^\circ\text{C}$ lower than observed here. While the particle size of UO_2 is not mentioned in Mukerjee et al., the reacted graphite is two orders of magnitudes finer as compared to the starting material used in this work. Because the roles of each reactant are unclear, we can only conclude that grain-size seems to affect the transformation temperature.

The carbon dioxide generation indicated by Equation (1.1) was also noticeable as a slight increase in the recorded vacuum pressure.

We observed changes during isothermal holding when plotting strains relative to the room temperature lattice parameter a with $4.961 \text{ \AA}$, which we attribute to increasing carbon

concentration in the uranium carbide. These strains have been derived in two ways: from a single peak fit of the 200 reflection of cubic UC and with the sequential refinement of the lattice parameter from the full spectrum. This led to qualitatively similar results (Figure 8, top). In both cases, the reference strain is the room temperature lattice parameter. Single peak fits have shown to be useful in calculating transition temperatures, but the dimensional change in a unit cell should be far more accurate when considering the full d-spacing range of all five histograms. Thus, we will consider only the latter results (shown in red of Figure 8, top).

Figure 8: Thermal strain of UC_x lattice showing negative CTE due to carbon diffusion. Top: Temperature profile with isothermal measurements shaded in yellow. Bottom: Strain relative to first data point at each isothermal holding temperature.

To further investigate these changes, we also computed the strain relative to the first data point at each temperature, Figure 8, bottom. We clearly see an increased rate of change during the first ~600 seconds at the higher holding temperature, consistent with an increased mobility of carbon atoms at a higher temperature. After ~600 seconds, the rates of lattice parameter change at 1500°C and 1750°C are about the same, indicating the same rate limiting factor becoming active. As was shown in previous work studying in situ carburization [16], modeling can aid to interpret these rates, however, this was outside the scope of the present work.

Analog to UO_x , the unit cell of UC_x also shrinks with increasing amount of anions. During the isothermal hold at 1500°C the lattice strain decreases from $22.395 \cdot 10^{-3}$ to $21.919 \cdot 10^{-3}$ within 39 min, before the thermally activated reaction reaches equilibrium and the lattice parameter remains approximately constant for the remaining 20 minutes of the holding time at that temperature. A linear regression calculates a strain rate of $3.09 \cdot 10^{-7} \text{s}^{-1}$ with an accuracy of $R^2=0.988$ for this diffusion region. At 1750°C, the strain rate increases to $4.24 \cdot 10^{-7} \text{s}^{-1}$ determined during the 42 min of isothermal holding, which can be explained due to the higher available thermal activation energy. A polynomial regression of second order increases the R^2 value from 0.876 to 0.977 suggesting that the reaction rate at 1750°C is controlled by diffusion rather than interface controlled [34]. The second order strain rate approximation is found to be described by:

$$\frac{\Delta d}{d} = 2.292 \cdot 10^{-2} + 9.701 \cdot 10^{-7}T + 3.081 \cdot 10^{-10}T^2 \quad (1.2)$$

After 42 minutes equilibrium conditions are not reached, implying that more carbon would have diffused into the UC crystal forming UC_2 at this temperature. Unaware of this at the time the experiment was conducted, we raised the temperature to 2000°C.

Post Heating Evaluation

The first sample, after the heating cycle, appears porous due to the release of CO₂ gas according to Equation (1.1). The cylinder also shrank ~16% in each dimension, a 41% reduction in volume, from initially 16 mm diameter by 4 mm cylinder length to 13.4 mm by 3.3 mm. The main reason for this is the more compact crystal structure of UC with a lattice parameter of 4.961 Å, compared to the likewise fcc UO₂ unit cell with 5.47 Å accounting for 25% of the volumetric reduction. The remaining 16% volume change is likely due to the release of CO₂ and possibly sintering effects.

An observed 3 wt% UC₂ tetragonal phase in the ex situ measurement is evident from the occurrence of its two strong reflections, the 110 at 2.5728 Å and the 002 at 3.0038 Å in the recorded histogram (Figure 5). This small phase fraction however was not detectable during the experiment in the high-temperature furnace owing to higher noise levels, lower neutron intensities (due to 4 mm collimation) and lower counting times in order to capture reaction kinetics. The 002 of the 2H graphite phase at 3.3555 Å is not matched well by the refinement shown in Figure 5 due to its sizeable texture evident by strong fluctuations in peak intensity throughout the different detector banks.

Conclusion

We observed the synthesis of uranium carbide from uranium oxide and graphite in situ using high temperature neutron diffraction. Our diffraction results clearly show that the reaction occurs within a few minutes without any detectable intermediate phases. By means of lattice parameter changes we were able to follow the diffusion of carbon atoms into the uranium carbide lattice during isothermal holding at 1500°C and 1750°C, leading to the formation of the UC₂ phase. Of

the three opposing structure models reported in the literature for the non-quenchable cubic UC₂ phase, stable between 1769°C and 2560°C, our experimental results endorse the NaCl-type structure according to Bowman et al. Recent publications on thermal modeling of safety critical factors in nuclear reactors which were based on the fluorite structure, agree the least with our experimental data. This underlines the necessity of experimental verification of models and predictions. We provide first experimental data of a reversible order-disorder transition in this δ -phase with its onset at ~1800°C which is likely due to oscillating C₂ molecules in the sublattice described by Wen et al. [39].

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References

- [1] B. Frost, "The Carbides of Uranium," *J. Nucl. Mater.*, vol. 10, no. 4, pp. 265-300, 1963.
- [2] D. R. Olander, "Nuclear Fuels - Present and future," *J. Nucl. Mater.*, vol. 389, no. 1, pp. 1-22, 2009.
- [3] M. T. Simnad, "Uranium Carbide Fuels," in *Inorganic Reactions and Methods: Formation of Ceramics*, vol. 18, Hoboken, NJ, USA, John Wiley & Sons, Inc., 1999, pp. 346-349.
- [4] R. De Coninck, W. Van Lierde and A. Gijs, "Uraniumcarbide: Thermal diffusivity, thermalconductivity and spectral emissivity at high temperatures," *J. Nucl. Mater.*, vol. 57,

pp. 69-76, 1975.

- [5] D. Martin, "A re-appraisal of the thermal conductivity of UO₂ and mixed (U,Pu) oxide fuels," *J. Nucl. Mater.*, vol. 110, pp. 73-94, 1982.
- [6] [Online]. Available: <http://icsd.fiz-karlsruhe.de/>.
- [7] M. Bredig, "The High-Temperature Cubic Phases of Uranium and Lanthanum Dicarbides," vol. 43, p. 493, 1960.
- [8] T. Massalski, Binary Alloy Phase Diagrams, William W. Scott, Jr. Materials Park, Ohio, 1990, p. 893.
- [9] A. Bowman, G. Arnold, W. Wittman, T. Wallace and N. Nereson, "Crystal Structure of UC₂," vol. 21, pp. 670-671, 1966.
- [10] W. Wilson, "High-temperature X-ray diffraction investigation of uranium-carbon system," vol. 43, pp. 77-81, 1960.
- [11] P. Chevalier and E. Fischer, "Thermodynamic modelling of the C-U and B-U binary systems," vol. 288, pp. 100-129, 2001.
- [12] M. Freyss, "First-principles study of uranium carbide: Accommodation of point defects and of helium, xenon, and oxygen impurities," vol. 81, p. 014101, 2010.
- [13] L. Carraz, S. Sundell and H. Ravn, "High-temperature carbide targets for fast on-line mass separation of alkali and noble gas elements," *Nucl. Instrum. Methods*, vol. 158, pp. 69-80, 1979.
- [14] K. Davidson, W. Martin, D. Schnell, J. Taub and J. Taylor, "Development of Carbide-Carbon Composite Fuel Elements for Rover Reactors," *Los Alamos Scient. Laboratory Report LA-5005*, 1972.
- [15] S. C. Vogel, "A review of neutron scattering applications to nuclear materials," *ISRN Materials Science*, vol. 2013, p. 302408, 2013.
- [16] B. Winkler, D. Wilson, S. Vogel, D. Brown, T. Sisneros and V. Milman, "In situ observation of the formation of TiC from the elements by neutron diffraction," *J. Alloys and Compd.*, vol. 441, no. 1-2, pp. 374-380, 2007.
- [17] E. Juarez-Arellano, B. Winkler, S. Vogel, A. Senyshyn, D. Kammler and M. Avalos-Borja, "In situ observation of the reaction of scandium and carbon by neutron diffraction," *J. Alloys and Compd.*, vol. 509, no. 1, pp. 1-5, 2011.
- [18] A. Friedrich, B. Winkler, E. Juarez-Arellano and L. Bayarjargal, "Synthesis of Binary Transition Metal Nitrides, Carbides and Borides from the Elements in the Laser-Heated Diamond Anvil Cell and Their Structure-Property Relations," *Materials*, vol. 4, no. 10, pp.

1648-1692, 2011.

- [19] N. Lane, S. Vogel, G. Hug, A. Togo, L. Chaput, L. Hultman and M. Barsoum, "Neutron diffraction measurements and first-principles study of thermal motion of atoms in select Mn+1AX_n and binary MX transition-metal carbide phases," *Pys. Rev. B*, vol. 86, no. 21, p. 214301, 2012.
- [20] H. Matzke, "On the rim effect in high burnup UO₂ LWR fuels," *J Nucl. Mater.*, vol. 189, pp. 141-148, 1992.
- [21] H. Wu, Y. Yang and C. Cao, "Synthesis of Colloidal Uranium - Dioxide Nanocrystals," *J. Am. Chem. Soc.*, vol. 128, no. 51, pp. 16522-16523, 2006.
- [22] F. Weigel, The Chemistry of the Actinide Elements, 2nd Edition ed., G. T. S. & L. R. M. J. J. Katz, Ed., London: Chapman & Hill., 1986.
- [23] L. Desgranges, G. Baldiozzi, Rousseau, J.-C. Niepce and G. Calvarin, "Neutron Diffraction Study of the in Situ Oxidation of UO₂," *Inorg. Chem.*, vol. 48, no. 16, pp. 7585-7592, 2009.
- [24] O. Roth, H. Hasselberg and M. Jonsson, "Radiation chemical synthesis and characterization of UO₂ nanoparticles," *J. Nucl. Mater.*, vol. 383, pp. 231-236, 2009.
- [25] T. Nenoff, B. Jacobs, D. Robinson, P. Provencio, J. Huang, S. Ferreira and D. Hanson, "Synthesis and low temperature in situ sintering of uranium oxide nanoparticles," *Chem. Mater.*, vol. 23, no. 23, pp. 5185-5190, 2011.
- [26] S. Hasan, T. Ghosh, D. Viswanath, S. Loyalka and B. Deng, "Synthesis of Uranium Oxide Nanoparticles in Aqueous Solutions," *T. Am. Nucl. Soc.*, vol. 96, no. 1, pp. 180-182, 6 2007.
- [27] Q. Wang, G.-D. Li, S. Xu, J.-X. Li and J. Chen, "Synthesis of uranium oxide nanoparticles and their catalytic performance for benzyl alcohol conversion to benzaldehyde," *J. Mater. Chem.*, vol. 18, no. 10, pp. 1146-1152, 3 2008.
- [28] H.-R. Wenk, L. Lutterotti and S. Vogel, "Rietveld texture analysis from TOF neutron diffraction data," vol. 25, no. 3, pp. 283 - 296, 2010.
- [29] S. Vogel, C. Hartig, L. Lutterotti, R. Von Dreele, H.-R. Wenk and D. Williams, "Texture measurements using the new neutron diffractometer HIPPO and their analysis using the Rietveld method," *Powder Diffr.*, vol. 19, no. 1, p. 65, 2004.
- [30] S. Vogel and H. Priesmeyer, "Neutron production, neutron facilities and neutron instrumentation," vol. 63, p. 27, 2006.
- [31] P. W. Lisowski and K. F. Schoenberg, "The Los Alamos Neutron Science Center," vol. 562, no. 2, pp. 910-914, 2006.

- [32] H. M. Reiche, Advanced sample environments for in situ neutron diffraction studies of nuclear materials, Las Cruces, NM, USA: New Mexico State University, 2012.
- [33] S. Vogel, "gsaslanguage: a GSAS script language for automated Rietveld refinements of diffraction data," vol. 44, pp. 873 - 877, 2011.
- [34] S. Vogel, E. Ustundag, J. Hanan, V. Yuan and M. Bourke, "In-situ investigation of the reduction of NiO by a neutron transmission method," *Mat. Sci. Eng. A-Struct.*, vol. 333, pp. 1-9, 2002.
- [35] S. Vogel, H. Reiche and D. Brown, "High pressure deformation study of zirconium," *Powder Diffr.*, vol. 22, no. 2, pp. 113-117, 2007.
- [36] S. Pojprapai, Z. Luo, B. Clausen, S. Vogel, D. Brown, J. Russel and M. Hoffman, "Dynamic processes of domain switching in lead zirconate titanate under cyclic mechanical loading by in situ neutron diffraction," *Acta Mater.*, vol. 58, no. 6, pp. 1897-1908, 2010.
- [37] H. Nickel and H. Saeger, "Ueber die Bildung des U_2C_3 ," vol. 28, pp. 93-104, 1968.
- [38] A. Austin, "Carbon Positions in the Uranium Carbides," vol. 12, pp. 159-161, 1959.
- [39] X.-D. Wen, S. Rudin, E. Batista, D. Clark, G. Scuseria and R. Martin, "Rotational rehybridization and the high temperature phase of UC_2 ," *unpublished*.
- [40] C. Basak, "Classical molecular dynamics simulation of uranium monocarbide (UC)," *Comp. Mater. Sci.*, vol. 40, pp. 562-568, 2007.
- [41] J. Ralph and G. Hyland, "Empirical confirmation of a Bredig transition in UO_2 ," *J. Nucl. Mater.*, vol. 132, pp. 76-79, 1985.
- [42] W. Hayes, "Premelting," *Contem. Phys.*, vol. 27, no. 6, pp. 519-532, 1986.
- [43] F. Kracek, E. Posnjak and S. Hendricks, "Gradual transition in sodium nitrate II. The structure at various temperatures and its bearing on molecular rotation.," *J. Am. Chem. Soc.*, vol. 53, pp. 3339-3348, 1931.
- [44] M. Harris, "A new explanation for the unusual critical behavior of calcite and sodium nitrate, $NaNO_3$," *Am. Mineral.*, vol. 84, pp. 1632-1640, 1999.
- [45] K. Lokshin, Y. Z., D. H., W. Mao, H.-K. Mao, R. Hemley, M. Lobanov and M. Greenblatt, "Structure and Dynamics of Hydrogen Molecules in the Novel Clathrate Hydrate by High Pressure Neutron Diffraction," *Phys. Rev. Lett.*, vol. 93, no. 12, p. 125503, 9 2004.
- [46] S.-I. Nishimura, G. Kobayashi, K. Ohoyama, R. Kanno, M. Yashima and A. Yamada, "Experimental visualization of lithium diffusion in $LiFePO_4$," *Nat. Mater.*, vol. 7, no. 9, pp. 707-711, 9 2008.

- [47] Y. Idemoto, K. Ueki and N. Kitamura, "Dependence of Average and Local Structures and Cathode Performance on Synthetic Condition of $\text{Li}_x(\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3})\text{O}_2$ as a Cathode Active Material for Li Ion Battery," *Electrochemistry*, vol. 78, no. 5, pp. 475-481, 2010.
- [48] S. Mukerjee, J. Dehadraya, V. Vaidya and D. Sood, "Kinetics and Mechanism of $\text{UO}_2 + \text{C}$ Reaction for UC/UC₂ Preparation," *J. Nucl. Mater.*, vol. 210, no. 1-2, pp. 107-114, 1994.