

In situ synthesis and characterization of uranium carbide using high temperature neutron diffraction



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ABSTRACT

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 UO₂ + 2C → UC + CO₂ 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 UC₂ phase which agree with proposed rotational rehybridization found from simulations by Wen et al.

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1. 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 UO₂) coupled with a considerably higher thermal conductivity (Fig. 1) and higher fissile density than UO₂ [1]. As a direct result of the higher thermal conductivity age induced thermal expansion known as 'bambooning' which has been observed in UO₂ 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 UO₂. Additionally UC₂ can further be employed as a reduction agent when mixed with UO₂ to maintain its stoichiometry as proposed for Very High Temperature Reactors [2].

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,

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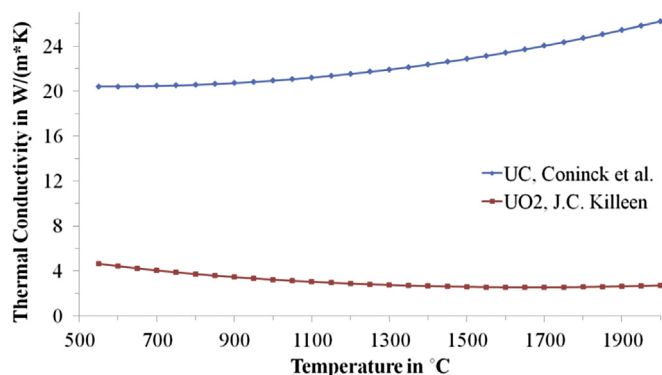


Fig. 1. Thermal conductivity of stoichiometric UC and UO_{2.0} (fully dense) as a function of temperature [4,5].

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 Ref. [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 carbides [16–19], we investigated the synthesis of uranium carbide. We chose to start our experiment with the carbothermic reduction of UO₂ as the synthesis from the elements would have created pyrophoric hazards prior and during the experiment.

Avoiding structural changes of nuclear fuel during its lifetime is beneficial as internal stresses, cracks, etc. are reduced. Within a 100–200 μm thick outer layer of reactor fuel pellets, originally 10–20 μm large UO₂ grains subdivide into ~ 1000 grains of less than 1 μm size after about $2 \cdot 10^{21} \frac{\text{fissions}}{\text{cm}^3}$ (about 8.5% burnup) at low temperatures [20]. Here, we studied the reaction of such nanoparticle UO₂ fuel with graphite powder. Because the physical and chemical properties of UO₂ 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 UO₂ 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.

2. Experimental setup

2.1. 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 UO₂ as well as the high temperature UC₂ 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 min every 250 °C between 250 °C and 2000 °C. The 30 min were collected as six data sets of 5 min 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 Fig. 2.

In a second experiment we collected diffraction data for 30 min 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.

2.2. Sample preparation

We pressed 12.5 mmol UO₂ 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 UO₂ and 75 at.% C with a molar ratio of C:UO₂ = 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 CO₂, while the remaining two carbon atoms per uranium are available to produce UC₂ at high temperatures. To increase structural integrity we added 60 mg of Naphthalene (C₁₀H₈) to the sample. The 99.999% pure graphite powder with grain size < 7 μm was obtained from Alfa Aesar. We synthesized the UO₂ powder from an aqueous solution of uranyl acetate by dissolving 4.24 g (10 mmol) of uranyl acetate dihydrate in 100 ml of H₂O. 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 h 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

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