Oxidation of UC: An *in situ* high temperature environmental scanning electron microscopy study

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ABSTRACT

In situ HT-ESEM oxidation of sintered UC fragments revealed the morphological changes occurring during the transformation between UC to UO_2 and UO_2 to U_3O_8 at 723−848 K and in an atmosphere of 10 −100 Pa O_2. Two main oxidation pathways were revealed. Oxidation at 723 K in atmospheres $\leq$25 Pa O_2 showed the transformation from UC to UO_{2+x}, as confirmed by *post mortem* HRTEM analysis. This oxidation pathway was comprised of three steps: (i) an induction period, where only surface UC particles oxidised, (ii) a sample area expansion accompanied by crack formation and propagation, (iii) a stabilisation of the total crack length inferring that crack propagation had stopped. Samples oxidised under 50 Pa O_2 at 723 K and at 773−848 K for 10−100 Pa O_2 showed an "explosive" oxidation pathway: (i) sample area expansion occurred as soon as oxygen was inserted into the chamber and crack propagation and crack length followed an exponential law; (ii) cracks propagated as a network and the oxide layer fragmented, (iii) an "explosion" occurred causing a popcorn-like transformation, typical for oxidation from UO_2 to U_3O_8. HRTEM characterisation revealed U_3O_8 preferentially grow in the [001] direction. The explosive growth, triggered by ignition of UC, proceeded as a self-propagating high-temperature synthesis reaction, with a propagation speed of 150−500 ± 50 μm/s.

1. Introduction

Uranium monocarbide (UC) has potential application as nuclear fuel for Generation IV reactors. The main advantages of this material compared to the current UO_2 fuel are its higher fissile material density (1.34 times) and better thermal conductivity (25.3 W/(m·K) which is 2.6 times higher) [1]. While UC offers improved properties during use, at the end of the fuel cycle it cannot be safely stored or disposed of without undergoing preliminary conditioning to a suitable oxide form as it may be potentially pyrophoric and reactive with moisture and gases [2,3].

The mechanism of oxidation of uranium carbide was investigated in the 1960s and 1970s when interest in UC as a breeder

reactor fuel was high [4—9]. It was found to be affected by several parameters such as temperature, oxygen partial pressure, morphology of the oxide layer formed, separation of the reaction products and stoichiometry of the initial material [10]. The oxidation mechanism of UC is complex as similar studies [5,11] performed over the same temperature range and under the same oxygen atmosphere, suggest different oxidation mechanisms which are affected by the formation of a protective oxide layer or a low density non-protective pulverised oxide layer [12,13]. Indeed U_3O_8 appears to be a detachable powder whilst the thin layer adherent at the surface of uranium carbide is usually characterised as UO_2 [14,15]. Many aspects of the intermediate oxidation process that occur when UO_2 is oxidised to U_3O_8 are not well understood. Oxidation of UO_2 powders usually occurs in two stages represented by a pseudo-parabolic weight gain curve followed by a sigmoidal curve [16]. The first part of the curve is characterised by a low oxidation rate, an induction period, that is associated with the diffusional oxidation of UO_2 to $UO_{2.34}$ with formation of U_4O_9 and

U_3O_7 as intermediate products while the latter part of the curve assumes sigmoidal kinetics associated with the U_3O_8 nucleation and growth process [16−18] that occurs when U_3O_8 is formed from U_3O_7 [16] or UO_2 [18,19]. The fcc cubic fluorite−type crystal structure of UO_2 can accommodate extra oxygen atoms and therefore is able to form the polymorphs U_4O_9 and U_3O_7. These are described as UO_2 matrices enriched with oxygen atoms [20]. Solubility of oxygen in UO_{2+x} depends on temperature [21]: above 773 K uranium oxides from $UO_{2.26}$ - $UO_{2.33}$ can be converted to U_3O_8 [22].

UC oxidation occurs with the characteristic Maltese cross [23] shape of the oxide, typical for carbides and borides of the group IV,V,VI of the transition metals [24,25] when oxidised in CO_2 atmosphere [26] at 1073 K or in an atmosphere $\geq$ 13.3 kPa in oxygen from 823 to 1073 K [14,27].

Iyer et al. [28] proposed a mechanism of oxidation for UC which involves: first the diffusion of oxygen into the uranium carbide matrix with the precipitation of carbon, reported to be highly reactive. The resulting oxycarbide is converted into uranium dioxide with subsequent precipitation of carbon as a second phase. This oxide acts as a diffusion barrier for oxygen transport through the carbide matrix [28]. It is unclear whether the oxide product readily spalls off or stays adherent to the carbide core, as contradictory results have been reported [11−13]. Mukerjee et al. [11] proposed that at low oxygen partial pressures (<5 kPa) the slow release of CO_2 does not generate stresses in the oxide layer and therefore an intact oxide layer at the end of the reaction is formed.

The main reactions that can occur during the oxidation of UC are:

$$UC + O_2 \rightarrow UO_2 + C \qquad (1)$$

$$C + O_2 \rightarrow CO_2 \qquad (2)$$

$$3UO_2 + O_2 \rightarrow U_3O_8 \qquad (3)$$

Reactions (1) and (2) occur at the same time, however reaction (3) is believed to occur when all the carbon is oxidised to CO_2 [28]. Slightly different reactions have been reported [7] where the intermediate products of oxidation are UC_2, UO_2, $UC_{1-x}O_x$, UO_3 or directly U_3O_8 and carbon could be oxidised either to CO or CO_2 [14] depending on temperature and oxygen availability [29]. The presence of carbon increases the complexity of the oxidation mechanism of UC in comparison with oxidation of UO_2 or metallic U as carbon can be found in the oxide as either free carbon, as carbide, as oxycarbide, as carbon monoxide or dioxide [14]. UC is well known to be pyrophoric [3,28] and its ignition temperature is system dependant and is affected by several parameters such as heating rate, partial pressure of oxygen, and at least ten other factors including mass and specimen geometry [2]. The proposed UC ignition reaction [28] is:

$$UC + \frac{7}{3}O_2 \rightarrow \frac{1}{3}U_3O_8 + CO_2 \qquad (4)$$

It has been previously proposed that ignition in UC powder is triggered by the formation of a poorly crystallised and cracked layer of UO_2 which does not offer protection to the UC core when being exposed to oxygen [15]. On the other hand, a stable and protective layer made of a solid solution UCO/UO_{2-x} would prevent ignition. The second path was found to be possible thanks to slow heating rates [15].

The work presented in this paper is the first of its kind as it follows the *in situ* observation of morphological changes occurring during oxidation of sintered fragments of UC at low oxygen partial pressures ($\leq$100 Pa O_2). This was made possible thanks to the use of state-of-the art techniques: high-temperature environmental scanning electron microscope (HT-ESEM) used for monitoring *in situ* oxidation of UC samples and *post-mortem* characterisation of the oxide products performed via high resolution transmission electron microscopy (HRTEM).

2. Experimental

High density disc shaped, ^{235}U depleted UC pellets (>91% of the theoretical density, TD, with U/C stoichiometry of 1.00 ± 0.03), were manufactured at CEA (Commissariat à l'Energie Atomique) Cadarache, France. They were crushed into fragments of various sizes and shapes with masses in the range 3.3−17.5 mg and stored in an inert glovebox. A value for the samples surface area before oxidation was evaluated by measuring the 3D sample dimensions from a SE image, approximating the third dimension as this was taken on a 2D image. The approximated samples height was considered to be even on all sides as this measurement could not be performed on each sample corner, the evaluated surface area was then divided by the sample mass and the values found were in the range of 1.6−9.7 cm^2/g. The insertion of the sample in the HT-ESEM was performed in air after removal of the UC fragment from the glovebox. The oxidation experiments were performed at the Institut de Chimie Séparative de Marcoule (ICSM) in Marcoule, France, in a HT-ESEM (FEI Quanta 200 FEG ESEM) equipped with a hot stage under an atmosphere of oxygen between 10 and 100 Pa oxygen. Samples were heated to the desired temperature, from 723 to 848 K, under vacuum, and only after the required temperature was reached and stabilised, was the oxygen flux introduced into the chamber. A sample corner region, to study flat surfaces, edges and corners all at once, was continuously monitored for the entire length of the experiment and pictures were recorded every 3 or 5 s as soon as oxygen was inserted in the chamber and by default every 15 s after. All images were recorded with the same field of view, corresponding to an area of 908 × 836 μm^2. The general procedure and details of the HT-ESEM platform may be found in Refs. [30−32]. Image analysis, using the Fiji ImageJ [33] software, was used to monitor surface changes during isothermal heat treatments. Expansion of the sample surface and crack propagation due to the oxidation process was monitored by choosing specific features that identify a portion of the surface (the area highlighted in yellow in Fig. 1a and b) and by manually tracking their change in position over time. The same area used to measure the dilatometric expansion of the sample was used to analyse crack coverage (Fig. 1b). Cracks were highlighted in the figure, by choosing a threshold level in the image values contrast (in this case threshold = 10 out of 255 where 0 is black and 255 is white) allowing the dark regions lying below the threshold, to be identified as cracks. The result of the analysis is a two-dimensional value of the area covered by the cracks on the selected region. Data were then normalised to the value measured at time t = 0 which represents the moment when oxygen was inserted in the chamber, so that values are expressed in %. The initial value was subtracted from the following measurements so that the increment of sample expansion and crack propagation is tracked from an initial zero value and therefore comparison between different experiments is possible. A process called skeletonization was applied in order to evaluate the crack network. This involve a binary thinning process which is used to find the centrelines, or skeletons, of objects [34]. By using the plugins Skeletonize (2D/3D) and Analyse Skeleton (2D/3D) [35] available in ImageJ it is possible to quantify crack length and crack network by counting crack junctions (Fig. 1c). Cracks branching were evaluated with the number of junctions provided through the Analyse Skeleton technique. Sample overall expansion was evaluated with Fiji ImageJ by tracking sample borders and measuring this area before and after oxidation (Fig. 2a and b).