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Innovative preparation route for uranium carbide using citric acid as a carbon source

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ABSTRACT

The preparation of uranium carbide (UC) by carbothermal reduction and its sintering into dense pellets by conventional means require high temperatures for long periods. We have developed a preparation route yielding fine UC powder with significantly increased sinterability. At first, a mixture of nanocrystalline UO_2 embedded in amorphous carbon (nano-UO_2/C) was obtained by thermal decomposition of a gel containing solubilised uranyl nitrate and citric acid. Later, the nano-UO_2/C powder was treated in a conventional furnace or in a modified spark plasma sintering facility at elevated temperatures ($\geq$ 1200 °C) in order to obtain uranium carbide powder. The effects of initial composition, temperature, gas/vacuum atmosphere and the overall reaction kinetics are reported.

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1. Introduction

Uranium and mixed uranium-plutonium carbides are considered as fuels for fast breeder reactors. Recently, comprehensive reviews of the use of carbide fuels [1] and their thermophysical properties [2] have been published.

Typically, the preparation of U(Pu)C involves UO_2 (PuO_2) powder mixing and blending with graphite or carbon black followed by carbothermal reduction (CTR, Eqs. ((1), 2)) at temperatures above 1500 °C for several hours [2,3]:

$$UO_2+4C \rightarrow UC_2+2CO \quad (1)$$

$$UO_2+3UC_2 \rightarrow 4UC+2CO \quad (2)$$

For example, Suzuki et al. [4] used a UO_2, PuO_2 and graphite powder mixture (molar ratio of $C/(UO_2+PuO_2)=2.975$) that was ball-milled for 48 h. The CTR proceeded at 1500 °C for 4 h. The results showed that all the powder contained a minor $UPuO_{2-x}$ phase, whatever the atmosphere (0.2, 10^{-3} Pa or He) employed. Moreover, the powder had to be ball-milled again before pressing and sintering. Ganguly et al. [5] ball-milled UO_2, PuO_2 and a graphite mixture for 12 h, compacted at 105 MPa and performed CTR at 1475 °C for 4 h at 1 kPa. The powder contained 10–15 wt% U (Pu)$_2C_3$ and up to 0.45 wt% oxygen. Duguay and Pelloquin [6] used a similar procedure: blending, milling, pressing and CTR at 1500–1750 °C for 15 h under vacuum, with a oxide/carbon ratio of 3.09. Vaudez et al. [7] used the same process, while setting the CTR conditions to 1550 °C for 15 h.

All the above investigations can be considered as "conventional" carbide preparation routes, which use an oxide/graphite blend as a starting material. Recently, a big step has been taken in the preparation of non-nuclear carbides. Organic species are used as a source of fine carbon with high surface area consequently leading to milder conditions needed for the CTR. For example, Matović et al. [8], Yan et al. [9] and Lu et al. [10] reported the synthesis of HfC using citric acid as a carbon source. Similarly, citric acid was used for the preparation of VC [11], B_4C [12] or WC [13]. Apart from citric acid other organic compounds may be used as a carbon source, for example chitosan [14], ascorbic acid [15], phenolic resin [16,17] or divinylbenzene [18].

In this work, we describe a preparation of uranium carbide derived from a solution of uranyl nitrate and citric acid. Uranyl cation forms a 1:1 complex $[UO_2(cit)]^-$ with the citrate at pH $\leq$ 1, while at higher pH the molecules start to form a dimer $[(UO_2)_2(cit)_2]^{2-}$ bridged by the alcohol group of the citric acid [19,20]. Complexation of the uranyl ion assures a perfect homogenous distribution of the carbon and the metal source. This solution is decomposed by increasing the temperature to 1000 °C in Ar to form nanocomposite UO_2/C. Suzuki et al. [21] performed a

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kinetic study on CTR and identified the most limiting factors as the oxygen diffusion in UO_2 particles at the reaction interphase or the diffusion of CO gas through a compact layer. This can be overcome by nanocomposite UO_2/C due to the high interface area and interconnected porosities after citrate decomposition. The nanocomposite is then treated at elevated temperatures ($\geq$ 1200 °C) in a spark plasma sintering (SPS) apparatus devoted to radiotoxic materials [22], which was modified for CTR purposes similarly as in Feng et al. [23].

2. Experimental part

2.1. Materials and preparation

The preparation route can be divided into several steps as presented in the flowchart of Fig. 1:

(1) Uranyl nitrate and citric acid (Alfa Aesar, 99%) solutions were mixed in desired molar ratios.

(2) The solution was treated with the following decomposition program under Ar atmosphere – heating at 50 °C/h to 200 °C with no dwell time; from 200 to 1000 °C at 200 °C/h and a 1 h dwell; cooling at 200 °C/h to room temperature. The resulting powder was crushed and homogenized in a mortar, and was denoted as "nanocrystalline UO_2/C". Two options may follow, either CTR in a conventional furnace (3A) or in the modified spark plasma sintering facility (3B).

(3A) Nanocrystalline UO_2/C powder was introduced into a conventional metallic furnace at 1600 °C under argon flow with a 1 h dwell (heating and cooling ramps at 200 °C/h), where the CTR took place.

(3B) Nanocrystalline UO_2/C powder was hand-pressed into a modified SPS die and the CTR was conducted under vacuum in the modified SPS (described in the following subsection 2.2.).

From the step (2), powders manipulations were done in glove boxes designed for radioactive materials handling under inert atmosphere (nitrogen or argon). The water content in the glove boxes atmosphere is generally less than 10 ppm, but O_2 content can rise up to 0.7%.

2.2. Spark plasma sintering device adapted for CTR

Spark plasma sintering in its normal configuration belongs to the group of electric field assisted sintering techniques. Normally, it is used to simultaneously press and sinter compacts using graphite dies and punches. Here, the classical set-up was modified so that it can be used as pressureless furnace as shown in Feng et al. [23]. Fast heating and cooling ramps that prevent grain growth and necking are the advantages of this special use of the SPS, thus the resulting powder has increased sinterability. The SPS facility (FCT Systeme GmbH, Rauenstein, Germany) is described in [22]. The graphite set-up used for CTR is presented in Fig. 2. The main innovation is the annular punch fitted with a horizontal orifice to permit the fast CO release thanks to vacuum in SPS chamber. Use of the conventional SPS arrangement resulted in a quasi-sealed containment, which did not permit CO release. In this case there is no carbothermal reaction at all, confirming Suzuki's hypothesis [21]. The typical heating cycle was – heating ramp at 200°C/min to the desired temperature (1200, 1400, 1600°C), desired dwell (0, 5, 10, 20, 30min) with a cooling ramp of 200°C/min to room temperature.

2.3. Analytical techniques

2.3.1. Powder X-ray diffraction

The structure of the products was determined at room temperature by X-ray diffraction (XRD) using a Bruker D8 X-ray diffractometer mounted in a Bragg–Brentano configuration with a curved Ge monochromator (1, 1, 1) and a ceramic copper tube (40 kV, 40 mA) equipped with a LinxEye position sensitive detector. For the measurement, the powder was deposited on a silicon wafer to minimize the background and dispersed on the surface with 2 or 3 drops of isopropanol. Structural analyses were performed by the Rietveld method with the JANA 2006 software [24].

2.3.2. ^{13}C nuclear magnetic resonance

^{13}C Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) experiments were performed at 100 MHz on a Bruker 9.4T dedicated for the study of radioactive materials [25]. A 4 mm probe was used and the sample spun at 10 kHz. A Hahn echo sequence was performed with 90° and 180° pulse lengths of 8.2 µs and 16.4 µs respectively with an echo delay of 1 rotor period. A recycle delay of 500 ms was used. The sample was referenced to tetramethysilane (0 ppm). The spectrum was fitted using the dmfit software [26].

2.3.3. Electron microscopy

Crystallite size and morphology of the samples were studied using a transmission electron microscope (TEM) TecnaiG2 (FEI™) 200 kV equipped with a field emission gun, modified during its construction to enable the examination of radioactive samples. The TecnaiG2 TEM is equipped with a Gatan™ Tridiem GIF camera, an energy-dispersive X-ray (EDX) analysis system, and a high-angle annular dark-field (HAADF) detector for the scanning transmission electron microscope (STEM) imaging. The samples for the TEM investigations were prepared by crushing tiny fragments of

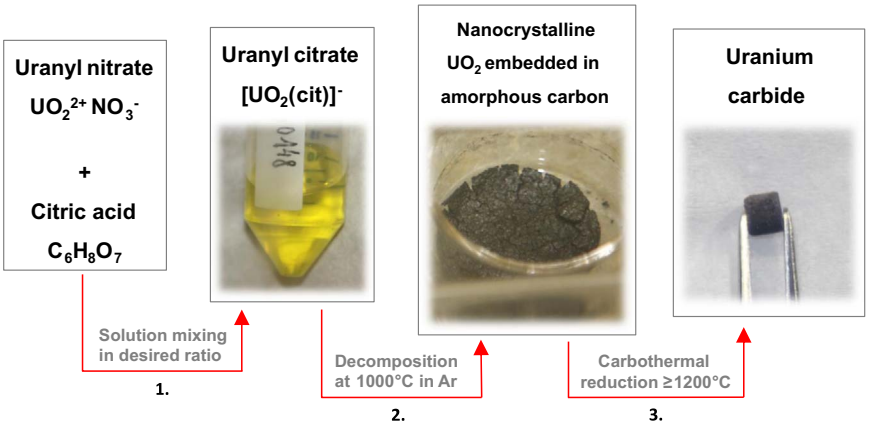

Fig. 1. Flowchart representing the preparation steps for uranium carbide starting from uranyl nitrate and citric acid solutions.

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