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Short communication

Spark plasma sintering of fine uranium carbide powder

D. Salvato[a,b], J.-F. Vigier[a,*], M. Cologna[a], L. Luzzi[b], J. Somers[a], V. Tyrpekl[a,1]

[a] European Commission, Joint Research Centre (JRC), Postfach 2340, 76125 Karlsruhe, Germany
[b] Politecnico di Milano, Department of Energy, CeSNEF (Enrico Fermi Center for Nuclear Studies), via La Masa 34, 20156 Milano, Italy

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ABSTRACT

Results of uranium carbide sintering using a spark plasma sintering facility are presented here. The initial uranium carbide powder is produced from the thermal decomposition of a citric acid and uranium nitrate mixture. The study shows that spark plasma sintering is a very efficient compaction tool for uranium carbide material. Both onset of sintering and final density are strongly correlated to the UC synthesis conditions.

1. Introduction

Uranium carbide (UC) or uranium-plutonium carbide are potential fuels for fast reactors [1–3]. One of their main drawbacks is the difficult preparation and sintering. Typically, carbide powder is obtained through carbothermal reduction (CTR, reaction of metal oxides with graphite or carbon black) at temperatures above 1400 °C for several hours [3]. In Suzuki's study [4] carbide pellets with densities over 90% of theoretical density (TD) require 47 h of ball milling before compaction (300 MPa) and sintering (1700 °C for 3 h in flowing Ar). Furthermore, addition of Ni can increase the density up to 97%. In another study $U_{0.45}Pu_{0.55}C$ pellets were prepared from a ball-milled powder (4 h), which was pre-compacted, granulated and compacted (375 MPa). The sintering (1627 °C for 10 h) yielded pellets with 86% of TD [5]. Recently, a study of $U_{0.8}Pu_{0.2}C$ pellet fabrication was published [6] including the effect of lubrication (zinc stearate, calcium stearate, azodicarbonamide up to 3.0 wt%). Green pellets were obtained at 500 MPa and sintered at 1750 °C for 5 h under Ar-H_2. Increasing the lubricant amount led to decrease sintered density (acting as a pore former) from about 91% of TD for 0 wt% of lubricant to 78% for 2 wt%.

Herein, we present the densification of UC powder using a spark plasma sintering (SPS) device, which was implemented in a glovebox operating under an Ar purified atmosphere [7]. It has been already applied for the preparation of fine grained UO_2 pellets [8], UO_2/CsI composite [9] or dense ThO_2 pellets [10]. Recently, the SPS technique was used to prepare dense uranium nitride pellets [11–13]. To our knowledge, results obtained on uranium carbide sintered with SPS have never been published. Nevertheless, Tougait et al. have presented preliminary results on UC sintering using SPS facility at Actinide 2013 conference [14]. The technique was applied on UC produced with conventional CTR at 1700 °C and shows a sintering onset in SPS facility at the same temperature. In our study, uranium carbide sintering using SPS at 1700 °C with a 10 min dwell time is presented. The study focus especially on the effect of the initial UC synthesis conditions on the sintering behavior.

2. Experimental part

2.1. Powder synthesis

It was shown in a preliminary study that combining:

- the use of a highly reactive precursor coming from thermal decomposition of uranyl nitrate and citric acid and
- the use of a modified SPS facility to act as a furnace to perform CTR under vacuum with a fast temperature ramp

is an efficient way to produce uranium carbide in very mild conditions [15,16]. This procedure gave fine UC powder with few percent of UO_2 as second phase. Powders obtained this way at 1200, 1400 and 1600 °C

* Corresponding author.
E-mail address: jean-francois.vigier@ec.europa.eu (J.-F. Vigier).
[1] Current address: Belgian Nuclear Research Centre SCK·CEN, Boeretang 200, 2400 Mol, Belgium.

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Table 1
Parameters of the initial powder and pellets after sintering.

Initial UC powder				Onset of sintering [°C]	After sintering			
Synthesis temperature [°C]	Synthesis dwell time [min]	UC [wt%]	UO_2 [wt%]		Density [% of TD]	UC [wt%]	UO_2 [wt%]	UC_2 [wt%]
1200	10	97	3	~1175	95	85	7	8
1400	10	97	3	~1410	88	90	5	5
1600	10	95	5	~1700	68	83	4	13

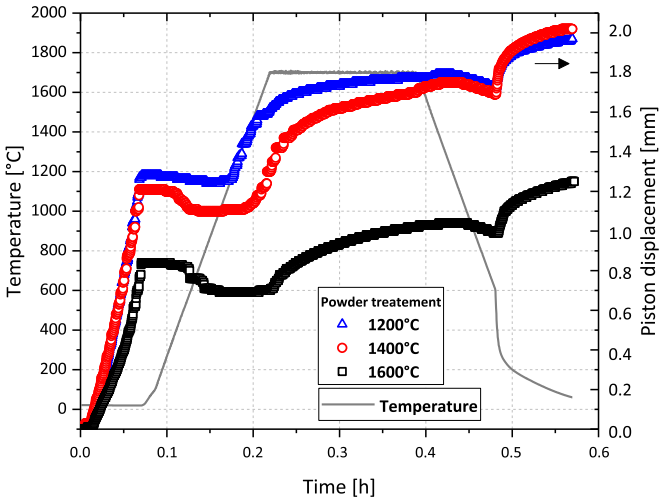

Fig. 1. Spark plasma sintering plots for powders obtained at 1200, 1400 and 1600 °C. The applied pressure is linearly increased to the nominal value (100 MPa) at room temperature before heating, and is linearly decreased to 0 MPa during the cooling step from 1700 °C to 600 °C. The increase of piston displacement during the heating step and the dwell time are characteristic of the powder sintering. Other displacements are consequences of temperature and/or applied pressure changes.

with a 10 min dwell time were selected for this sintering study. They were used as received, neither milled nor sieved.

2.2. Spark plasma sintering

A small scale SPS facility (FCT Systeme GmbH) integrated in a glovebox [7] was used for the compaction of the powders. Graphite dies and punches (6 mm inner diameter) were used. About 0.3 g of starting powder was loaded in the graphite die, prepressed at 0.5 kN and sintered to a disk of about 1 mm in height. The SPS procedure consisted of 50/5 ms current/pause intervals, 100 MPa applied pressure, 200 °C/min heating-cooling rate and 1700 °C final temperature with a 10 min dwell time, under vacuum.

2.3. Analytical techniques

The XRD powder patterns were collected on a Rigaku MiniFlex 600 diffractometer with a θ–2θ configuration using Cu $K_{\alpha 1\text{-}\alpha 2}$ radiation. The patterns were treated using the JANA 2006 software [17]. Scanning electron microscopy was performed on a Philips XL 40 using a tungsten filament (200 V–30 keV). The density was obtained by mass/volume ratio. The volume was measured using a X-ray Tomography (Nikon XT H 225 Industrial CT scanning device, equipped with a 225 kV microfocus X-ray source with a 3 µm focal spot size).

3. Results and discussion

Important information about the initial, final composition and sintering behavior of the powders is summarized in Table 1. Sintering of the powders obtained at 1200, 1400 and 1600 °C starts at 1175, 1410 and 1700 °C respectively (see Fig. 1). The onset of sintering depends significantly on the powder preparation temperature, which affects the initial grain size and degree of necking (Fig. 2). The highest density (95% of TD) was achieved for the powder obtained at 1200 °C. Such density is obtainable by conventional means only after hours of sintering or use of sintering additives.

Similarly as for uranium nitride [12], the SPS provides an efficient compaction tool, when temperatures above 1600 °C and pressures about 100 MPa are applied. The morphology of the initial powders and fresh fracture surfaces of the sintered pellets by SEM are shown in Fig. 2. The SEM pictures show that lowering initial CTR temperature leads to a more finely divided material and then lower porosity after sintering. The variation of internal porosity observed in the sintered pellets as a function of the powder preparation temperature is in good agreement with the density measurements. For pellets prepared from UC powder obtained at 1200 °C the pore size is ~100 nm in diameter and increases to ~1 µm for the powder synthesized at 1600 °C. These observations confirm that the UC powders produced under mild conditions have increased sinterability.

During the sintering phase, the composition calculated from powder XRD changed slightly (Fig. 3). Initially, the amount of secondary phases in UC is very low (up to 5 wt% UO_2 and no UC_2 phase). After sintering, at least 5 wt% of UC_2 phase was observed together with a small rise of the UO_2 proportion. The appearance of UC_2 is not fully understood, but may be explained by the presence of carbon from two possible sources: (i) the SPS compaction was done in a graphite punch/die system, thus, it is a source of possible reactant; (ii) the initial powder contained some unreacted amorphous carbon or uranium oxy-carbide that was not revealed by powder XRD. The increase of the UO_2 amount could be explained by precipitation of oxygen impurities or decomposition of oxy-carbide. Another possible moment of oxidation of the material was during pulverization before measurements, which was, however, done in a glovebox with an inert atmosphere (O_2≈0.6%, H_2O≈7 ppm).

4. Conclusion

We present a SPS study of powders that were prepared from a solution of uranyl nitrate and citric acid as a carbon source. Such powders have increased sinterability compared to powders obtained after carbothermal reduction in a conventional route. Indeed, a SPS cycle of 1700 °C with a 10 min dwell time and 100 MPa of applied pressure is sufficient to obtain pellets with 95% of theoretical density using initial powder generated at 1200 °C. Therefore, this study showed that spark plasma sintering is a very efficient compaction tool applicable to uranium carbide powders, especially if this material is produced under mild conditions.

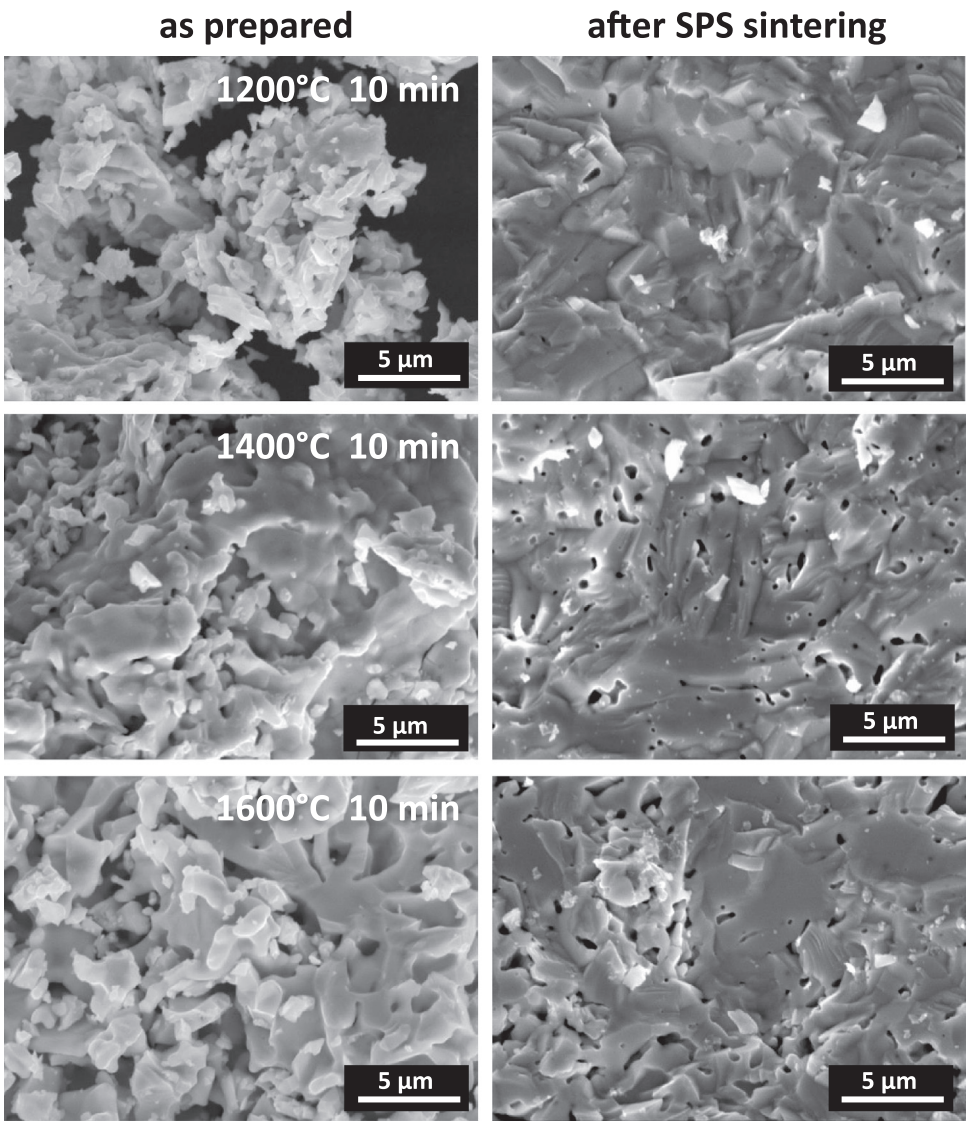

Fig. 2. Morphology of the initial UC powders (left) and fresh fracture surfaces of the pellets generated by SPS (right) by scanning electron microscopy.

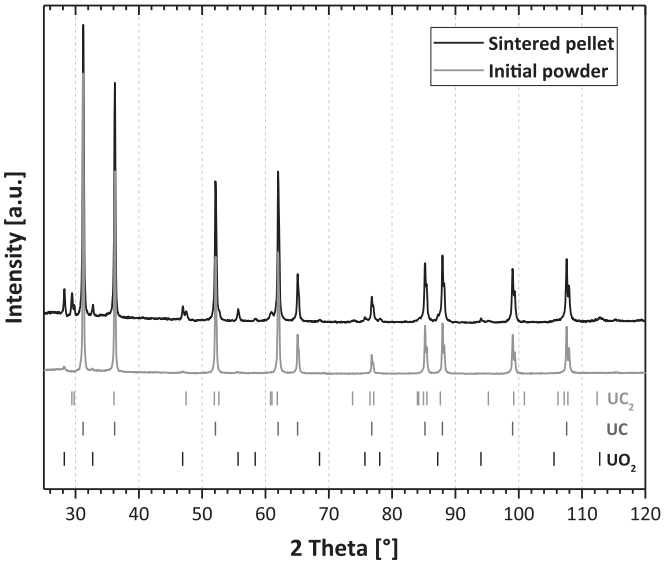

Fig. 3. Powder X-ray diffraction of the initial UC powder (1200 °C) and pellet; diffraction lines are attributed to UO_2 [18], UC [19] and UC_2 [20] phases.

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