

Grain growth in uranium nitride prepared by spark plasma sintering

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ABSTRACT

Uranium mononitride (UN) has long been considered a potential high density, high performance fuel candidate for light water reactor (LWR) and fast reactor (FR) applications. However, deployability of this fuel has been limited by the notable resistance to sintering and subsequent difficulty in producing a desirable microstructure, the high costs associated with ¹⁵N enrichment, as well as the known proclivity to oxidation and interaction with steam. In this study, the stimulation of grain growth in UN pellets sintered using SPS has been investigated. The results reveal that by using SPS and controlling temperature, time, and holding pressure, grain growth can be stimulated and controlled to produce a material featuring both a desired porosity and grain size, at least within the range of interest for nuclear fuel candidates. Grain sizes up to 31 μm were obtained using temperatures of 1650 °C and hold times of 15 min. Evaluation by EBSD reveal grain rotation and coalescence as the dominant mechanism in grain growth, which is suppressed by the application of higher external pressure. Moreover, complete closure of the porosity of the material was observed at relative densities of 96% TD, resulting in a material with sufficient porosity to accommodate LWR burnup. These results indicate that a method exists for the economic fabrication of an ¹⁵N-bearing uranium mononitride fuel with favorable microstructural characteristics compatible with use in a light water-cooled nuclear reactor.

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1. Introduction

Uranium mononitride (UN) has been a widely studied nuclear fuel candidate owing to its high density and high thermal conductivity, both of which are superior to the reference uranium dioxide fuel standard in most reactors today, while its high melting point is several hundred degrees higher than competing accident tolerant fuels such as U₃Si₂. Together these properties represent an overall improvement in the economy of operation as well as safety. Intense research was conducted into the material in the 1960's and 1970's but, for various reasons - notably the extreme difficulty in sintering, the cost penalty associated with the enrichment of ¹⁵N, and undesirable reactions with air and steam - interest in light water applications waned. Previous studies have required extremely high temperatures - in excess of 2300 °C - to achieve relative densities near and above 95% TD using conventional sintering techniques [1]. These high temperatures - known to carry a high cost penalty - also led to a rapid growth in grain size - in

excess of 40 μm - and an undesirable increase in the oxygen content of the material during sintering [1]. [2] [3] The tendency of UN to decompose at high temperatures has also necessitated the use of an N₂ cover gas, the quantity of which being large enough to prohibit the use of an ¹⁵N cycle, leading to the well-founded conclusion that high density, high purity U¹⁵N possessing a favorable microstructure would not easily or economically be provided via a conventional sintering route. Parasitic thermal neutron capture in ¹⁴N and the subsequent production of moderately long-lived ¹⁴C considerably degrade the neutronic performance and back-end safety of U¹⁴N fuel, which effectively ended consideration of the fuel for use in a thermal neutron spectrum in favor of fast reactor concepts where ¹⁴N and moderate porosity (>10%) do not limit performance [4].

Recently, studies have shown that the use of SPS sintering can permit very high densities - up to 99.9% - to be obtained at 1650 °C and using hold times of around 3 min, with closure of porosity occurring at relative densities greater than 97.5% TD [5]. Studies on the oxidation behavior of uranium nitride pellets have shown that the presence of open porosity substantially increases the rate of oxidation of the material and therefore must be eliminated for the fuel to be used in an oxidizing environment [6]. [7] However, a

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further requirement of LWR fuel is that sufficient residual porosity must be present in order to accommodate fission products and reduce swelling at higher burn ups, which, while highly dependent on operating temperature, has been observed to be similar to uranium dioxide under irradiation at LWR conditions [8]. [9] [10] Additionally, a variety of important fuel performance behaviors can be coupled with microstructure, namely creep, yield strength, thermal conductivity, fission gas retention, and fuel swelling, and thus the ability to control the fuel microstructure with respect to all of the aforementioned characteristics is highly motivated [11]. Some studies have reported a limited ability to stimulate very modest grain growth using extended hold times. Ge, for example, showed that by increasing hold times from 1 min to 10 min, the grain size of UO₂ could be increased from 3.8 to 6.6 μm without substantially increasing the relative density of the final product [12]. Makino, meanwhile, demonstrated the importance of the applied pressure in suppressing grain growth in ceramic alumina, even if other studies on metals and ceramics have shown the opposite or no effect of pressure [13]. [14] [15] [16] [17] [18] An objective of this study, then, was to investigate the influence of SPS processing parameters, particularly applied pressure, on grain growth in UN and enable an earlier onset of pore closure such that the final product would exhibit a relative porosity of 96% TD, typical of LWR applications, using a nitrogen-free sintering method [19].

2. Methodology

2.1. Sample synthesis and preparation

High purity uranium nitride powder was fabricated at KTH using a hydriding-nitriding method described previously, and which has been observed to produce powders with a median particle size of 4.3 μm [20] These powders were then characterized using XRD, SEM, XRF, and elemental analysis of oxygen and nitrogen, using a LECO TC436DR, and carbon, using a LECO series CS440. For powders used in this study, oxygen content was less than 800 ppm, carbon less than 500 ppm, and nitrogen was determined to be 5.4 %wt. XRD (shown in Fig. 1 revealed a single-phase cubic structure corresponding to a lattice parameter of 4.889 Å, consistent with previous reports of uranium nitride with low carbon and oxygen impurities [21]. Analysis of other impurities found trace amounts of silicon, niobium, and aluminum, representing <500 ppm, <25 ppm

and <10 ppm, respectively, as measured by XRF and ICP-OES. Following characterization, the as-synthesized powders were sintered using a modified Dr. Sinter SPS machine, contained within a glovebox under an inert, argon atmosphere. A 12 mm inner-diameter graphite die was used, along with thin graphite paper to protect the sample and die from interaction during sintering. These were provided by the National SPS Facility at Department of Materials and Environmental Chemistry at Stockholm University. All runs were conducted in low vacuum (≈ 10 Pa) and using constant heating and cooling rates of 100 °C/min. After sintering, this bonded graphite paper was removed from the samples via grinding.

After grinding, samples of each pellet were taken for the elemental analysis of oxygen, nitrogen, and carbon, which did not reveal an appreciable change from the powder state. XRD of the pellet surface was also performed and is shown in Fig. 1, indicating a lattice parameter of 4.89 Å. The density of each pellet was measured using a modified Archimedeian method, with chloroform as the immersion medium [5]. Chloroform has the advantage of being chemically non-reactive with UN as well as being highly penetrating, which offers more accurate estimations of open porosity compared with water. In these experiments, the dry mass of each pellet was measured, followed by the submersion of the pellet into the chloroform and the measurement of the pellet buoyant force. The initial immersed mass was used for the determination of the pellet total volume. Following this the pellet – submerged in chloroform – was subjected to a vacuum just above the vapor pressure of chloroform, allowing for a very complete evacuation of air from the open pores of the pellet. This vacuum was held until no additional air bubbles could be discerned. After vacuum the pellet was again suspended and its buoyant force recorded, without removal from the chloroform medium, which ensures no additional air is reintroduced into the pores.

2.2. Microscopy and electron back-scatter detection

Following bulk physical and chemical analysis, axial and transversal sections of each sample were sectioned off, whereafter chemical etching and optical microscopy was performed in order to assess the grain size of the material in accordance with ASTM E112 [22]. [23].

For select specimens, radial cross sections were taken for analysis using high resolution field emission gun scanning electron microscopy (FEG SEM) and electron back scatter detection (EBSD), model LEO 1530-FESEM-EBSD.

3. Results and discussion

3.1. Grain growth

Analysis of the as-synthesized powders by SEM (shown in Fig. 2) reveal a highly flaky, lightly agglomerated morphology with average particle sizes not exceeding 5 μm, consistent with literature observations of uranium powders derived from the hydriding process [24]. [25].

Initial studies focused on determining the effects of sintering time, temperature, and pressure on the stimulation of grain growth. Pellets were sintered at temperatures of 1450 °C and 1650 °C, using pressures between 45 MPa and 135 MPa, for times between 2 and 15 min. These parameters are presented in Table 1 and shown in Fig. 3.

From this series it is possible to see that the parameters affecting final grain size are complex: involving sintering temperature, sintering pressure, holding time, but also porosity, which is consistent with microstructure coarsening occurring during the end of the

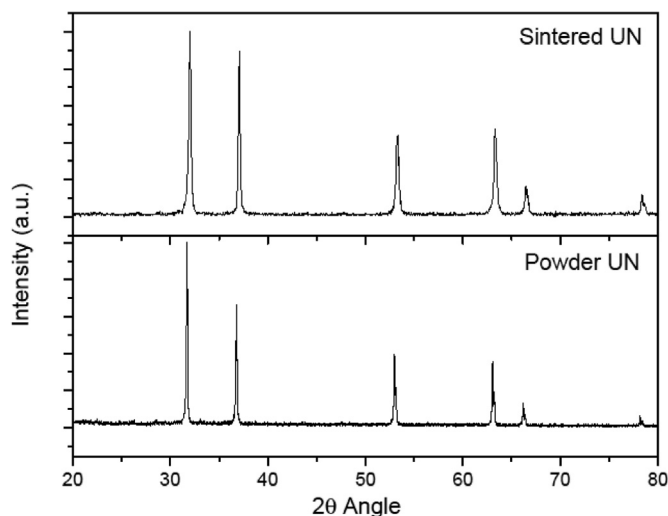


Fig. 1. X-ray diffraction patterns of UN in as-synthesized powder (bottom) and sintered (top).

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