Journal of Nuclear Materials 473 (2016) 13–17

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Spark plasma sintering and porosity studies of uranium nitride

Kyle D. Johnson*, Janne Wallenius, Mikael Jolkkonen, Antoine Claisse

Albanova Universitets Centrum, Kungliga Tekniska Högskolan, Stockholm, Sweden

HIGHLIGHTS

- UN pellets are fabricated over a wide array of densities using the SPS method.
- The sintereing parameters necessary to produce pellets over a wide array of density space are charted.
- Pellets of extremely high density (99.9% of TD, absolute density of 14.25 g/cm^3) are fabricated.
- Full-closure of the porosity in this material is obtained at around 2.5% of total porosity.

ARTICLE INFO

Article history:
Received 4 September 2015
Received in revised form
15 January 2016
Accepted 20 January 2016
Available online 21 February 2016

Keywords:
Generation IV
Nuclear fuel
Uranium nitride
SPS
Sintering
Pore closure

ABSTRACT

In this study, a number of samples of UN sintered by the SPS method have been fabricated, and highly pure samples ranging in density from 68% to 99.8%TD – corresponding to an absolute density of 14.25 g/cm^3 out of a theoretical density of 14.28 g/cm^3 – have been fabricated. By careful adjustment of the sintering parameters of temperature and applied pressure, the production of pellets of specific porosity may now be achieved between these ranges. The pore closure behaviour of the material has also been documented and compared to previous studies of similar materials, which demonstrates that full pore closure using these methods occurs near 97.5% of relative density.

1. Introduction

Interest in actinide nitrides as fuels in transmutation and fast reactor schemes has propelled interest in their research throughout the world. The use of UN in fast reactors has been studied in Sweden and Russia, amongst others. High thermal-conductivity, high metal density, and good chemical tolerance with steel cladding make nitrides highly attractive for lead-cooled systems such as the LMFBR and MYRRHA, as well as various space reactor systems [1,2]. The sintering behaviours of nitrides have been studied extensively using conventional, pressure-less sintering, as well as hot pressing, in the 1960's and 1970's, but advances in powder metallurgical methods have opened up new avenues for the fabrication of uranium nitride pellets [3,4].

Alternative sintering schemes such as spark plasma sintering (SPS), also known as field-assisted sintering (FAST), have also been investigated in recent years [5]. The use of SPS, in particular, provides a unique glimpse into the sintering process of the material, as online monitoring yields valuable information. In Japan, studies have been conducted into the effects of the SPS technique on the physical properties of UN [5], specifically comparing them with samples produced via more conventional sintering methods. This paper seeks to build on this work, and provide an insight into the SPS parameters which can be used to meet requirements for UN as a nuclear fuel, namely the influence of SPS parameters on the fuel density and porosity.

Aside from increasing the understanding of the influence of SPS parameters on the sintering behaviour of UN, there is interest in itself in observing the relationship between open and closed porosity of this material during sintering. As discussed by Claisse [6], the nature of porosity within the fuel can have a substantial impact on the behaviour of the fuel, particularly with respect to fission gas release and swelling, during irradiation conditions. As such it is of particular interest to understand the process of pore

* Corresponding author.
E-mail address: kylej@kth.se (K.D. Johnson).

http://dx.doi.org/10.1016/j.jnucmat.2016.01.037
0022-3115/

closure during sintering in this material prior to any possible irradiation testing.

2. Experimental

High purity uranium nitride powder was fabricated at KTH using a hydriding-nitriding method described previously, which has been observed to produce powders with a median particle size of 4.3 μm [7,8]. These powders were then characterised using XRD and XRF, and elemental analysis was performed. Following characterisation, the as-synthesized powders were sintered using a modified Dr. Sinter SPS machine, contained within a glovebox under an inert, argon atmosphere. For sintering, a 12 mm inner-diameter graphite die was used, with thin graphite paper used 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. After sintering, this bonded graphite paper was removed from the samples via grinding.

After grinding, pellets were cracked and samples were taken for the elemental analysis of oxygen, nitrogen, and carbon. For the measurement of oxygen and nitrogen, a LECO TC436DR was used for simultaneous determination, while carbon measurement was performed using a LECO series CS440. These instruments report the absolute weight fraction of the respective elements based upon the weight of the entire sample analysed. XRF was also used to identify the presence of heavier elements, of which silicon was the only detected element. In this case it is worth mentioning that the silicon fraction reported is the weight fraction relative only to uranium, as the light elements – oxygen, carbon, and nitrogen – are not detected.

The density of each pellet was measured using a modified Archimedean method, also referred to hydrometry, with chloroform as the medium. 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, m_{dry}, was measured, followed by the submersion of the pellet into the chloroform and the measurement of the pellet buoyant force. The initial immersed mass, $m_{immersed}$, is used for the determination of the pellet total volume. Following this the pellet – submerged in chloroform – was subjected to a vacuum just above the vapour 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, m_{vacuum}, recorded, without removal from the chloroform medium, which ensures no additional air is reintroduced into the pores. Equations (1)–(3) were used for the measurement of density performed in these experiments, where ρ and ϕ represent density and porosity, respectively. These terms will hereafter be expressed in terms of volume percent rather than fractions.

$$\rho_{pellet} = \rho_{chloroform}\frac{m_{dry}}{m_{dry} - m_{immersed}} \quad (1)$$

$$\phi_{open} = \frac{m_{vacuum} - m_{immersed}}{m_{dry} - m_{immersed}} \quad (2)$$

$$\phi_{closed} = \frac{\rho_{pellet}}{\rho_{theoretical}} - \phi_{open} \quad (3)$$

It bears mentioning that while this technique offers high precision for samples with large mass, i.e. greater than 3 g, and low open porosity, the ingress of chloroform for highly open porous samples occurs quite rapidly, and produces a non-negligible error for samples of this type.

3. Results

3.1. Evaluation of impurities

While the measurement of density may seem straightforward, the calculation of theoretical density is certainly less so, and requires careful analysis of trace elements and impurities in order to accurately quantify which phases are present in the material such that total porosity may be reliably determined. For this purpose, oxide was assumed to exist in the UO_2 phase, while carbon was assumed to be fully dissolved in a U(N,C) phase. Both assumptions were confirmed using XRD to analyse the lattice parameters of the material. Included in Fig. 1 are XRD spectra of the synthesized powder as well as a sintered pellet. The lattice constants in each case were evaluated using the Rietveld Method and the program MAUD [9].

Typical values for impurities are listed in Table 1, with oxygen, nitrogen, and carbon derived from inert fusion and combustion, respectively, while silicon was obtained using XRF, as described previously. Additionally, the volume fraction of each phase was calculated using the concentration of each constituent and the molar volume of its presumed phase.

Further investigations were conducted to determine the nature of silicon impurities noted to be present in the material by Malkki and shown in Fig. 2. In that study, the presence of silicon in sintered samples was identified in the grain boundaries of the material and treated as having formed a separate U_3Si_2 phase for the purpose of calculating the theoretical density of the material. Through the use of EBSD, XRF, and EDS techniques, this was instead found to not be the case, as the identified defects were determined to contain trace amounts of silicon, iron, and other metal impurities from the source material. In Fig. 2 and Table 2, various nodules and their corresponding quantification using EDS are presented and compared with a typical UN phase on a sintered, polished, but non-etched pellet.

Having rejected the formation of a U_3Si_2 phase, the preponderance of silicon was instead regarded as having dissolved into UN in the form of U(N,Si), which has been suggested to be stable up to

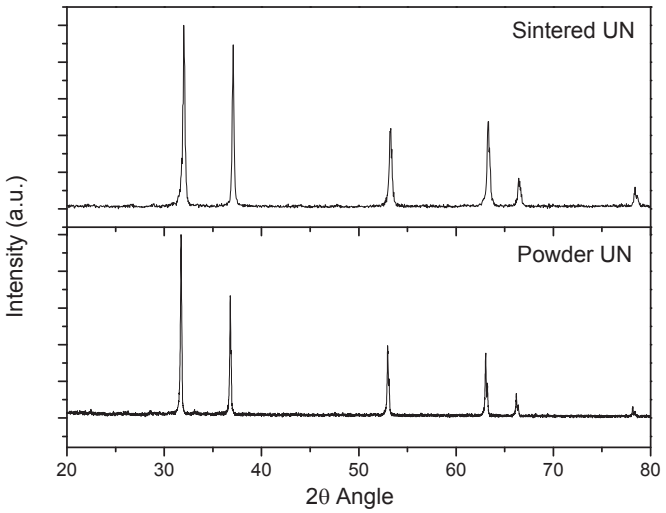

Fig. 1. XRD spectrum of sintered UN pellet, with an evaluated lattice parameter of 4.890, and (Bottom) XRD spectrum of manufactured UN powder, with an evaluated lattice parameter of 4.888, using MAUD.