



Letter to the Editor

Synthesis of uranium nitride by a mechanically induced gas–solid reaction

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ABSTRACT

A high energy, low-temperature, ball-milling route was used to directly produce uranium nitride. Pure uranium metal particles (~100 μm) were ball milled under a 420 kPa nitrogen atmosphere for 24 h at ambient temperature to yield phase pure U₂N₃ powder as confirmed by X-ray diffraction and energy dispersive spectroscopy. The median particle size was measured to be approximately 6 μm.

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1. Introduction

Uranium mononitride (UN) has been considered as an advanced nuclear fuel for a few, developmental fast-spectrum nuclear reactors since the 1970s [1]. Such fast reactors include: the gas-cooled fast reactor (GFR), the lead-cooled fast reactor (LFR), and the sodium-cooled fast reactor (SFR). The nitride fuel forms are excellent candidates for these fast-spectrum reactor types due to high melting temperatures combined with greater actinide densities and greater thermal conductivities than the oxide fuel forms [2–4].

Many authors have studied various synthesis routes for economically producing large quantities of high purity nitride powders [1–13]. Much of this previous work has focused on optimizing the carbothermic reduction of uranium dioxide (UO₂) prior to nitriding to form UN. However, the carbothermic reduction synthesis route requires many steps and costly infrastructure. The many processing steps could potentially introduce impurities such as oxygen and carbon. Moreover, significant handling concerns arise due to the propensity for oxidation of these nitride powders. The costly infrastructure is due, in part, to the high temperatures required to complete the conversion of UO₂ and the equipment typically used (including refractory metal furnaces) requires large amounts of space. Directly synthesizing a nitride from the pure metal reduces the number of steps involved, thereby minimizing the time and risks associated with handling nitride powders. In

addition, separating uranium from spent nuclear fuels as a pure metal via electrochemical refining implies that the most economical synthesis techniques would utilize the pure metal, not the oxide, as the primary starting material.

Regarding methods employing the pure metal, it has been previously reported that pure uranium metal was used as the starting material for a direct nitridation route via hydriding as well as various aqueous routes [5,7]. Another synthesis technique that uses the pure metal as the starting material is the mechanically induced gas–solid reaction (ball-milling) method. This technique has been demonstrated for producing TiN, BN, ZrN, and Fe₃N from the respective metals in a nitrogen or ammonia milling atmosphere [14–19] and requires significantly less infrastructure when compared to the thermal synthesis routes. Recent work, associated with this study, has shown that lanthanides, such as dysprosium and cerium, can be directly nitrided to form DyN and CeN using such a ball-milling technique.

The work presented in this paper demonstrates a novel and economical ball-milling synthesis route for synthesizing high purity uranium nitride at room temperature. The success of this low-temperature, mechanical route for producing uranium nitride should have profound implications on the advanced fuel cycle because it potentially offers the advantages of a simple, inexpensive method for producing nitride fuels for use in fast-spectrum reactors.

2. Experimental procedure

A 99.78% pure depleted uranium ingot was obtained from the Idaho National Laboratories and used as the starting material for this work. Approximately five grams of uranium metal was filed from the

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ingot in an argon atmosphere glovebox with a carbon–steel metal file. The filings were collected and placed in a 250 mL chrome steel milling vessel with the milling media under an Argon atmosphere. The milling container contained 70 g of 5 mm diameter yttria stabilized zirconia (YTZ, TOSOH, Tokyo, Japan) milling media (Fig. 1(a)) providing an optimum metal filing to media mass ratio of 1:14. The milling vessel, seen in Fig. 1(b), was sealed prior to purging and charged with ultra-high purity (UHP) N₂ to approximately 420 kPa. The nitrogen gas was purified by passing it through copper turnings at 500 °C, which reduced the oxygen content to less than 0.1 ppb as measured by a Neutronics OA-1 oxygen analyzer (Exton, Pennsylvania, USA). The jar was fixed in a Retsch planetary ball mill (PM 100, Haan, Germany) and the uranium was milled for 24 h at 500 rpm with intermittent nitrogen purges and recharges every 2 h to replace the environment.

After milling, the powder was separated from the milling media in an inert atmosphere glovebox and prepared for X-ray diffraction (XRD) and particle size analysis. The XRD system used for this analysis did not have inert atmosphere capabilities. Therefore, the powder was temporarily protected from oxidation by loading it into a stainless steel powder holder and sealing with an x-ray transparent thin film. The XRD data was collected in air at room temperature using a Philips X'pert XRD with a Cu K α source ($\lambda = 0.15418$ nm) and a 4°/min scan rate in Bragg–Brentano geometry. The chemical composition of the powder was further analyzed in the scanning electron microscope (SEM) by energy dispersive spectroscopy (EDS). For particle size distribution data, the uranium nitride powder was dispersed in de-ionized water and analyzed with a Horiba LA-950 laser scattering particle size distribution analyzer. This was done using a refractive index of 2.2 + 0.1i. Where “i” denotes the imaginary component of the refractive index and accounts for irregularities (deviations from spherical) of the powders.

3. Results and discussion

On five different occasions, XRD results confirmed that ball-milling uranium metal at ambient temperature is capable of producing phase pure U₂N₃ (Fig. 2). Furthermore, EDS results indicate a very low oxygen concentration that measured below the detectable limits of the EDS system. Based on these results, the reaction of uranium metal with nitrogen at ambient temperature to form uranium nitride has proceeded to completion. It should be noted that if the temperature of the milling process were elevated, it is presumed that the reaction would occur more rapidly. However,

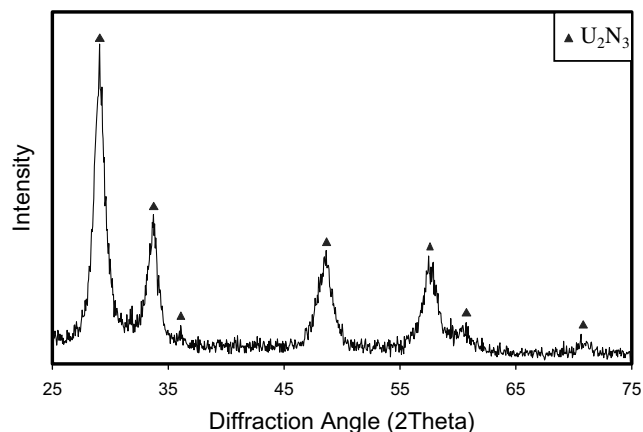


Fig. 2. X-ray diffraction spectrum of U₂N₃ powder produced by mechanically induced gas–solid reaction (ball-milling) method in a N₂ atmosphere at room temperature.

no work has been done to confirm this. Optical images of the pure metal particles and the resulting U₂N₃ particles were obtained by suspending the particles in an aqueous solution prior to imaging them with an inverted stage optical microscope. The pure metal particles were observed to have irregular and elongated shapes with approximate lengths of a few hundred microns (Fig. 3(a)). An optical micrograph showing the spherically shaped U₂N₃ powders resulting from the reaction ball-milling is shown in Fig. 3(b). Particle size analysis measured the median particle size of U₂N₃ to be 6.2 μ m with a particle size distribution from 1 to 45 μ m.

Future work in the Advanced Materials Laboratory at Boise State University includes reducing the sesqui-nitride to a mononitride, which according to the literature the decomposition of pure U₂N₃ above 1350 °C results in pure UN [2,11,12,20–22]. Also, future work entails the percentage of reaction completion by varying the time and atmosphere of the milling process.

4. Summary

A novel, low-temperature, mechanical approach for directly nitriding uranium metal has been demonstrated. U₂N₃ was successfully synthesized from pure uranium metal using a high energy ball-milling route at ambient temperature. This is a very simple process (therefore has a lower associated cost) and permits a direct nitridation synthesis route from metal produced by electrochemi-

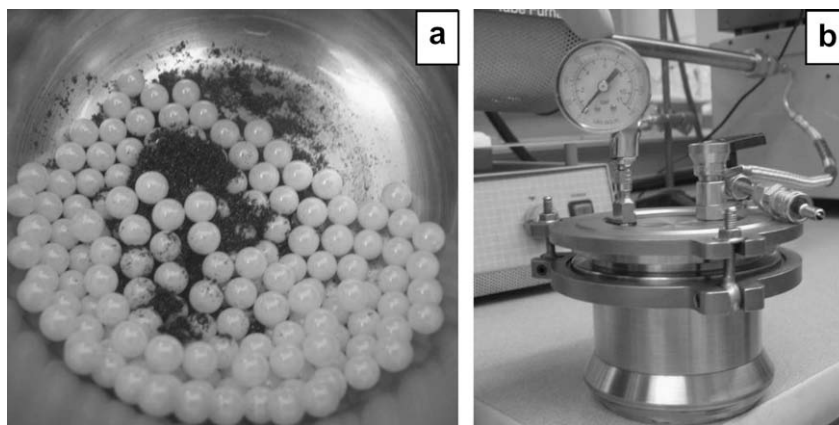


Fig. 1. (a) Photograph of uranium metal shavings and YTZ milling media in chrome steel ball-milling container. (b) Planetary ball mill container used to synthesize UN via a mechanically induced gas–solid reaction (ball-milling) method with a N₂ atmosphere at room temperature. This vessel allows for multiple charges/purges to 420 kPa with oxygen-gettered UHP N₂ during the milling process.

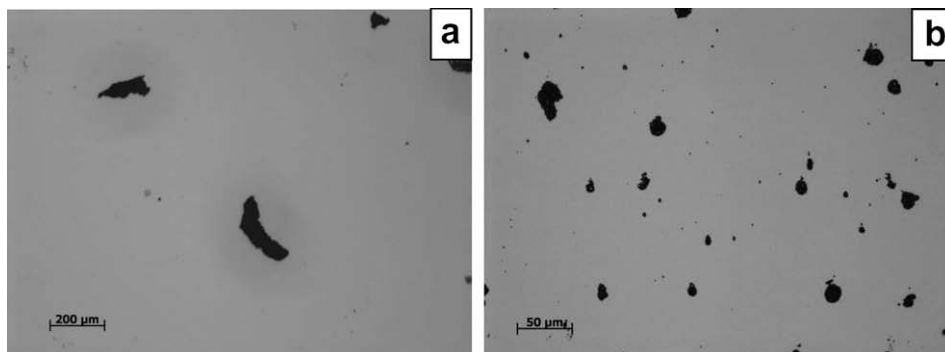


Fig. 3. (a) Optical micrograph (50 \times) showing the ellipsoid shaped uranium metal particles prior to reaction ball-milling in N_2 . (b) Optical micrograph (200 \times) showing the spherically shaped U_2N_3 powders resulting from the reaction ball-milling. Particle size analysis measured the median particle size of U_2N_3 to be 6 μm with a particle size distribution from 1 to 45 μm .

cal refining techniques. The results of this work could have a profound impact on the potential future uses of nitride nuclear fuels in both fast-spectrum reactors and space reactors by providing a closed, low-temperature, and economical synthesis route with a small footprint (requiring little infrastructure).

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