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Letter to the Editor

Synthesis of dysprosium and cerium nitrides by a mechanically induced gas–solid reaction

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ABSTRACT

A high energy ball milling process was used to produce dysprosium nitride and cerium nitride powders at room temperature. Dysprosium and cerium metal flakes were milled in a 275 kPa nitrogen atmosphere for 24 h at ambient temperatures. X-ray diffraction confirmed the formation of phase pure dysprosium nitride and cerium nitride powders. The median particle size of the resultant dysprosium nitride was measured as 4 μm using a laser scattering technique. The particle size of the cerium nitride was not measured due to its reactive nature.

1. Introduction

Advanced nuclear fuel cycles are being developed in the US, Asia, and Europe to provide a transition from the current once through fuel cycle to a more environmental and effective energy solution. Such advanced fuel cycles require the use of complex nuclear fuels that are comprised of fissile materials such as plutonium, americium, neptunium, and curium in the form of oxides, metals, hydrides, and nitrides. Traditionally, oxide materials have been used as nuclear fuels due to desirable properties they exhibit but a few critical properties of the nitrides have been found to be better than those of the oxides. When compared to typical oxide fuels, nitrides require lower 'burning' temperatures and exhibit decreased cladding compatibility concerns due to their higher actinide densities, higher thermal conductivities, higher melting temperatures, and lower thermal expansion coefficients [1,2]. Although the nitrides are more efficient fuel forms, there are some disadvantages associated with them. Single phase mononitrides can be difficult to synthesize, difficult to handle (especially in the powder form due to their pyrophoric nature when exposed to oxygen), and difficult to analyze. Also, a great concern is the transmutation of ^{14}N into ^{14}C, a long-lived radiotoxic isotope which affects the neutronics of the fuel. Consequently, the fuels will need to be synthesized using ^{15}N, a costly alternative to ^{14}N.

It is known that working with even minute quantities of radioactive materials requires numerous engineering and administrative controls and it is therefore more efficient to begin work with non-radioactive elements with similar properties to their radioactive counterparts, also known as surrogates. Dysprosium nitride (DyN) and cerium nitride (CeN) have been identified as surrogates for americium nitride (AmN) and plutonium nitride (PuN), respectively, because of their similar nitriding properties and from past studies [3–8]. Dysprosium nitride (DyN) also has a relatively high vapor pressure, which is similar to that of americium nitride (AmN) [4]. By using DyN and CeN as surrogates for AmN and PuN, many of the challenges that arise when working with actinides are reduced (or removed), worker exposure is minimized, and synthesis processes can be assessed without producing high level nuclear waste.

There are a few published methods for synthesizing nitrides from metals and oxides of dysprosium and cerium [9,10,4,11,12]. Such synthesis methods include: the heat treatment of pure metal in a nitrogen and hydrogen atmosphere followed by nitridation in a pure nitrogen atmosphere at high temperatures [9,10], reducing the oxide via a carbothermic reduction prior to nitridation in a nitrogen atmosphere [4,11], and a solution route [12]. These routes can require: relatively long synthesis times, multi-steps, excessive handling, production of waste from intermediate synthesis steps, and are expensive due to the required infrastructure. The

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mechanical synthesis route presented in this work is an economic alternative to existing thermal routes that require high purity atmospheres, high temperature furnaces, and much infrastructure. This mechanical synthesis technique is considered economic because its starting materials (pure metal) can be obtained directly from the products of spent fuel separations techniques (such as pyroprocessing or electrochemical refining). This mechanical route is viewed as advantageous because it converts a metal to a nitride at room temperature with a reduced number of handling/processing steps thereby minimizing the time and risks typically associated with handling the nitrides. This technique is also conducted within a closed system, thus reducing the amount of material lost to evaporation and handling.

Mechanical synthesis routes have been used to produce various nitrides from their respective metals such as TiN and ZrN [13,14]. This paper reports the first work demonstrating the direct nitridation of dysprosium and cerium metal via a mechanical ball milling route. This work was conducted in parallel with successful efforts to develop economical nitride synthesis methods for uranium nitride [15,16]. The results suggest direct nitridation of plutonium and americium as well as other actinides may be possible by this method, offering a relatively inexpensive, closed system for processing.

2. Experimental procedure

Dysprosium and cerium metals and their nitrides have a propensity to react with oxygen exothermically when exposed to air under ambient conditions. Therefore, the preparation and experimentation of the powders prior to and after milling were carried out in an argon atmosphere glove box. Throughout this work, it was found that CeN had a much higher propensity for oxidation compared to DyN.

2.1. Synthesis of DyN

To synthesize DyN, 5 g of 99.9% pure 420 μm (−40 mesh) dysprosium metal flakes (ESPI, Ashland, OR, USA) were placed in a 250 ml chrome steel milling vessel under an argon atmosphere. About 70 g of 5 mm diameter yttria stabilized zirconia (YSZ) grinding media (TOSOH, Tokyo, Japan) were added to the milling vessel yielding a powder to mass ratio (PMR) of 1:14. The vessel was charged with ultra high purity nitrogen to 275 kPa. The dysprosium metal was milled at room temperature in a PM 100 planetary ball mill (Retsch, Haan, Germany) at 500 rpm for 24 h total in four sessions. The milling vessel was intermittently purged and recharged with nitrogen. The purges and recharges were performed after 2 h of milling, after an additional 4 h, and after an additional 8 h.

2.2. Synthesis of CeN

To synthesize CeN, 5 g of 99.9% pure 420 μm (−40 mesh) cerium metal flakes (ESPI, Ashland, OR, USA) were placed in a 250 ml chrome steel milling vessel under an argon atmosphere. About 70 g of 5 mm diameter YSZ grinding media were used yielding a PMR of 1:14. The milling vessel was charged with ultra high purity nitrogen to 275 kPa. A single purge and recharge of nitrogen was performed after 2 h of milling. Milling was performed for 24 h. There were fewer purge and recharge cycles performed with the cerium experiment to minimize the amount of oxygen exposure to the sample as there is likely to be some oxygen introduced into the system each time the gas connections are attached and detached from the milling vessel.

2.3. Powder characterization

The resulting powders were characterized by X-ray diffraction (XRD) and their particle size distributions were measured using multiple laser scattering techniques. The XRD data were collected in air at room temperature using a Philips X'pert XRD system with a Cu Kα source ($\lambda = 1.5418$ Å) and a 4°/min scan rate in Bragg-Brentano geometry. Lorentzian fits of the first four XRD peaks were used to analyze the data. Powders were transferred from the milling vessel to an XRD sample holder in a glovebox under an argon atmosphere. The sample holders were sealed with vacuum grease and an X-ray transparent film to reduce the chance of oxidation during handling and analysis outside of the argon atmosphere glovebox. A Horiba LA-950 Laser Scattering Particle Size Distribution Analyzer (Minami-ku Kyoto, Japan) was used to determine particle size of DyN. The DyN was dispersed in deionized water and the system was given a refractive index of $2.2 + 0.1i$. The CeN was not analyzed with the particle size analyzer due to its reactivity with water.

3. Results and discussion

The XRD spectrum of the DyN sample which had a PMR of 1:14 and was milled for 24 h in 275 kPa nitrogen at room temperature is shown in Fig. 1. The only peaks present in the XRD spectrum are the DyN peaks (by comparison with the accepted data given by the Joint Committee of Powder Diffraction Standards (JCPDS)), indicating that the reactive ball milling route produced a phase pure DyN powder. Analysis of the XRD spectrum was performed using Lorentzian fits of the first four diffraction peaks and Bragg's equation (1):

$$n\lambda = 2d_{hkl}\sin\theta \qquad (1)$$

where n is assumed to be 1, λ is the wavelength of the incident X-rays, and θ is the position of the diffracted peak. The lattice constant of the ball milled DyN was found as 0.487 ± 0.001 nm, which is in agreement with the published value of 0.490 nm [16,17]. Further analysis of the XRD spectrum was performed using the Lorentzian fits of the diffraction peaks and the Scherrer equation (2):

$$L = \frac{k\lambda}{\beta\cos\theta} \qquad (2)$$

where k is a geometry constant and set to 0.9, and β is the breadth of the diffraction peak at half of its maximum value. The average crystallite size of the DyN was found to be 8.0 nm. A plot of particle

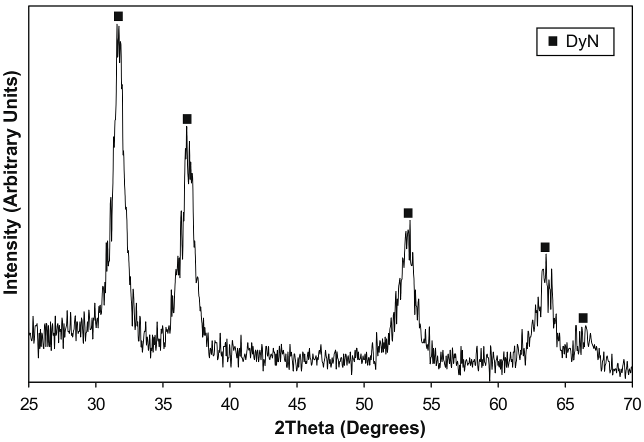

Fig. 1. XRD pattern of DyN that was synthesized by milling 420 μm (−40 mesh) dysprosium metal flakes in a 275 kPa nitrogen atmosphere for 24 h at room temperature. Only DyN peaks are present.

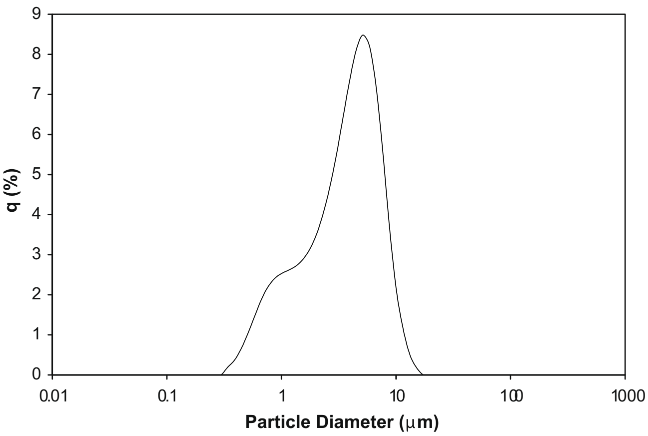

Fig. 2. Particle size distribution of DyN that was synthesized by milling 420 μm (−40 mesh) dysprosium metal flakes in a 275 kPa nitrogen atmosphere for 24 h at room temperature. The median particle size was found to be approximately 4 μm.

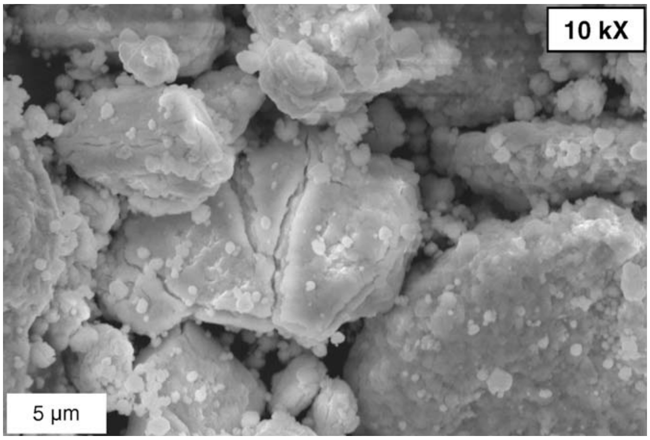

Fig. 3. SEM image of DyN powder that was synthesized by milling 420 μm (−40 mesh) dysprosium metal flakes in a 275 kPa nitrogen atmosphere for 24 h at room temperature.

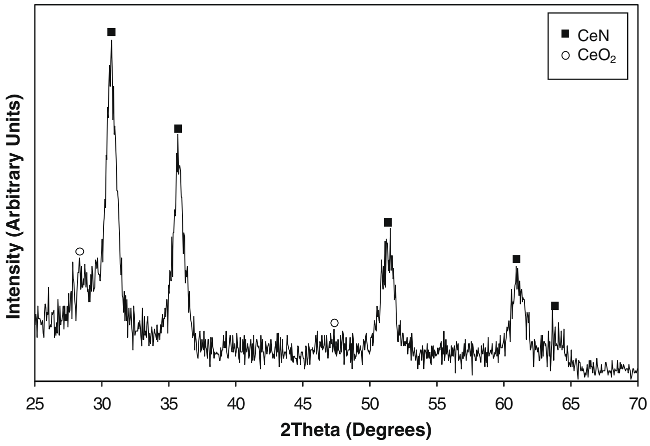

Fig. 4. XRD pattern of CeN that was synthesized by milling 420 μm (−40 mesh) cerium metal flakes in a 275 kPa nitrogen atmosphere for 24 h at room temperature. CeN and minor CeO_2 peaks are present.

size distribution is shown in Fig. 2 and a corresponding scanning electron image (SEM) is shown in Fig. 3. The volume-based median and mean of the bimodal particle size distribution of the sample was approximately 4.0 and 3.6 μm, respectively, after 24 h of milling.

The XRD spectrum of the CeN sample which had a PMR of 1:14 and was milled for 24 h in 275 kPa nitrogen at room temperature is shown in Fig. 4. The dominant peaks are CeN peaks but there are also CeO_2 peaks present in the XRD spectrum. The oxygen peaks in the XRD spectrum of the CeN are likely due to its very reactive nature and the fact that it was exposed to minute amounts of oxygen when transferring to (and during) the phase analysis. However, the results show that phase pure CeN can be produced by this mechanical method. Similar analysis (to that performed with the XRD spectrum of the DyN) was performed on the XRD spectrum of the CeN. The lattice constant of the ball milled CeN was found as 0.504 ± 0.001 nm, which is in agreement with the published value of 0.502 nm [18]. Further analysis of the XRD spectrum indicates that the average resultant crystallite size is 9.4 nm.

The XRD spectrums for both of the milled nitrides exhibited broad diffraction peaks with low intensities and relatively large peak to noise ratios. These characteristics are attributed to two primary factors: the first being very small crystallites and the second being the amorphization of the solids. The average crystallite sizes were estimated through the Scherrer relation Eq. (2) in the preceding paragraphs. The amorphization of the materials is expected to be due to the high energy impacts between the milling media and the metal/nitride that is endured throughout the milling process. It is presumed that the large mechanical energy provided to the system produces large internal stresses and strains in the crystal structure of the materials, which is seen in the SEM image of the DyN powder (Fig. 3).

4. Conclusions

Direct nitridation of both dysprosium and cerium metal was achieved using a high energy ball milling technique under a 275 kPa nitrogen atmosphere at room temperature. XRD results verified that the ball milling route is able to produce phase pure DyN and CeN powders in relatively short times at low temperatures in a completely closed system. The results of this mechanical synthesis route are significant because it provides a simple, direct nitridation route as an alternative to thermal and chemical routes available for producing phase pure DyN and CeN. This direct nitridation synthesis route occurs at ambient temperatures, suggesting a substantial reduction in costs as compared to traditional thermal routes. In addition, due to the limited amount of equipment required for this route, both the infrastructure required to implement this process and the number of handling steps is substantially reduced. The results suggest that direct nitridation of AmN and PuN as well as other actinides may be possible by this method.

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