



In situ characterization of the nitridation of dysprosium during mechanochemical processing



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ABSTRACT

Processing of advanced nitride ceramics traditionally requires long durations at high temperatures and, in some cases, in hazardous atmospheres. In this study, dysprosium mononitride (DyN) was rapidly formed from elemental dysprosium in a closed system at ambient temperatures. An experimental procedure was developed to quantify the progress of the nitridation reaction during mechanochemical processing in a high energy planetary ball mill (HEBM) as a function of milling time and intensity using *in situ* temperature and pressure measurements, SEM, XRD, and particle size analysis. No intermediate phases were formed. It was found that the creation of fresh dysprosium surfaces dictates the rate of the nitridation reaction, which is a function of milling intensity and the number of milling media. These results show clearly that high purity nitrides can be synthesized with short processing times at low temperatures in a closed system requiring a relatively small processing footprint.

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1. Introduction

Interest in rare earth element production and management has increased significantly in the United States (US) in the past few years. Such “strategic materials” have substantially increased the US dependence on the Republic of China, which exported 99% of the approximately \$186 million worth of rare earths to the US in 2008 for use in metallurgical applications and alloys, electronics, catalysts, and cathode ray tubes [1]. Compared to the light rare earth metals, relatively little published literature exists for praseodymium, promethium, thulium, lutetium, and dysprosium although scientific interest in these metals is on the rise. In the next forty years, Hoenderdaal et al. [2] project that the demand for dysprosia (Dy_2O_3) and other dysprosium compounds will increase to between 7 and 25 times (to 14–50 ktons) the 2010 demand. This increase in projected demand largely stems from magnetic applications in electric motors due to dysprosium's exceptional magnetic moment of 10.6 Bohr magnetons, which is second only to holmium, and its ability to induce coercivity as an alloying agent or dopant [3]. DyN has also been investigated as a material for ferromagnetic and semiconductor superlattice

structures for spintronic applications [4–6]. Dysprosium's isotopes strongly absorb neutrons and could be applied as moderator materials in nuclear reactors. Additionally, due to its physical attributes and high vapor pressure, dysprosium mononitride (DyN) has been postulated as a suitable surrogate for americium mononitride (AmN) in studying its sintering and alloying effects in spent nuclear fuel reprocessing [7–12].

Traditional synthesis routes to advanced nitride ceramics are based on thermal treatments, which can require large amounts of infrastructure, long processing times, and can introduce excessive amounts of anion impurities. High energy ball milling (HEBM) is an alternative technique that can be used to synthesize high purity nitride ceramics in relatively short times in a sealed and controlled environment, which reduces exposure to unwanted atmospheres. HEBM is used in many processes that have been described in the literature: Mechanical alloying (MA), mechanical milling (MM) and mechanical grinding (MG), mechanical disordering (MD), reactive milling (RM), reactive mechanical milling (RMM), cryomilling, mechanically activated annealing (M2A), double mechanical alloying (DMA), and mechanically activated self-propagating high-temperature synthesis (MASHS) [13,14]. HEBM is a versatile processing technique that has demonstrated useful for producing nanometer-structured materials, crystalline and amorphous materials, as well as equilibrium and metastable phases [13]. A ball milling process that is considered high energy is one that utilizes high media

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impact velocities and large media impact frequencies to efficiently mill the powder charge. This can be accomplished in numerous ways. Most notably, dynamic mechanical energy can be delivered to a powder charge using a few different milling techniques, including: horizontal ball milling, planetary ball milling (PBM), magne to ball milling, and shaker milling (SPEX) [13–16]. Different milling apparatuses vary in capacity, efficiency of milling, and spatial arrangements requiring each to be characterized independently when attempting to understand the mechanisms of the processes.

Mechanical alloying has been used to synthesize oxide dispersion strengthened alloys since the 1960s and, approximately a decade later, the same process was shown to be useful as a ceramic synthesis method, later noted as RM [13]. For the past 40 years, RM has been investigated for the low temperature, solid state synthesis of advanced ceramics. According to Huot et al. [14], RM has been demonstrated on hydrogen storage materials using various milling techniques for the past 10 years, resulting in approximately one thousand publications. However, the study of RM in the synthesis of non-oxide and non-hydride materials has not been studied as extensively; there are fewer than 50 publications on the use of RM to form nitrides and fewer than 20 that used PBM. The limited number of studies that focused on producing nitride ceramics tended to investigate transition metals and class IIIA elements such as: Al, B, Cr, Fe, Ga, Nb, Si, Ta, Ti, V, and Zr [13,17–33]. To the best of the authors' knowledge, the synthesis of lanthanide or actinide nitrides via RM has not been published other than the earlier work of this group [7–10]. In particular, to study nitridation reaction kinetics during RM in a PBM using *in situ* temperature and pressure data is very limited; there are no studies found in the literature on RM in a PBM to form nitrides with *in situ* temperature and pressure measuring capabilities. The only studies found that have demonstrated such capabilities during PBM are limited and stem from the research on hydrogen storage materials [34–40].

The work described here is part of a larger effort in the understanding of RM (also referred to as a mechanochemical synthesis or a mechanically induced gas–solid reaction) by high energy planetary ball milling elemental dysprosium in a nitrogen atmosphere to form dysprosium mononitride (DyN), as follows:



The mechanochemical reaction was monitored (as a function of milling intensity and time) using *in situ* temperature and pressure measurements to calculate the extent of the reaction. A more detailed kinetics study is presented on the nitridation of dysprosium in a

PBM in our concurrent publication [41], where a fundamental milling dynamics model is used to describe the behavior of the RM process.

2. Experimental details

To study the RM during PBM of the nitridation reaction, milling experiments were performed in ultra-high purity (UHP) nitrogen with high purity dysprosium filings (99.9% purity, ESPI) sieved through a 40 mesh (420 μm) sieve (Fig. 1). The filings had a surface area of $0.196 \pm 0.058 \text{ m}^2 \text{ g}^{-1}$, as determined by nitrogen adsorption Brunauer–Emmett–Teller (BET) techniques. In order to gain insight into the reaction kinetics, the internal temperature and pressure of the milling vessel were monitored during milling in a Retsch planetary ball mill (PM100) at milling intensities varying from 350 to 650 rpm. Each milling run was completed using a Retsch 250 mL hardened steel milling vessel (85Fe, 12Cr, 2.2C, 0.45Mn, 0.4Si) and 5 mm diameter, spherical yttria stabilized zirconia media (Tosoh, Tokyo, Japan). According to the respective vendors, the milling vessel and milling media had a hardness of 62 HRC and 72 HRC, respectively. The ball to powder ratio (BPR) was held constant at 14:1 with a total dysprosium mass of 5 g (70 g of YSZ media which equates to 184 spheres). The temperature and pressure were monitored using a Retsch sensing lid (PM GrindControl), which has capabilities of 273–473 K, 0–500 kPa, and can wirelessly send data at 200 Hz to a remote computer. The temperature (measured by a thermistor) and pressure sensors are integrated into recessed locations in the steel sensing lid.

During each run, the milling vessels were loaded with media and dysprosium and sealed with the temperature and pressure monitoring lid in an argon atmosphere glovebox. It was then charged to approximately 450 kPa with oxygen-gettered UHP nitrogen (oxygen content less than 0.1 ppb as measured by a Neutronics OA-1 oxygen analyzer). The vessel was charged to 450 kPa and relieved (3 cycles) prior to a final charge of 450 kPa in order to ensure a pure nitrogen milling atmosphere.

The stages of the milling process were observed through mass measurements, SEM imaging, and powder X-ray diffraction (XRD) during a 500 rpm milling run. The 500 rpm milling run was periodically interrupted between 0 and 6 h of milling. Each time the process was halted, the milling vessel was transferred into an argon atmosphere glovebox where the lid was removed and the measurements or representative powders were taken. The same powder and media was then sealed, evacuated and charged with nitrogen, and secured to the mill for subsequent milling.

The effect of milling intensity was assessed by milling for 6 h at different intensities from 350 to 650 rpm. After milling, the powder was separated from the milling media in the argon-filled glovebox and characterized using SEM imaging, laser-scattering particle size analysis (PSA), and XRD. Additionally, temperature and pressure data were used to assess the reaction kinetics at each milling intensity.

In each case, XRD was performed at room temperature on a Bruker D8 Discover using Cu K α radiation ($\lambda = 0.15418 \text{ nm}$). However, some of the patterns were collected with a scintillation counter and some were collected with a 2-dimensional area detector. Due to the oxygen sensitivity of the material, the XRD samples were prepared in an argon glovebox and a semi-X-ray transparent film was placed over the powder filled sample holders in order to prevent oxidation during the XRD scans.

The particle morphology after 6 h of milling at 350–650 rpm was investigated using a Hitachi (S-3400N) thermionic cathode scanning electron microscope (SEM) as well as a Horiba (LA-950) laser scattering particle size analyzer (PSA). The powders were first adhered to carbon tape prior to carbon coating in order to obtain SEM images with reduced electron charging. For PSA, the DyN powders were dispersed in an isoparaffinic fluid (Isopar V, ExxonMobil) by external ultrasonication using a 750 W sonication probe prior to loading into the mixing chamber of the Horiba analyzer. The refractive indices used for the free powder and the Isopar V were 2.5–0.43i and 1.452, respectively.

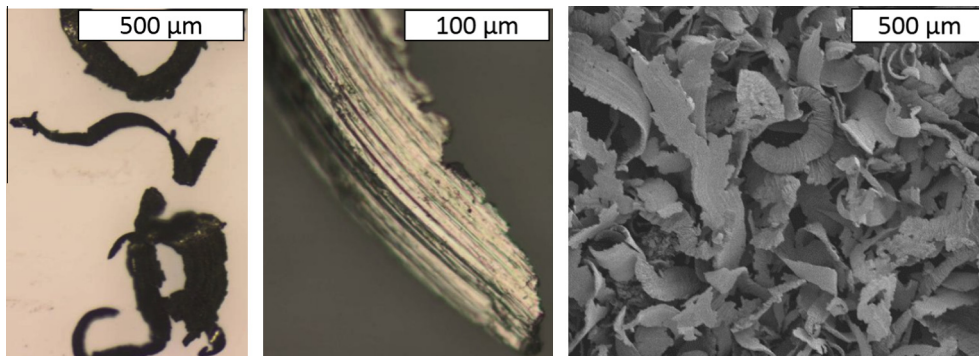


Fig. 1. Images of the dysprosium filings used as the starting materials for the kinetics study of the nitridation reaction to form DyN using a dry planetary ball milling process in nitrogen atmosphere. The filings have a surface area of $0.196 \pm 0.058 \text{ m}^2/\text{g}$.

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