



# Kinetics of the nitridation of dysprosium during mechanochemical processing



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## ARTICLE INFO

### Article history:

Received 26 May 2014

Received in revised form 16 August 2014

Accepted 12 September 2014

Available online 20 September 2014

### Keywords:

Mechanochemistry

Nitrides

Rare earths

High energy ball milling

Reaction kinetics

## ABSTRACT

Dysprosium nitride was synthesized by the reactive milling of the rare earth metal under 400 kPa nitrogen gas in a planetary ball mill. The nitrogen consumption rate was calculated from *in situ* temperature and pressure measurements to find the reaction extent as a function of milling time at milling speeds from 350 to 650 rpm. The results are analyzed in terms of a fundamental milling dynamics model in which the input milling energy is the primary driving force for reaction and the rate limiting step of the nitridation kinetics is the formation of chemically active surfaces. The model differs from traditional gas–solid reactions which are often limited by diffusion of a species through a surface layer or by dissociation of the gas molecule. These results give fresh insight into reactive gas–solid milling kinetics.

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## 1. Introduction

Reactive milling is an adaptation of the high-energy ball milling techniques that have been used for materials processing for some 50 years [1]. In reactive milling, sometimes termed mechanochemical synthesis, the system is designed to use the energy imparted by the milling tools to assist in driving a chemical reaction. The reaction may be solid–solid, solid–liquid, or solid–gas. The latter is often applied in studies of hydrogen storage materials [2–4]. There has been some work done describing the kinetics of gas–solid reactions during reactive milling, in which observed kinetics have included nucleation accelerated by grain refinement in transition metal-doped MgH<sub>2</sub> [3], autocatalysis/self-propagation in Zr and Hf hydrides [4], and nucleation and growth in HfN [5], ZrN [6], and ZrO<sub>2</sub>/ZrC [7,8]. While many closed-form analytical models have been developed to describe the mechanical energy imparted during high energy milling [9–14], very few reactive milling investigations explicitly consider this energy while discussing reaction kinetics, and to the best of the author's knowledge no investigation has analyzed how the rate of energy transfer could change during reactive milling.

Reactive milling is interesting from both a fundamental standpoint and with a view to applications, as the self-contained, low temperature nature of the process could enable the synthesis of many materials that are difficult or hazardous to prepare [15–17] as well as reducing the environmental impact of synthesis [18].

### 1.1. Dysprosium and dysprosium nitride

Dysprosium, like the other rare earth metals, displays extreme reactivity on fresh surfaces with most gasses [19,20]. An X-ray photoelectron spectroscopy study of the reaction of nitrogen on clean dysprosium demonstrated that nitrogen dissociatively chemisorbs with the formation of one or two monolayers of nitride at 300 K [21]. Gas phase reactions arrested in frozen argon provide evidence for direct scission of the N≡N bond by adjacent dysprosium atoms and do not indicate high complexation of the nitride by molecular nitrogen [22]. Similar behavior is observed for the early lanthanides [23] in contrast to the higher tendency of light transition [24] and some actinide [25] metals and nitrides to complex molecular nitrogen. Although the kinetics of the dysprosium nitridation reaction have not yet been reported in any detail, the demonstrated tendency for dissociative chemisorption over physisorption or dissolution of nitrogen suggests that the rate limiting step in the nitridation process will be either gas transport to the metal or through the nitride. This makes DyN an interesting model system for a reactive milling study: since milling is widely understood to break up and disperse surface films, nitride formation during reactive milling under a high

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nitrogen pressure might be expected to be kinetically limited by the formation of fresh chemically active surfaces rather than by transport mechanisms or nitrogen dissociation. A schematic of this proposed process is found in Fig. 1a–c. The impact event diagrammed in Fig. 1d is analyzed in terms of a kinematic model in order to determine the energy available for material refinement.

### 1.2. Ball milling modeling

The planetary ball milling model developed by Chattopadhyay [14] was used as a starting point for analysis of milling mechanics. The model includes assumptions that limit the applicability to the stochastic process of ball milling. Modeled media move in a no-slip condition, being governed by the normal force while “attached” to the vessel wall, by rigid body mechanics while not attached, and stick without slip on impact. Modeled impact is described by Hertzian mechanics [26] and assumes perfectly elastic impacts rather than the elastic–plastic behavior found in real milling systems. Even considering these limitations, the milling model provides a helpful point of reference and was employed to extract the angular frequency dependencies of various process variables. The physical constants of the planetary ball mill and milling media used are provided in Table 1, and the dependencies of impact conditions on milling speed are summarized in Table 2. The kinetics analysis considered here is specific to counter-revolving planetary ball mills, although the analysis could be extended to other high-energy mill geometries by modifying the model.

### 1.3. Energy requirements for surface formation

The continual input of energy during milling media impacts leads to crystallite size reduction. The exact mechanism is debated and probably varies from system to system. In brittle materials, fracture is assumed to be dominant, while in ductile materials there is probably dislocation coalescence leading to dynamic recrystallization of new subgrains [27] that asymptotically approach a limiting size of 10–20 nm. This limit condition is different for each material and thought to be related to the cohesive strength and to the maximum dislocation stacking density [28]. Unfortunately, very few studies on ball milling of pure metals have reported the crystallite size as a function of milling time [29,30], while most studies report only ending crystallite size. The reduction of dimension with increasing milling energy dose is a well known relationship in mineral processing typically represented by the empirical laws of Rittinger, Kick or Bond, which were proposed by Hukki [31] to be approximations to a size-dependent energy consumption of the general form:

$$dE = -C \frac{dx}{x^{f(x)}} \quad (1)$$

**Table 1**  
Mill and media physical constants.

Constant	Symbol	Value	Units
<i>Mill parameters</i>			
Vial/disk speed	$\omega_v/\omega_d$	–2.00	
Disk radius	$r_d$	70.5	mm
Vial radius	$r_v$	37.5	mm
Corrected $r_v$	$r'_v = r_v - r_b$	35.0	mm
Vial/disk radius	$r'_v/r_d$	0.496	
<i>Media parameters</i>			
Radius	$r_b$	2.5	mm
Density	$\rho_b$	5.89	g/cm <sup>3</sup>
Mass	$m_b$	0.39	g
Poisson's ratio	$\nu_b$	0.31	
Elastic modulus	$E_b$	234.8	GPa

**Table 2**  
Conditions at media impact (modeled).

Angular frequency dependencies				
Variable	Symbol	Coefficient	$\nu^x$	Units
Deflection	$\delta_h$	1.267	$\nu^{0.8}$	$\mu\text{m}$
Hertz radius	$a_h$	0.056	$\nu^{0.4}$	$\mu\text{m}$
Net velocity	$V$	0.286	$\nu^1$	m/s
Impact energy	$E_b$ (v)	0.056	$\nu^2$	mJ/hit

where  $x$  is the critical dimension of a comminuted material,  $C$  is a material constant, and  $f(x)$  describes a dependence of  $dE$  on the current size. Rittinger's law makes the approximation  $f(x) = 2$  in Eq. (1) and predicts the energy required for size reduction in very small (<10  $\mu\text{m}$ ) particles to be proportional to the area of new surface created. Fractal analysis has suggested  $f(x) = 2.3 + x \ln(x)$  with  $x$  measured in micrometers [32]. Thus, reactions in milled systems that are kinetically limited by surface formation or surface reactions should be expected to display a linear or nearly linear dependence on the mechanical energy imparted to the reacting material.

Closed form milling theory based on Hertzian contact solutions generally assumes completely elastic impacts, although the obtained solutions are sometimes modified by a constant scalar to correct for an assumed value of the coefficient of restitution  $C_R$ . In the case of normal impact with negligible spin, the energy state of the media after impact may be described solely by  $C_R = v_f/v_i$ ,  $0 \leq C_R \leq 1$ . A value of 1 indicates a completely elastic impact as described by Hertzian impact theory, while a value of 0 represents completely plastic impact. In high energy milling, both theory and experiment call for values in the range 0.5–0.9. In general, the value of  $C_R$  for a given media at a given moment depends on the thickness of material coating the media (and thus the volume available for plastic deformation). In any attempt to accurately describe the kinetics of a reaction during high energy milling, it is imperative to quantify if and how the coefficient of restitution changes throughout the milling process.

## 2. Materials and methods

### 2.1. Gas–solid reactive milling experiments

Milling experiments were conducted on a planetary ball mill (Retsch PM100, Haan, Germany) in a hardened steel vessel with a 250 mL nominal volume. The actual volume of the vessel + lid was measured to be 269.7 mL by measuring the amount of deionized water required to completely fill the vessel along with the gas ports in the milling lid. In a typical experiment, 5 g of dysprosium filings were added to the milling vessel along with 184 yttria-stabilized zirconia 5 mm diameter milling media, resulting in a ball-to-powder charge of 14:1. The vessel was then sealed and purged with ultra-high purity nitrogen, purified further by copper gettering, before pressurizing to 400 kPa nitrogen, which is greatly in excess of the 140 kPa required to fully convert 5 g of Dy to DyN under the given experimental conditions. In a few experiments, the starting pressure was varied in the range 300–600 kPa without a noticeable effect on the reaction rate. Milling was conducted at speeds ranging from 350 to 650 rpm for 6 h and at 500 rpm for between 15 min and 24 h. Nitrogen consumption was monitored *in situ* by pressure and temperature sensors mounted in the milling lid. As-milled powders were checked for phase purity by X-ray diffraction (Rigaku Miniflex, Tokyo, Japan). Full details of these experiments are currently being published in a concurrent manuscript by Jaques et al. [33].

### 2.2. Milling media energetics

Two experiments were performed on milling media coated by pure metals milled under argon for 0–24 h and for media coated by metal–metal nitride composites formed by milling metal under nitrogen for 0–1 h. The coefficient of restitution  $C_R$  was measured by removing media from the milling vial and dropping media 40 cm onto a milling vessel lid, resulting in a maximum impact velocity of approximately 2 m/s. Vacuum tweezers were used to hold the media before dropping to avoid imparting spin. The rebound height was measured and the coefficient of restitution calculated by assuming that the relationship  $mgh = 0.5 mv^2$  held such that  $C_R = (H_f/H_i)^{0.5}$ . At least 20 trials were performed for each combination of material

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