

Evolution of metal nitriding and hydriding reactions during ammonia plasma-assisted ball milling

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ARTICLE INFO

Keywords:

Plasma milling
Solid–gas reaction
Metal nitride
Metal hydride

ABSTRACT

Nanocrystalline metal nitride and hydride powders were prepared using plasma-assisted ball milling in ammonia gas (NH₃-P-milling) via an in situ synthesis reaction. The gas–solid reactions were triggered by a short duration of plasma milling of Mg and Ti under a constant pressure of ammonia gas, and the products in the two systems were nanocrystalline Mg₃N₂ and TiN, TiH₂ after 10 h, respectively. During the NH₃-P-milling of Ti powder, TiH₂ and TiN were formed during the initial stages of milling, and then, the TiH₂ decomposed during further milling upon reaction with N radicals, transforming into the TiN phase. In contrast, no chemical reaction occurred between NH₃ and Mg/Ti after 10 h of C-milling. The discharge plasma activated and decomposed the ammonia gas and activated the surface of the powders, which, together with the mechanical effect of high-energy ball milling, accelerated the gas–solid reactions.

1. Introduction

Metal nitrides are widely applied in ceramics, energy storage materials, and catalysts and can also be used to complement metal oxides in various applications [1]. For example, TiN exhibits enhanced hardness and is therefore applied as an abrasive material [2], and Mg₃N₂ has been widely used in high-thermal-conductivity ceramics, hydrogen storage materials, and catalysts in the synthesis of metal or non-metal nitrides [3–7]. Other metal nitrides (such as AlN, GaN) formed from group III metals are wide-bandgap semiconductors and can be used as optoelectronic materials [7,8]. Metal hydrides also have a large range of applications in hydrogen purification, nuclear reactors, and hydrogen storage [9]. Thus, the rapid and highly efficient synthesis of metal nitride and hydride powders has attracted much attention.

Various traditional synthesis methods including direct nitridation or hydrogenation at high temperatures or pressure, vapor deposition, and ion implantation are used to prepare metal nitride and hydride powders [10–13]. However, these methods either require multi-step chemical reactions or time-consuming processes [13]. For example, TiN powders are usually synthesized by direct nitridation of titanium hydride or dioxide, carbon-reduced nitridation of titanium dioxide, and self-propagating combustion synthesis [12,14]. Some works have demonstrated that combining gas absorption with ball milling may result in new types of phase transitions that cannot be realized using either method alone

[15]. Many metal nitrides have been synthesized by ball milling pure elements under nitrogen or ammonia gas at room temperature [16–18]. Furthermore, hydrogen absorption into metals using traditional processes (at elevated temperature and/or pressure) has been observed to occur more rapidly than nitrogen absorption [15]. For the milling of Ti in ammonia gas, the formation of the TiH₂ phase is first observed during the early stage of milling [17]. However, successful synthesis of the above nitrides or hydrides by ball milling requires a very long time (e.g., 300 h) [17].

A new material processing method called plasma-assisted ball milling that combines ball milling with dielectric barrier discharge (DBD) plasma was developed in our previous work [19]. A combination of heating and high-energy electron bombardment effects produced by the plasma and the mechanical effect of milling are simultaneously induced in plasma milling, which can effectively promote powder refinement, activation, and chemical reaction. Furthermore, the use of DBD, as a non-thermal plasma, might be an important addition for improving the efficiency of metal nitriding and hydriding, and leads to many unique advantages, such as high electron energy and a high concentration of active species of N and H from the ionization of the working gas in the glow plasma field [20]. Huang et al. [21] reported simple, single-step, catalyst-free, plasma-assisted growth of dense patterns of uniform-size single-crystalline AlN nanorods at a low substrate temperature without the need for a catalyst or hazardous precursors.

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<https://doi.org/10.1016/j.ceramint.2018.07.048>

Received 12 June 2018; Received in revised form 4 July 2018; Accepted 5 July 2018

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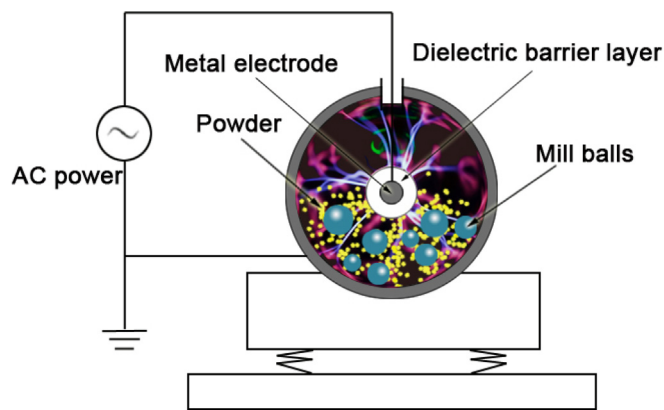


Fig. 1. Schematic illustration of DBD P-milling set-up.

Our previous works have also shown that the presence of a plasma field can accelerate the kinetics of compound synthesis and powder activation, although the precise mechanisms responsible for these phenomena are not yet understood. In this study, the evolution of metal nitriding and hydriding processes by triggering a simple gas–solid system under DBD plasma-assisted ball milling were evaluated at room temperature and atmospheric pressure. The results provide considerable insight into the mechanochemical process occurring during plasma milling. This approach is a promising method for fabricating ultra fine powders and synthesizing nitrogen or hydrogen compounds.

2. Experimental

Fig. 1 illustrates the working principle of plasma milling. The technique uses a vibratory mill, with DBD-plasma introduced into the vial of the mill during the milling process [19]. The electrodes, balls, and solid-state powders constitute a single-electric barrier discharge reactor during the plasma milling process, which produce homogeneous non-thermal plasma at a high-voltage alternating current with a frequency of 8–15 kHz. In this work, ammonia plasma was generated in the ball milling cylinder (NH₃-P-milling) under a high voltage of 15 kV and electric current of 1.5 A using a DBD Plasma-assisted ball-milling device (SCUT, China). Details of the preparation of the NH₃-P-milling Mg or Ti composite powder are provided in Fig. 2. The starting Mg or Ti powder (200 mesh size, 99.95% purity, supplied by Aladdin Chemistry Co., Shanghai, China) was sealed in a stainless steel vial at a powder-to-ball ratio of 1:60, the amplitude peak-peak value and acceleration

effective value of the ball milling jar were 127 mm and 4.5 g at a speed of 960 rpm, the air was removed from the chamber by purging with high-purity NH₃ gas (99.8% purity) at a flow rate of 100 ml/min; an atmospheric pressure of 0.1 MPa was maintained in the milling vial, and the off-gas of the reaction was introduced into water. For comparison, conventionally milled Mg or Ti composite powder under NH₃ without plasma discharge (NH₃-C-milling) was investigated under the same conditions as those used for the NH₃-P-milling process.

X-ray diffraction (XRD; Philips X'Pert MPD) using Cu-K α radiation ($\lambda = 0.1541$ nm) and scanning electron microscopy (SEM; Zeiss SUPRA 40) coupled with energy-dispersive X-ray spectroscopy (EDS) were used to characterize the alloy microstructures. Transmission electron microscopy (TEM; JEOL JEM-2100) at an operating voltage of 200 kV was also applied to characterize the samples. For the TEM observations, the samples were prepared by dispersing the as-prepared powders on Cu grids. Temperature-programmed desorption-mass spectroscopy measurements were conducted using an Autosorb-1C with a PrismaPlus QME 220 MS detector (TPD-MS, Quantachrome) under Ar gas flow. The temperature for characterization ranged from 60 °C to 600 °C with a ramping rate of 5 °C/min.

3. Results and discussion

3.1. Rapid synthesis of Mg nitride during ammonia plasma-assisted ball milling

Fig. 3 presents XRD patterns of the Mg powder treated by NH₃-P-milling and NH₃-C-milling for different milling times. For the plasma milling, the Mg, Mg₃N₂, and MgF₂ diffraction peaks coexisted in the as-milled samples. After 1 h of plasma milling, very small amounts of the Mg₃N₂ and MgF₂ phases were first detected. Their presence is attributed to some chemical reactions occurring in the Mg phase; however, the dominant phase of the milled powder remained metallic Mg with obvious broadening peaks (Fig. 3(b)). Upon increasing the milling time to 3 h, both the Mg₃N₂ and MgF₂ diffraction peaks showed a significant increasing trend and became the dominant phases (Fig. 3(c)). After 6–10 h of plasma milling, the metallic Mg diffraction peaks almost completely vanished with transformation of Mg into Mg₃N₂ and MgF₂ phases (Fig. 3(d) and (e)). The intensities of these phases, in particular the Mg₃N₂ phase, clearly increased with increasing plasma milling time, whereas the intensity of the MgF₂ phase maintained unchanged. Finally, after 10 h of plasma milling, the milled powders consisted of the dominant Mg₃N₂ phase, some MgF₂, and a small amount of remnant Mg. These results indicate that two types of chemical reactions occurred

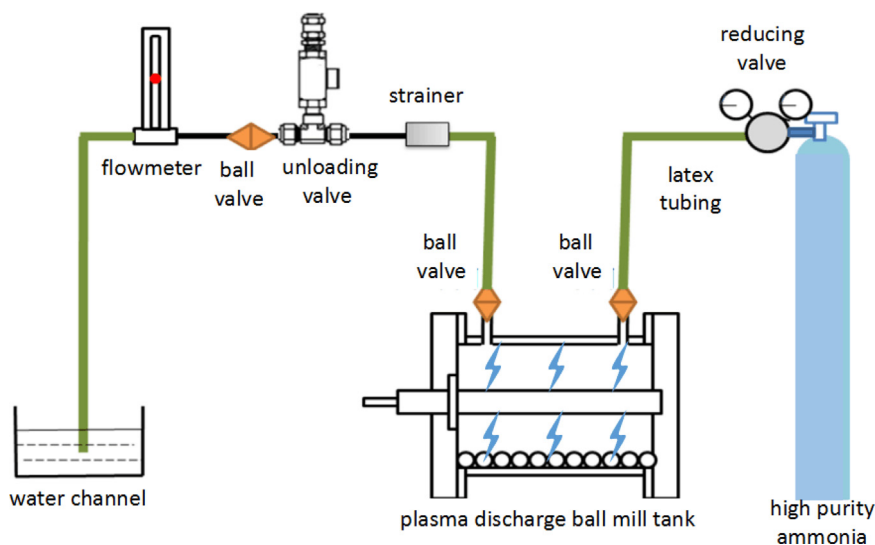


Fig. 2. Schematic illustration of ammonia control unit in DBD plasma milling set-up.

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