

## Effect of Milling Time on Hydrogen Desorption Properties of Nanocrystalline MgH<sub>2</sub>

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### ABSTRACT

Nanocrystalline magnesium hydride powder was synthesized by mechanical milling of MgH<sub>2</sub> in a planetary ball mill for various times. The effect of MgH<sub>2</sub> structure, i.e. crystallite size, lattice strain, particle size, and specific surface area on the hydrogen desorption properties was investigated. A single peak of hydrogen desorption observed for as-received powder, exhibiting an average particle size of 30 μm. In contrast, all milled powders with much reduced particle size exhibited desorption peak doublet in DTA. It shown that the dehydrogenation temperature of MgH<sub>2</sub> decreased from 421 °C to 319 °C after 30 h of mechanical milling. Here, the average crystallite size, specific surface area, and accumulated lattice strain were 18 nm, 9.3 m<sup>2</sup>/g and 0.7%, respectively. There was no significant difference on the onset temperature of dehydrogenation between powders milled at different times. However, the amount of hydrogen release decreased, i.e. from 5.9 wt.% to 4 wt.% with increasing the milling time from 5 h to 30 h.

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### 1. Introduction

Hydrogen is an ideal energy carrier and renewable fuel which is considered for future transport applications [1]. Magnesium hydride is an attractive energy storage material because of its hydrogen storage capacity (7.6 wt. %), low cost, and light weight [2, 3]. However, high hydrogen desorption temperature, relatively poor hydrogen absorption-desorption kinetics, and a high reactivity toward air and oxygen can restrict the use of MgH<sub>2</sub> in practical applications [4, 5].

In recent years, many efforts have focused on Mg-based hydrides to reduce the desorption temperature and to fasten the

re/dehydrogenation reactions which could be accomplished, to some extent, by changing the microstructure of the hydride by mechanical alloying which reduces the stability of the hydrides, as well as by using proper catalysts to improve the absorption/desorption kinetics [1]. Mechanical milling simultaneously produces mechanical deformation, defect formation and surface modification. These structural modifications can lead to the formation of metastable phases, refinement of the microstructure into the nanometer range, extension of solubility limits, development of amorphous phases, etc. [6]. It has been reported that nanocrystalline magnesium

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hydride exhibits fast absorption and desorption kinetics at 300 °C when compared with its non-milled counterpart. This behaviour can be attributed to the faster diffusion of hydrogen along the grain boundaries and the high number of heterogeneous nucleation sites of the hydrogen on absorption or the pure magnesium phase on desorption [7]. Simchi et al. [8] have investigated the effect of MgH<sub>2</sub> structure, i.e. crystallite size and lattice strain, on the hydrogen–desorption kinetics of MgH<sub>2</sub> using a SPEX shaker/mill for various times. Polanski et al. [7] investigated microstructural and hydriding/dehydriding properties of nanocrystalline MgH<sub>2</sub> prepared in different laboratory ball mills.

The aim of this work has been to study the effect of milling time on the dehydrogenation properties of MgH<sub>2</sub> powder obtained by mechanical milling in a planetary ball mill. So far, many researchers have investigated mechanical milling of MgH<sub>2</sub>. However, there are different types of high energy ball mills which are used for the engineering of MgH<sub>2</sub> in its nanocrystalline form. These milled differ in their milling energies, milling modes and uniformity of milling which have strong influence on end milling product. On the other hand, scaling-up of mechanical milling process is an important issue for the large scale production of MgH<sub>2</sub> powder as a precursor for the storage materials [9]. In view of that, a deeper understanding of microstructural and morphological formation of nanocrystalline structure of MgH<sub>2</sub> during long-time ball milling is required.

## 2. Experimental

The starting material MgH<sub>2</sub> (98%, <105 µm) powder was supplied from Merck, Germany.

Mechanical milling of MgH<sub>2</sub> was performed in a Retsch PM100 planetary ball mill at room temperature under a high purity argon atmosphere over various times. Ball to powder weight ratio of 20:1 was selected and the rotation speed was adjusted to 400 rpm. Weighing, filling and handling of the powders were performed in a glove box under argon atmosphere.

The phase formation and variation of grain

structure were investigated by X-ray diffraction method (X'Pert Pro MPD, PANalytical) with Cu-K<sub>α</sub> radiation. The crystallite size and lattice strain of β-MgH<sub>2</sub> phase were estimated by broadening XRD peaks using Williamson–Hall method [10]. The size and morphological changes of the powder particles upon mechanical milling were studied by scanning electron microscopy (SEM, KYKY EM-3200). The mean particle size of powders was measured using Clemex Vision image analyzer on SEM images. In order to characterize specific surface area of the milled powders, a Brunauer-Emmett-Teller analyser (BET, Belsorp-Mini II, Japan) was employed. The thermal behaviour was investigated with a simultaneous thermal analyzer (NETSCH STA 409) under argon atmosphere at a heating rate of 5 °C/min up to 500 °C.

## 3. Results and Discussion

Fig. 1 shows the effect of milling time on the dehydrogenation temperature of mechanically activated MgH<sub>2</sub>. As can be seen, mechanical milling affects the dehydrogenation of MgH<sub>2</sub> with the lowest desorption temperature obtained at 319 °C which corresponds to 30 h milling. The as-received MgH<sub>2</sub> exhibited a single endothermic peak at 421 °C corresponding to the decomposition of hydride. This value is similar to the values reported in previous studies [11]. However, the DTA curves for the milled samples show two endothermic peaks. The reason for the appearance of two peaks in DTA curves may be explained by Varin et al. [12] and Gennari et al. [13]. According to Varin et al. a two-step hydrogen desorption may occur due to the existence of two fractions of powder particles: small and large, which could desorb at lower and higher range of temperatures, respectively. However, Gennari et al. reported that the low-temperature endothermic peak corresponds to the complete dehydriding of γ-MgH<sub>2</sub> and the partial dehydriding of β-MgH<sub>2</sub>, whereas the high-temperature peak corresponds to hydrogen desorption from β-MgH<sub>2</sub>. Anyway, this aspect needs more fundamental studies which are now underway. In this work, the position of the first peak with the maximum rate (more

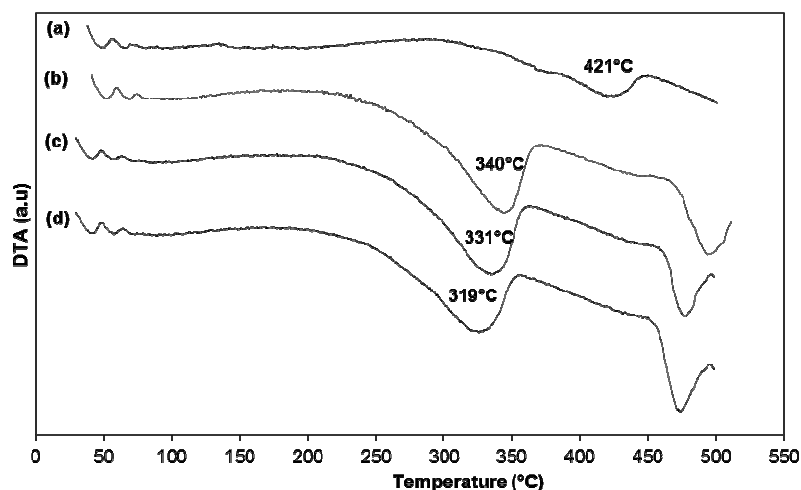


Fig. 1. DTA curves of  $\text{MgH}_2$  powder for unmilled (a) and milled for: 5 h (b); 15 h (c); 30 h (d).

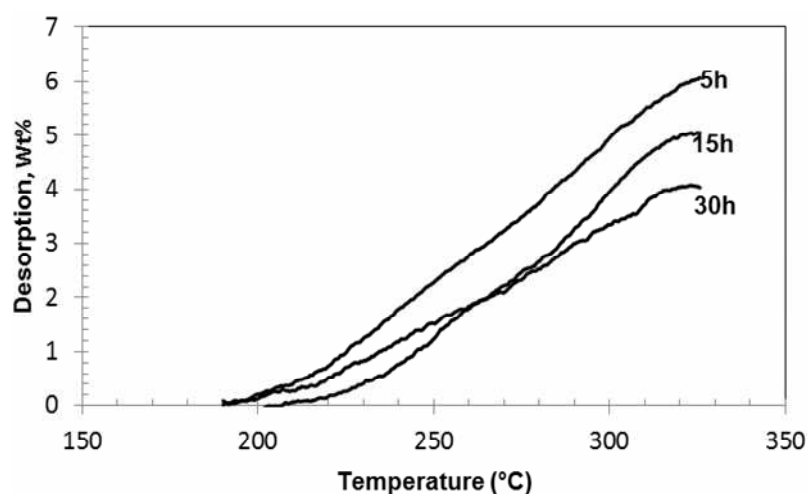


Fig. 2. Thermogravimetric (TG) profiles of  $\text{MgH}_2$  powder at different milling times.

endothermic) has been considered as the dehydrogenation temperature. Fig. 2 shows the thermogravimetry (TG) profiles of the  $\text{MgH}_2$  powder as a function of temperature milled for different times. As can be seen, no significant effect of the milling time on the onset temperature of dehydrogenation was noticed. However, the amount of hydrogen release decreases, i.e. from 5.9 wt.% to 4 wt.% with increasing the milling time from 5 h to 30 h.

In order to find the origin of differences, the characteristics of the milled powders at different milling times were investigated. Fig. 3 shows the XRD patterns of the  $\text{MgH}_2$  powder at the selected milling times. The XRD pattern of the un-milled  $\text{MgH}_2$  powder has been included in the graph for comparison. As can be seen, with the increase in milling time, all diffraction

peaks of  $\beta\text{-MgH}_2$  broadened and decrease evidently due to the high-energy impact of the milling balls. After 5 h of milling, the diffraction peaks corresponding to  $\gamma\text{-MgH}_2$  were detected. The formation of a small amount of MgO phase was also observed. By increasing the milling time to 15 h and 30 h, the diffraction peaks corresponding to  $\beta\text{-MgH}_2$  became broader and less intense, while those corresponding to MgO were intensified, showing the presence of higher amounts of this phase by increasing the milling time. No new phase formation was noticed at these times. Morphological changes produced by mechanical milling at different times can be observed in Fig. 4. No significant difference in the particle morphology was observed during MA process, whereas a significant particle size

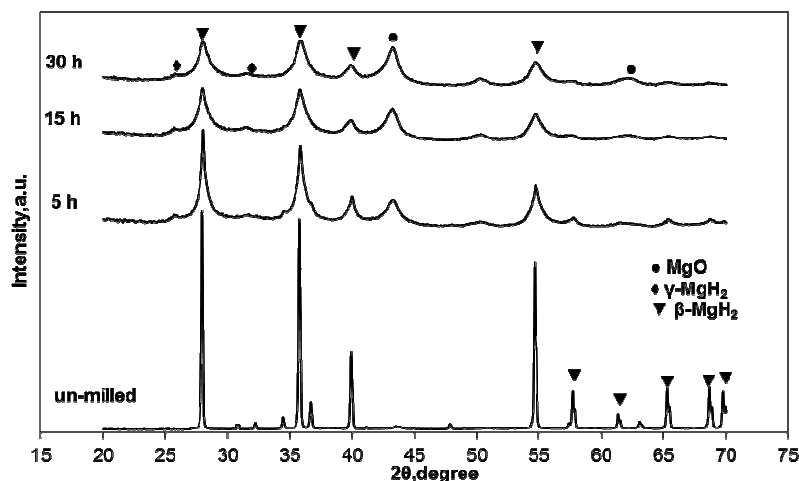


Fig. 3. XRD patterns of  $\text{MgH}_2$  powder at different milling times.

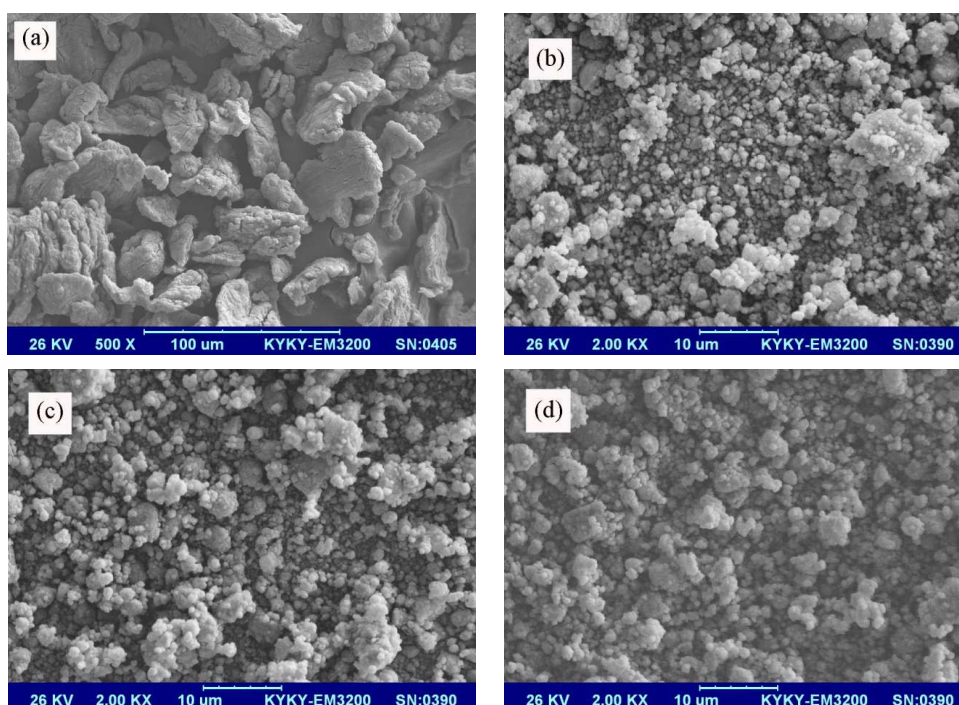


Fig. 4. SEM micrographs of as-received  $\text{MgH}_2$  (a) and ball milled for: 5 h (b); 15 h (c); 30 h (d).

refinement was obtained. The results obtained from various technical techniques including XRD, SEM and STA summarized in Table 1.

The results show that mechanical milling affects the dehydrogenation of magnesium hydride. This can be due to (i) formation of metastable  $\gamma\text{-MgH}_2$  phase, (ii) shorter diffusion paths for hydrogen within refined grains, and (iii) accumulation of lattice strain which affects the hydrogen desorption enthalpies, dehydrogenation temperature, and hydrogen

diffusion activation energy. It is worth mentioning that the formation of  $\gamma\text{-MgH}_2$  may affect the dehydrogenation process. The metastable high-pressure orthorhombic  $\gamma\text{-MgH}_2$  phase, which has a lower desorption enthalpy and temperature [14], would affect the thermodynamics and kinetics of dehydrogenation process, so its formation decreases the hydrogen desorption temperature of  $\text{MgH}_2$ . As can be seen in Table 1, the crystallite size gradually decreases from 60 nm

**Table 1.** Average particle size (D), specific surface area (S) and dehydrogenation temperature (T) of MgH<sub>2</sub> at different milling times. d and ε show the crystallite size and lattice strain of β-MgH<sub>2</sub> phase, respectively.

Time, h	Phase	D, μm	S, (m <sup>2</sup> /g)	d, nm	ε, %	T, (°C)
0	β	30	2.1	60	0	421
5	β, γ, MgO	2.2	8.4	25	0.3	340
15	β, γ, MgO	1.7	9	22	0.6	331
30	β, γ, MgO	1.6	9.3	18	0.7	319

to 18 nm by increasing milling time. Since the diffusion of atoms in grain boundaries is much faster than that of the entire lattice [15], it is acceptable that finer grain structure can promote the dehydrogenation. Additionally, a significant particle size refinement observed, i.e. from 30 μm to 1.6 μm after 30 h milling. MgH<sub>2</sub> is principally none-ductile material; so the mechanism of mechanical milling can be considered as continuous fracturing and micro welding till-approaching to the steady-state conditions [16]. The decrease in particle size should correspond to an increase in the specific surface area. BET measurement showed the variation of specific surface area in the range of 2.1-9.3 m<sup>2</sup>/g depending on the milling time. Polanski et al. [7] reported that specific surface area of MgH<sub>2</sub> increases from 1.1 to 7.3 m<sup>2</sup>/g after 20 h milling. Varin and Czujku [17] reported a profound effect of particle size on the decomposition temperature of MgH<sub>2</sub> after a certain critical threshold value (~2 μm). The present study has shown that the size of particles is approximately close to this value, so the effect of the particle size on the decomposition temperature should be considered. The results also show a gradual increase in the lattice strain with milling time. The lattice strain also significantly affects the hydrogen-desorption kinetics [18]. Zhang et al. [19] reported that the hydrogen desorption enthalpies, dehydrogenation temperature, and hydrogen diffusion activation energies decrease for strained MgH<sub>2</sub> relative to that of strain-free system, which is beneficial for the improvement of the dehydrogenation properties of MgH<sub>2</sub>. This implies a factor in the source of different dehydrogenation response of the powders. Nevertheless, MgO acts as a barrier between the solid and gas phases by limiting the diffusion of hydrogen atoms through its dense structure. Therefore, MgO can block

catalytic active centers and can prevent the dissociation of molecular hydrogen [20].

#### 4. Conclusions

Nanocrystalline MgH<sub>2</sub> powder was synthesized by milling of MgH<sub>2</sub> in a planetary ball mill for various times. The findings can be summarized as follows:

- 1- A single peak of hydrogen desorption was observed for as-received powder, In contrast, all milled powders with much reduced particle size exhibited desorption peak doublet in DTA.
- 2- Mechanical milling of MgH<sub>2</sub> up to 30 h decreased its decomposition temperature from 421 °C to 319 °C mainly due to the formation of a nanocrystal, accumulation of the lattice strain, formation of metastable γ-MgH<sub>2</sub> phase and the reduction of MgH<sub>2</sub> particle size from 30 μm to 1.6 μm. The lowest dehydrogenation temperature (319 °C) was attained at the crystallite size of 18 nm, the average particle size of 1.6 μm and accumulated lattice strain of 0.7%.
- 3- No significant difference on the onset temperature of dehydrogenation between powders milled in different times was noticed.
- 4- The amount of hydrogen release was decreased, i.e. from 5.9 wt.% to 4 wt.% with increasing the milling time from 5 h to 30 h due to the reduction of crystallite size and the introduction of lattice strain in MgH<sub>2</sub>.

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