

Nanocrystalline magnesium and its properties of hydrogen sorption

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Materials

ABSTRACT

Purpose: The goal of this paper is to study the possibility of obtaining of magnesium and magnesium hydride in nanocrystalline form and then to activate these materials for to be used in efficient systems of hydrogen storage.

Design/methodology/approach: The magnesium hydride (MgH_2) was directly synthesised from mechanically grinded magnesium powder obtained through ball milling of Mg (BM), and hydrogen of high purity. The MgH_2 was then chemical activation by surface modification of nanocrystalline Mg with nickel ultrafine particles addition. The hydrogen sorption properties of the nanocrystalline Mg were investigated by a conventional pressure-volume-temperature technique, X-ray diffraction, and scanning electron microscopy (SEM).

Findings: We found that the mechanical activation improved significantly the kinetics of hydrogen absorption in nanocrystalline magnesium, increasing sorption rates by up to 2 orders of magnitude. A profound effect of the powder particle size on the hydrogen desorption characteristics has been also observed. It was also determined that the Mg_2Ni compound absorbed hydrogen quickly and showed excellent hydrogen sorption properties at 300°C.

Research limitations/implications: The reduction of the particle size of magnesium and the creation of fresh surfaces by mechanical ball milling help the kinetics but does not affect the thermodynamics.

Practical implications: Further examination to obtain improved properties of hydrogen sorption process of magnesium based materials and investigations of achievement of new systems for hydrogen solid storage.

Originality/value: This work contains new aspects, which show the conditions of obtaining of nanocrystalline metal clusters with size under 30nm and represents new approach of improvement of hydrogen sorption process in light metals, such as magnesium, that can provide promising results for the hydrogen storage applications.

Keywords: Metallic alloys; Nanocrystalline magnesium; Hydride; Mechanical milling

1. Introduction

Hydrogen is considered to be one of leading candidates for clean energy sources in the future. For safe and efficient hydrogen storage, developments of new hydrogen storage materials are currently being researched [1-3]. The hydrogen storage capacity per unit weight of typical metal alloys is very low (about 2.2 mass%) and not sufficient for use in a fuel cell vehicle. Therefore, alloys containing light elements are focused on high performance storage materials. Most hydrogen absorbing metals are very reactive, easily forming surface oxides which then block

the uptake of hydrogen. They also require costly time consuming activation. Magnesium, in particular has a high storage capacity (7.6 wt.%) with the benefit of the low cost of the abundantly available magnesium [4-6].

For this reason, magnesium and its alloys are considered to be some of the most important candidates for reversible hydrogen storage materials. Unfortunately, magnesium hydrides have some impediments.

The main barriers for direct usage of pure MgH_2 are slow desorption kinetics, a high thermodynamic stability and a high reactivity toward air and oxygen which it has in common with most other lightweight metal hydrides [6-8]. The high

thermodynamic stability of MgH_2 results in a relatively high desorption enthalpy, which corresponds to an unfavourable desorption temperature ($> 300^\circ C$) at 1 bar H_2 [4,6]. Also, the formation of an oxide layer presents an impenetrable boundary to hydrogen gas molecules. [7]. To initiate uptake of hydrogen, the oxide layer must be cracked by activation, a long costly process. Even after activation, there is a limited dissociation rate of hydrogen molecules on the metal surface. This may be improved by a layer of catalyst, but this is also time consuming and costly [5]. Hydrogenation also depends upon the growth of the hydride on the magnesium surface. This outer layer of the hydride blocks hydrogen reaching the inner unreacted magnesium once the layer reaches a thickness of only 100 μm . This means that there is no physical way for magnesium to be fully hydrogenated [6]. The solutions for these impediments would be to form nanocrystalline magnesium hydride and then a chemical activation. Adjusting the powder size to $< 50 \mu m$ is thin enough to overcome the hydride blocking issue which require activation in polycrystalline magnesium hydride [4]. Using a mill, powders are fragmented into smaller and smaller particles and cold welded to form medium sized particles with small grain sizes [8-12].

This paper presents the possibility of obtaining of magnesium hydride (MgH_2) and then to activate this compound by reactive ball milling of Mg powder, followed of chemical activation by surface modification of Mg powder with nickel ultrafine particles addition. Thus magnesium can become an efficient material for hydrogen storage.

2. Experimental

Ball milling (BM) of Mg, was performed in a planetary mill (Fritch P5) using stainless steels balls and vials, under 1-10 bars of H_2 . It was used Mg powder ($-20 +100$ mesh, purity higher than 99.8%). Mg powder was placed in the milling chamber in the hydrogen atmosphere of a glove box. The ball to powder weight ratio used was 10:1. The purity of hydrogen was 99.995 vol.%. After MgH_2 was obtained by direct synthesis from mechanically grinded magnesium and hydrogen of high purity at temperature of $300^\circ C$ and 10 bar, this compound was mixed together with Ni powder (purity 99.9%) in a ratio of 1:0.5 in an argon atmosphere, glove box (O_2 content < 10 ppm) and then was placed in quartz tube where was vacuumed and heated at $300^\circ C$ for 8 hours. The purity of argon was 99.995 vol.%. For comparison, MgH_2 (typical size $\sim 80-100 \mu m$) was milled at 300 rpm in planetary ball mill, for 15 hours in an argon atmosphere in a stainless steel milling pot (250 ml) using 10:1 ball to powder ratio.

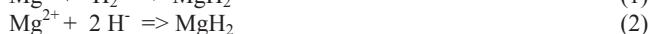
Small amounts of the powder of Mg and MgH_2 were taken from the mill at regular periods of time for morphological, structural and thermal analysis. Their structures were studied by X-ray diffraction (XRD, Philips Electronic Instruments, PW 1710). Then the samples were placed in a closed system with constant volume under pure hydrogen/argon atmosphere (99.995%) to study the hydrogen sorption (absorption/desorption) kinetics. The amount of absorbed hydrogen was estimated from the decrease of pressure in time and by determination of H_2 concentration in argon. The successive hydrogen absorption/desorption kinetic measurements were performed at $300^\circ C$.

The system used for thermal absorption/desorption process, utilizes a temperature controlled furnace and a fused silica tube where in hydrogen charged sample is heated at a constant rate under a constant argon or hydrogen carrier flow. For subsequent analysis, the release argon and hydrogen gas is fed into a gas chromatograph Hewlett Packard which permits quantitative analysis.

3. Results and discussions

3.1. Kinetic factors in the reaction of Mg and H_2

Magnesium metal transforms into magnesium hydride in a gas-solid reaction, according the following chemical reactions:



In the solid phase MgH_2 forms a hydride bridged polymer, such as presented in Figure 1, that confer a high stability.

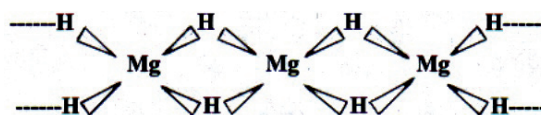


Fig. 1. Schematic representation of solid phase of MgH_2

The hydriding reaction of metallic magnesium involves several steps: (1) gas permeation through the particle bed, (2) surface adsorption and hydrogen dissociation, (3) migration of hydrogen atoms from the surface into the bulk, (4) diffusion through the particle and finally (5) nucleation and growth of the hydride phase. In principle each of these steps might be rate limiting.

The practical use of magnesium as a storage medium is limited especially if the size of the Mg particles is too large. A self-passivating layer of MgH_2 is formed, preventing any further hydrogen uptake due to the low diffusion rate of H through the MgH_2 β -phase. The thickness of this layer is about 200 nm at low hydrogen pressure but the thickness decreases with increasing pressure. Reducing of the size of the Mg particle, i.e. making it smaller than the thickness of the hydride layer, improves the uptake performances. However due to kinetics, i.e. too high absorption and desorption temperature (a temperature of more than $300^\circ C$ to dehydride of MgH_2) the practical use as a storage medium is severely hampered. Alloying Mg with other elements that do not form stable hydrides, d-elements like Ni or Pd, improves the thermodynamic and kinetic properties. However, this results in a significant reduction of the hydrogen uptake.

3.2. Effect of BM on pure Mg and MgH_2

On decreasing the particle size by ball milling (BM) of magnesium and magnesium hydride a high density of defects and

distortions is introduced. It is known from previously studies [7,13-15] that the abundant defects and distortions in the magnesium structure does not play a decisive role in the increase of the sorption rate as they are annealed out when the hydrogen content is cycled, while the kinetics remain fast. Therefore, the ball milling treatment is regarded mainly as a method to produce nanostructured and catalyzed magnesium particles in large quantities.

The effect of ball milling on pure magnesium is the breaking of the surface oxide layer and the exposure to hydrogen of fresh Mg surfaces creating during the deformation process explain the reduced need for activation. The hydrogen sorption kinetics are improved significantly, Mg with a crystallite size under 30 nm absorbs about 3.8 to 4.2 wt.% of hydrogen after 20 minutes at 300°C, under 10 bar, while conventional polycrystalline Mg powder practically does not absorb hydrogen under these conditions. The good hydrogenation kinetics of nanocrystalline Mg could be explained by a reduced surface barrier, an abundance of defects that act as nucleation sites for the hydride phase and by grain boundaries that facilitate hydrogen diffusion in the matrix.

The milling of pure Mg which is a ductile material, often results in excessive cold welding and formation of large agglomerates. One way to get around that problem is by milling MgH₂ which is a quite brittle material. X-ray diffraction shown that after 8 hours of milling, the stable structure β -MgH₂ partly transform into a metastable nanocrystalline γ -MgH₂ phase.

Additional milling to 20 hrs does not further decrease the crystallite size or increase the phase abundance of this new phase. The crystallite sizes are 30 and 45 nm for the β and γ phase respectively. The specific surface area increases by a factor of ten during milling. The reduced crystal size, increased surface area and the presence of numerous defects all contribute to improve the hydrogen sorption kinetics as shown in Figures 2 and 3.

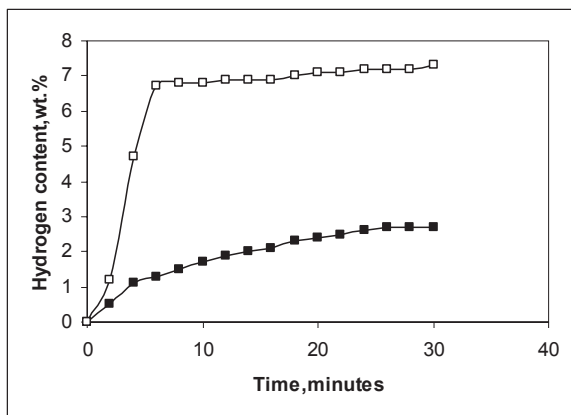


Fig. 2. Hydrogen absorption of unmilled (filled) and milled MgH₂ (open marks): Pressure 10 bar; Temperature 300°C

At 300°C, ball milled MgH₂ absorbs about 4.8 wt.% of hydrogen in 3 minutes. In comparison, unmilled MgH₂ absorbs about 2.8 wt.% of hydrogen in 30 minutes (see Figure 2). The absorption kinetic of milled MgH₂ is about 10 times faster than in the case of unmilled MgH₂. With regarding to the desorption process, at 300°C, the unmilled powder is not completely desorbed after 30 minutes. While milled MgH₂ is

approximately completely desorbed after about 12 minutes. On the other hand, both the milled and unmilled curves have a sigmoid shape which means that a nucleation and growth processes take place during desorption (see Figure 3).

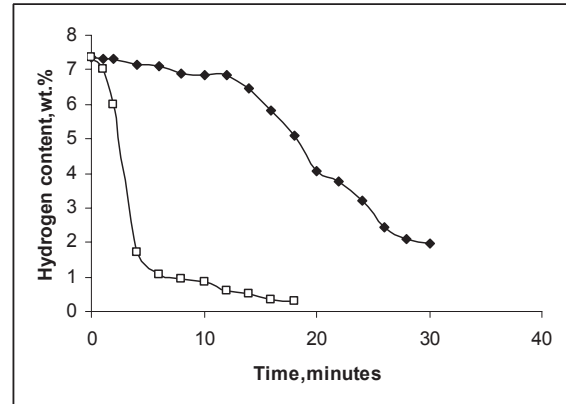


Fig. 3. Hydrogen desorption of unmilled (filled) and milled MgH₂ (open marks). Pressure under 0.1 bar; Temperature 300°C

The above results shown that the mechanical activation through ball milling reduces particle size, increases specific surface area, and introduces nanograins as well as a large amount of defects to magnesium and magnesium hydride particle. All of these changes induced by ball milling enhance the hydrogen absorption/desorption process in magnesium. The activation energy decreases as the ball milling time increases.

3.3. Chemical activation of MgH₂

It has been shown that the hydrogen sorption kinetics of Mg can be greatly improved if the material is prepared with a nanocrystalline microstructure through high velocity ball milling. An enhancement in the absorption/desorption kinetics of MgH₂ it was also observed through reaction with small amounts of Ni ultrafine particles. The reaction kinetics have been accelerated significantly, even at ambient temperature. The hydrogen desorption kinetics of MgH₂ with 0.5 wt.% Ni addition after six hydrogen desorption and reabsorption cycles are shown in Figure 4, compared to MgH₂ milled for 15 hrs.

It is apparent that MgH₂ with 0.5 wt.% Ni addition desorbed hydrogen significantly faster than both the unmilled and milled MgH₂. Figure 5 shows the scanning electron microscopy images before hydrogen desorption of: a) MgH₂ milled for 15 hrs and b) MgH₂ / 0.5 wt.% Ni. The combination of MgH₂ (Mg) with the smaller crystallites, the nano Ni catalyst and the high H₂ pressure gives rise to the excellent absorption /desorption kinetics.

The experimental results shown that the milling of the MgH₂ itself, improves the desorption and absorption kinetics over those of the unmilled MgH₂ because of the smaller crystallite size. The fine powder structure of magnesium and Ni ultrafine particles addition to MgH₂ observed by scanning electron microscopy, may be very important factors in the fast kinetics of both MgH₂ milled and MgH₂ / 0.5 wt.% Ni materials. Chemical activation of

magnesium is new route for activating the hydrogen store MgH_2 , that results in highly effective hydrogen uptake and release characteristics, comparable to those obtained from mechanically milled material.

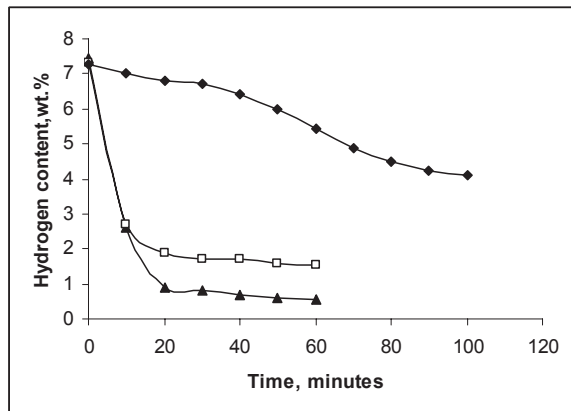


Fig. 4. Hydrogen desorption kinetics at 250°C, under 0.1 bar H_2 (■) MgH_2 unmilled; (□) MgH_2 milled for 15 hrs; (►) MgH_2 with 0.5 wt.% Ni addition.

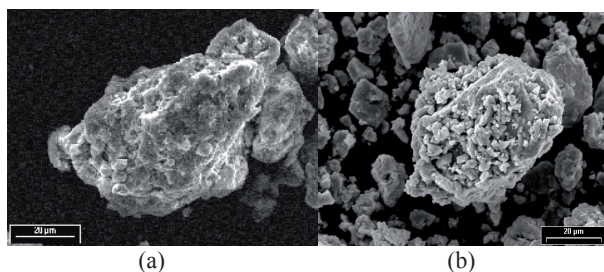


Fig. 5. Scanning electron microscopy images before hydrogen desorption of: a) MgH_2 milled for 15 hrs; b) $MgH_2/0.5$ wt.% Ni

4. Conclusions

Mechanical grinding can be used to synthesize low and high temperature metal hydride systems. The nanostructured materials is beneficial for the hydrogen absorption and desorption kinetics, especially in the case of Mg-based systems where the improvement in kinetics is very significant. For Mg-based systems, no significant loss of capacity is observed after ball milling and strain is usually released at the operating temperature. The changes induced to magnesium powder by ball milling enhance the hydrogen sorption process. Chemical activation of magnesium hydride is a new route to obtain superior hydrogen storage materials.

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