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Letter

A new approach to the processing of metal hydrides

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ABSTRACT

In this paper we show that severe plastic deformation techniques could be used to enhance hydrogen sorption properties of metal hydrides. Commercial magnesium hydride was processed in a vertical cold rolling apparatus. After only five rolling passes hydrogen sorption kinetics at 623 K were greatly enhanced without noticeable loss of capacity. The improvement in sorption kinetics is probably due to the nanocrystalline structure and number of defects. Investigation of the powder morphology and crystal structure indicates that cold rolling is equivalent to ball milling.

1. Introduction

Magnesium is one of the most abundant elements in the earth crust, it is inexpensive and its hydride has one of the highest hydrogen capacity of elemental hydrides. Unfortunately, the hydrogen sorption in magnesium is slow and occurs at elevated temperature. It is well established that ball milling greatly enhances the hydrogen sorption kinetics of Mg and Mg-based alloys [1]. Numerous authors have shown that high energy ball milling is a good way to improve hydrogen sorption kinetics and to add catalysts in the form of nanocomposites [2–7]. However, as this type of milling necessitates relatively high specific energy, production of nanoscale materials in industrial amount with this technique may be quite expensive in term of capital and operation costs.

Recently, severe plastic deformations (SPD) techniques such as equal angular channel pressing (ECAP), high pressure torsion (HPT), forging, and cold rolling have been investigated as means to synthesize and process alloys in order to give them enhanced hydrogen storage properties. Skripnyuk et al. used ECAP to process Mg-based alloys after which the alloys were powdered by filing with a rasp [8–10]. Processing of $MgNi_2$ by HPT has been studied by Kudasome et al. [11]. They found a significant reduction of crystallite size and an hydrogen sorption of 0.1 wt.% in the grain boundaries. Lima et al. also used HPT to process Mg–Fe powder mixture and showed that hydride was produced by subjecting the mixture to HPT followed by hydrogen exposure at 623 K and 3 MPa [12].

The effect of cold rolling on hydrogen sorption properties have been studied by various authors. Ueda et al. prepared a Mg–Ni laminated composite followed by heat treatment which produced Mg_2Ni [13]. Exposure of the heat treated sample to hydrogen lead to complete hydrogenation, producing Mg_2NiH_4. Zhang et al. investigated the effect of cold rolling on the hydrogen sorption properties of Ti–22Al–27Nb alloy [14,15]. They reported that hydrogen absorption and desorption properties are improved by small deformations; however this improvement is lost upon hydrogen cycling. Also, they found no sorption enhancements for highly deformed samples. Recently, Miyamura et al. have made a systematic investigation of the effect of cold rolling on various Mg-based compounds such as Mg/Cu, Mg/Al, Mg/Pd [16–19]. Dufour and Huot investigated the Mg/Pd system and found that preparation of the composites by cold rolling resulted in alloys that had much faster first hydrogenation (activation) and better resistance to air exposure [20,21].

To our knowledge, SPD techniques for hydrogen storage application have only been used on metal. Recently, Leiva et al. have investigated the effect of SPD (HPT, CR, Forging) on MgH_2 and MgH_2–Fe mixtures [22]. They found that SPD reduces crystallite size and, similar to ball milling, could also produce the high pressure high temperature γ-MgH_2 phase. This means that for magnesium hydride SPD methods could be considered as replacement for ball milling technique.

Amongst SPD techniques, cold rolling is probably the easiest to scale up for industrial applications. In the work of Leiva et al. to

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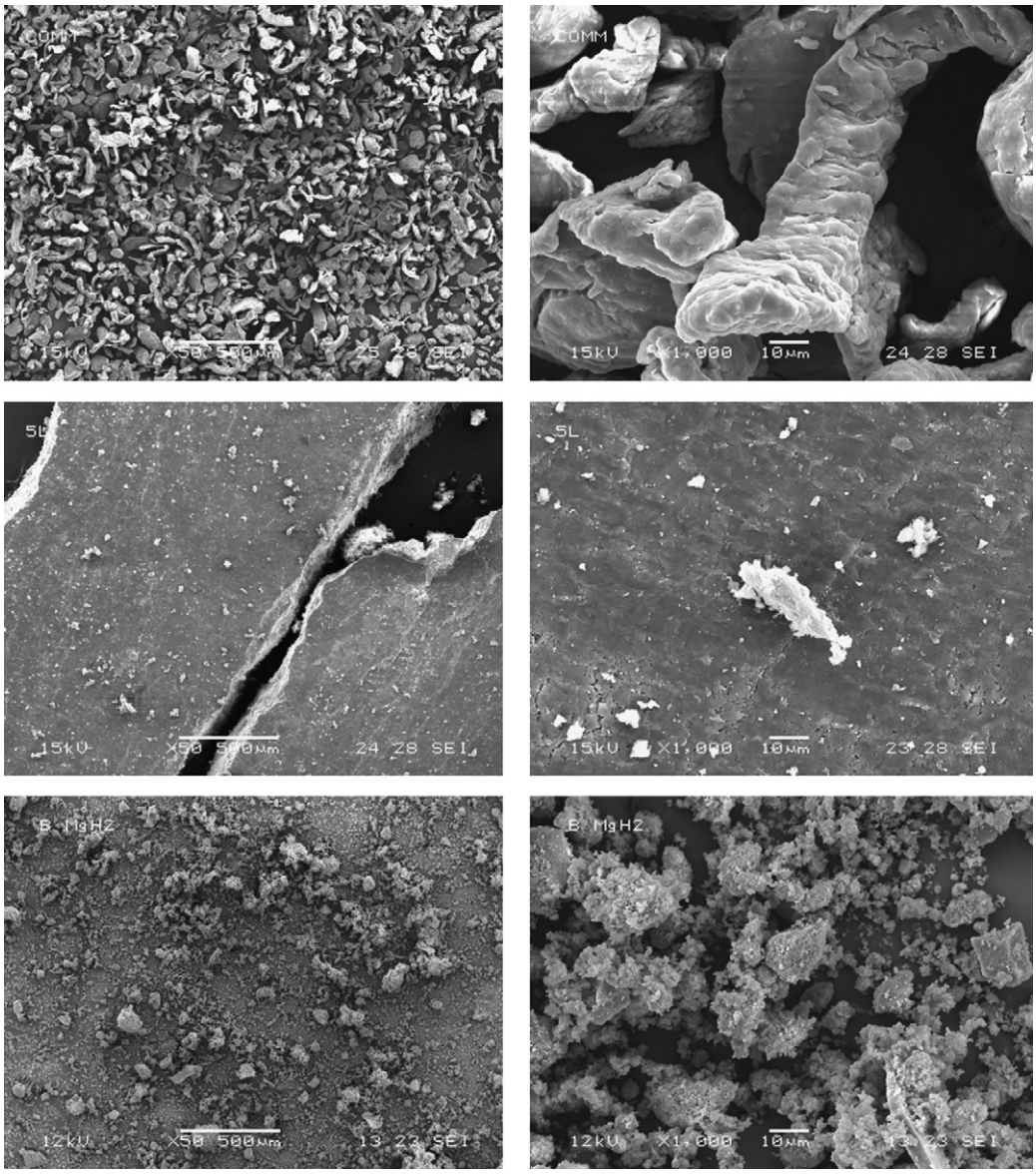

Fig. 1. Scanning electron microscope (SEM) micrographs of MgH_2: as received on top, cold rolled in the middle and ball milled on bottom. Magnification: left column 50×, right column 1000×.

process MgH_2 by cold rolling the powder was first sealed in a SS tube and then rolled [22]. Such a set up has the advantage of not exposing the powder to the air but it reduces the deformation experienced by the powder because the SS tube will take a good part of the deformation. Also, the numbers of rolls that could be performed before rupture of the tube is limited. Moreover, this method makes the preparation lengthy, expensive, and practically impossible to scale up.

As commercial magnesium hydride is quite stable and has a slow kinetic reaction, exposure to the air does not usually lead to violent oxidation. Evidently this phenomenon depends on the exact nature of the MgH_2:nanocrystalline MgH_2 is more reactive and may react in air at room temperature. Still, we decided to use this low reactivity of MgH_2 to air to investigate the possibility of cold rolling magnesium hydride in air.

In this paper we report the effect of cold rolling MgH_2 in air. As a mean of comparison, we also processed MgH_2 in a high energy ball mill under argon atmosphere. The effects on the morphology, crystal structure and hydrogen storage properties of cold rolling in air and ball milling in argon were investigated.

2. Experimental details

The cold-rolling apparatus used in this study was a Durston DRM 100 modified by the company to have the sample go in vertically. This set-up greatly facilitates the rolling of powders because the powder could be easily collected in a pan under the rolls. The rolling cylinders are made out of stainless steel and are 13 cm long with a diameter of 6.5 cm. They are driven by a 1.1 kW Rossi Motoriduttori DC electric motor. We processed 300 mesh MgH_2 powder (96% purity), provided by Alfa Aesar, between two #316 stainless steel plates. Cold rolling magnesium hydride agglomerates the powder into plates with thicknesses varying from 0.3 to 0.8 mm. The material is then collected in plate form and rolled again. The time for one rolling pass is one or 2 s. Therefore, for a sample rolled 5 times, the total time the powder was subjected to rolling is estimated to be 10 s.

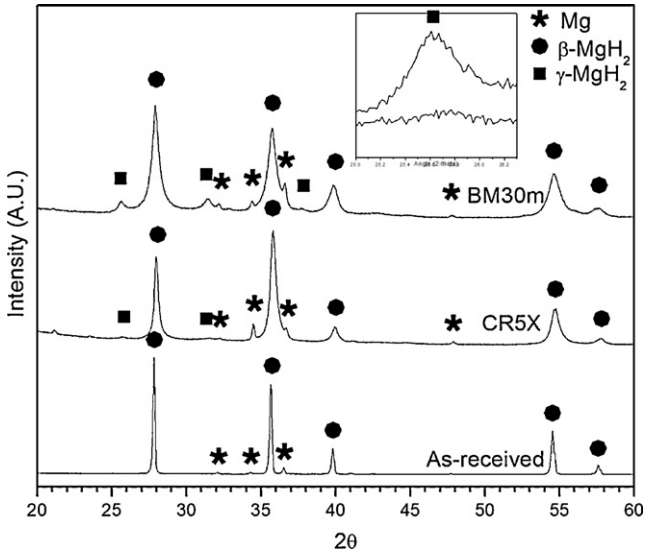

Fig. 2. X-ray diffraction patterns of MgH_2: as received (bottom), cold rolled five times (middle) and mechanically milled for 30 min (top).

Ball milled samples were processed in a SPEX high-energy mill for 30 min. As-received 300 mesh MgH_2 powder was inserted into a stainless steel crucible in an argon glove box. Stainless steel balls were added to have a ball to powder weight ratio of 10:1. After milling, the samples were stored in a glove box.

Absorption and desorption curves were made at 623 K, 2 Mpa and 0.06 Mpa, respectively, using a home-made PCT apparatus. The crystal structure was investigated by x-ray powder diffraction on a Bruker D8Focus apparatus with Cu-Kα1 radiation. Crystallite size and microstrain were evaluated from Pawley method [23] using Topas software [24]. Electron microscopy was made with a Jeol JSM-5500 SEM. The samples were metalized with a POLARON SC 7620 sputter coater. A gold deposit of 37 nm was sputtered on the samples to improve conductivity.

3. Results and discussion

Morphology of as received, cold rolled and ball milled MgH_2 is shown in Fig. 1. As seen on these micrographs, the as received MgH_2 has a long wormlike shape. It has a width of about 10–20 μm and a length of the order of 100 μm. Cold rolling the sample for five times agglomerate the powder into plates of approximately 300 μm thick. Therefore, despite the fact that magnesium hydride is a brittle material, cold rolling is seen to be a good method for agglomeration. The morphology of ball milled samples is drastically different than the cold rolled one. Ball milling had the effect of breaking up the big particles seen in the as-received samples into much smaller sphere-like shape particles of sizes ranging from 1 to about 15 μm. Some particles are also agglomeration of smaller ones.

Crystal structure was investigated by X-ray powder diffraction. X-ray patterns of as-received, cold rolled and ball milled samples are presented in Fig. 2. In the case of the cold rolled and ball milled samples, the broad peaks indicate a nanocrystalline structure. Crystallite sizes and microstrains deduced from Pawley method are shown in Table 1. As expected, the as-received sample shows relatively big crystallite size and small strain. Ball milling reduced the crystallite size and increased the strain in the β-MgH_2 phase. As for cold rolling, it could be seen that it also reduced the crystallite size but not as much as ball milling. However, the strain induced in the cold rolled sample is higher than in the ball milled sample. It may be because cold rolling will act more in a 'shear' mode than ball milling. In any case, it is clear that cold rolling is as effective as ball milling to produce a nanostructure and to induce microstrain.

Table 1
Crystallite size and strain for β-MgH_2 in the as received, cold rolled and ball milled states.

MgH_2 sample	Crystallite size (nm)	Strain %
As received	187 ± 4	0.263 ± 0.004
BM30m	13.7 ± 0.2	0.61 ± 0.05
CR5X	31.3 ± 0.4	0.84 ± 0.02

Another remarkable feature is the absence of magnesium oxide or hydroxide peaks in the diffraction pattern of the cold rolled sample. Therefore, even if rolling was performed in air the amount of oxides and hydroxides is smaller than the detection level of X-ray powder diffraction (a few wt.%). A common result of high energy milling is the formation of metastable states. In the present case of some β-MgH_2 was transformed to the high-temperature high-pressure γ-MgH_2 phase during ball milling. As seen in the insert of Fig. 2 the X-ray pattern of cold rolled sample also shows incipient peak belonging to the γ-MgH_2. Therefore, even if cold rolling was performed for less than 10 s compared to 30 min for ball milling, the process was energetic enough to start the conversion of some β-MgH_2 to γ-MgH_2.

The hydrogen absorption kinetics are shown in Fig. 3. For better comparison, the hydrogen content is given with respect to the theoretical maximum capacity of magnesium (7.6 wt.%). It is clear that the as-received MgH_2 has a very slow kinetic and that ball milling for 30 min drastically enhanced hydrogenation kinetic. The beneficial effect of ball milling on hydrogen sorption kinetics of magnesium hydride is a well established fact and is not surprising. The remarkable fact is that the sample rolled 5 times shows kinetics almost as fast as the sample ball milled for 30 min. It should be pointed out that the rolling was performed in air while ball milling was done under argon. Also, total rolling time was of the order of 10 s while milling was performed for 30 min.

Desorption kinetics are shown in Fig. 4. Desorption kinetic of as-received magnesium hydride is very slow. As in the case of absorption, cold rolling is almost as effective as ball milling to improve kinetics. Moreover, curves of ball milled and cold rolled samples have the same general shape. This means that the rate limiting step is probably the same for both. The main difference

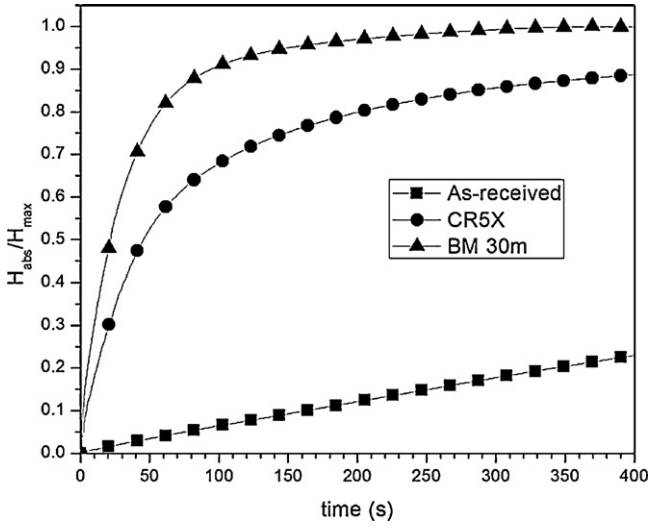

Fig. 3. Normalized kinetic absorption at 623 K and under 2 MPa hydrogen pressure of MgH_2 in as-received, cold rolled five times, and mechanically milled states.

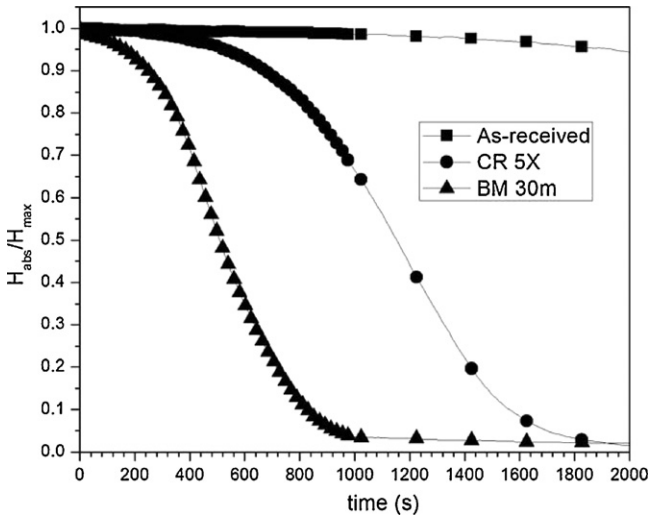

Fig. 4. Normalized kinetic desorption at 623 K and under 0.06 MPa hydrogen pressure of MgH_2 in as-received, cold rolled five times, and mechanically milled states.

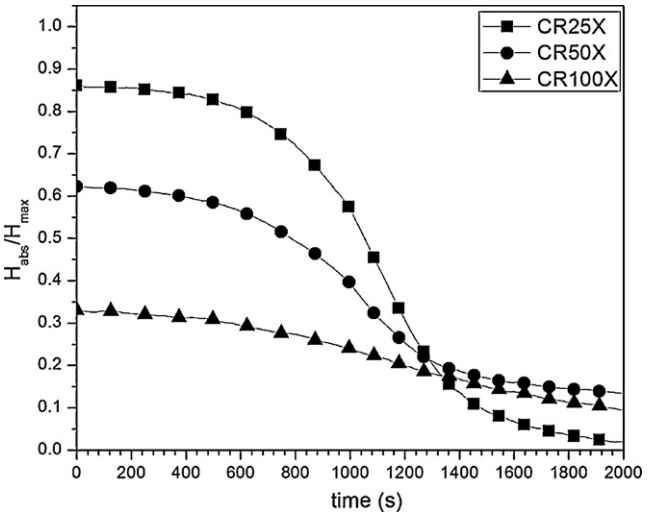

Fig. 6. Normalized desorption at 623 K and 0.1 MPa of hydrogen pressure for cold rolled MgH_2.

between these two curves is incubation time. In the case of ball milled sample the reaction onset is about 290 s while for the cold rolled sample the incubation time is 780 s. However, once the reaction started the slopes are similar.

Therefore, we could see that cold rolling is extremely effective for improving hydrogenation kinetics of metal hydrides. Its effect on magnesium hydride is the same as ball milling with the enormous advantage of being performed in air and with a processing time reduced by two orders of magnitudes.

In the same way as for ball milled samples, the increase in hydrogen sorption kinetics shown in our cold rolled samples could be attributed to its nanocrystalline structure and formation of defects. As cold rolling seems to be more efficient than ball milling to produce nanocrystalline structure, we investigated the effect of number of rolls on the hydrogen sorption properties of magnesium hydride. Magnesium hydride powder was cold rolled in air for 25, 50, and 100 times. In Fig. 5 we present the hydrogenation kinetics of these samples. It is clear that with the numbers of rolls, the reaction kinetics get slower and the capacity decreases.

Desorption curves are shown in Fig. 6. As for absorption, the kinetic get slower with the number of rolls. However, the incubation time (onset) decreases with number of rolls. This is an indication that the number of defect increases with number of rolls even if the total capacity is getting smaller. The reason for the drastic reduction of capacity is the presence of oxides as seen in the diffraction patterns shown in Fig. 7.

From the diffraction pattern taken after 25 rollings, we conclude that the crystal structure does not change much except that the MgO peak grows. As this peak is very broad, it indicates that the crystallite size of the oxide is very small (a few nm). The relative intensity of the oxide peaks goes up with rolling number. This confirms that the reduction of hydrogen capacity is due to the formation of oxide as expected. We saw that rolling is very efficient to increases reactivity in magnesium hydride. But, because all handling was done in air, as the reactivity increases the reaction with air will also increases thus leading to formation of oxide. This means that rolling has to be performed in an inert atmosphere when the number of rolling passes is high.

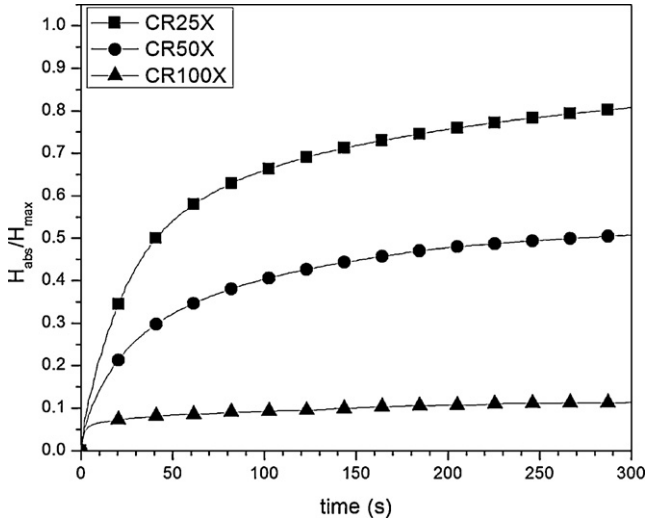

Fig. 5. Normalized absorption at 623 K and 2 MPa of hydrogen pressure for cold rolled MgH_2.

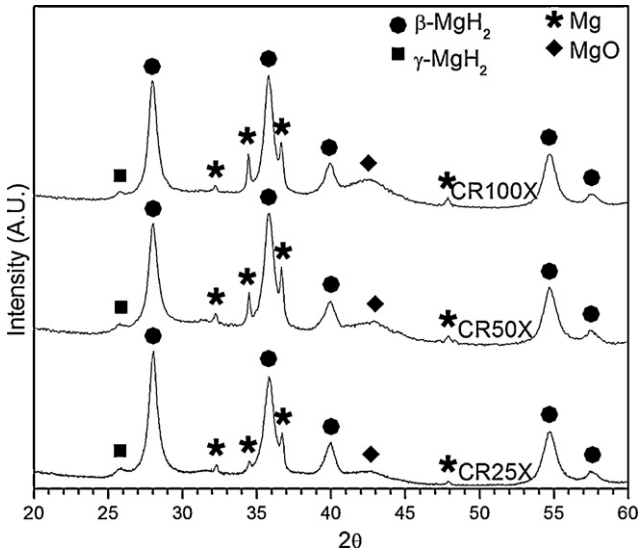

Fig. 7. XRD patterns of MgH_2 cold rolled for 25, 50 and 100 times.

4. Conclusions

In this investigation we showed that cold rolling is a good way to produce nanocrystalline structure in magnesium hydride. In term of processing time and energy spend it is much more efficient than ball milling. Moreover, it could be performed in air if the number of rolling is limited. After only 5 rolls, we measured an important enhancement of hydrogen sorption properties, comparable to ball milling for 30 min and without loss of capacity. This processing technique could easily be applied at the industrial level.

Acknowledgments

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