Exploring several different routes to produce Mg-based nanomaterials for Hydrogen storage

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Abstract. Severe mechanical processing routes based on high-energy ball milling (HEBM) or severe plastic deformation (SPD) can be used to produce Mg nanomaterials for hydrogen storage applications. In the last few years, we have been exploring in our research group different SPD processing routes in Mg systems to achieve good activation (first hydrogenation) and fast H-absorption/desorption kinetics, combined with enhanced air resistance. In this paper, we compare SPD techniques applied to Mg with HEBM applied to MgH2. Both advanced - melt spinning (MS), high-pressure torsion (HPT) - and more conventional - cold rolling (CR), cold forging (CF)- techniques are evaluated as means of production of bulk samples with very refined microstructures and controlled textures. In the best SPD processing conditions, attractive H-absorption/desorption kinetic properties are obtained, which are comparable to the ones of MgH2 milled powders, even if the needed temperatures are higher – 350°C compared to 300°C.CR and CF stand out as the processes with higher potential for industrial application, considering the level of the attained hydrogen storage properties, its simplicity and low cost.

1. Introduction

MgH2 is a very interesting material for hydrogen storage applications since it has very high gravimetric hydrogen capacity (7.6 %) and presents high reversibility and cyclability [1]. Besides, magnesium is a low cost and non-toxic metal and can be easily recycled. These features are very important to promote the wide application of hydrogen solid tanks [2]. Conventional (microcrystalline) MgH2 has very slow hydrogen absorption and desorption kinetics even at temperatures as high as 400°C [2]. However, it is well known that nanostructuring MgH2 by HEBM has a very positive impact on its hydrogen storage properties, leading to faster kinetics at much lower temperatures [3]. Nanocrystalline MgH2-based materials prepared by HEBM present high specific surface area, which favors faster kinetics of hydrogen reaction but it is also highly susceptible to air contaminants as oxygen or moisture, and therefore it should be processed and handled under inert atmosphere [4]. On the other hand, different processing techniques based on severe plastic deformation (SPD) are being explored to produce Mg or MgH2 materials suitable for hydrogen storage applications, combining acceptable hydrogen storage properties with better air resistance [5]. The main advantages of using SPD techniques instead of HEBM are that SPD techniques could be much simpler, cost effective and close to industry practice, since it is normally...
performed in air, requiring only a few minutes or even seconds to accomplish processing. Furthermore, it is often a variation of known techniques as rolling, extrusion or forging [6]. To illustrate the potential for innovation associated to the use of SPD processing routes, we have performed a patent search in the Derwent Innovation Index database [7], including all years and all sections, using the search expression that is detailed as supplementary data. A total of 275 patent documents were retrieved. Seventy three of them mentioned the alloys' base metals, of which 29% refers to Aluminum, 25% to Iron/Steel, 19% to Titanium, 15% to Magnesium and 12% to Copper. Two hundred and four documents mentioned the SPD method used, comprising: 65% Angular pressing, 30% Asymmetric Rolling, 6% Cold Rolling, 5% High Pressure Torsion and 4% Accumulative Roll Bonding. The main countries of origin were: 30% Russia (including USSR), 22% China, 15% South Korea, 11% United States and 10% Japan. Surprisingly, none of these patent documents was related to hydrogen storage materials, despite of the strong academic activity in the field, which can be exemplified by the studies cited below.

Extensive CR of Mg-2.5 at.%Pd was performed by Dufour and Huot [8]. The air-exposed laminated samples presented faster activation (first hydrogenation) and similar kinetics of hydrogen absorption and desorption when compared to a sample ball milled for 2 h. It revealed the potential of SPD for the production of hydrogen storage materials. Equal channel angular pressing (ECAP) was also explored as a mean to produce grain refined Mg alloys for hydrogen storage [e.g. 9-12]. However, in this case, to maintain the structural integrity of the billets and therefore allow the application of several ECAP passes, temperatures at least around 200°C are needed, which limits considerably the final grain size and density of defects [9]. In our research group, we have been exploring the potential of different SPD processing routes to produce nanostructured Mg alloys or composites for hydrogen storage applications [e. g. 9, 13 - 18].

In this paper, Mg samples were severely deformed trough different techniques as HPT, CR, CF and melt spinning followed by cold rolling (MS + CR). The results of microstructural refinement, texture and hydrogen storage properties are compared for the different used SPD routes and also with the ones obtained for ball-milled MgH$_2$, showing the potential of SPD techniques to produce hydrogen storage materials.

2. Experimental

A commercial Mg ingot (FOSECO, 99.8%) was cut into small samples of a few milimiters thickness. After surface cleaning, the material was processed by different SPD routes: HPT, CR, CF, MS + CR. The Mg melt spun ribbons were produced using a graphite crucible in a single roller melt-spinning wheel at a tangential wheel speed of 42 m/s in an argon atmosphere. HPT processing was performed using a pressure of 5 GPa and five turns. The Mg samples were confined between two stainless steel plates for processing by CR and CF. A FENN duo-reversible rolling machine was used for CR processing, and after several passes, around 95% of thickness reduction was obtained. Forging was carried out by dropping a 30 kg hammer thirty times from a height of 1.50 m onto the sample. For comparison, MgH$_2$ powders (Alfa Aesar, 98%) were processed by 10 h of HEBM in a FRITSCH P5 mill, with a ball-to-powder weight ratio of 50 : 1.

Structural characterization was made by scanning electron microscopy, SEM (Phillips FEG XL 30), and transmission electron microscopy, TEM (FEI TECNAI, 200 kV). X-ray diffraction (XRD) patterns were obtained in two different diffractometers: Rigaku Geigerflex (Cu cathode) and Siemens D5005 (Co cathode). In the case of the milled MgH$_2$, the XRD patterns were used to estimate the average crystallite size by the Scherrer method, as described by Lu e Lai [19]. The H-desorption behavior of the magnesium hydride sample was evaluated by differential scanning calorimetry (DSC) coupled to thermogravimetric analysis (TGA) and mass spectrometry(NETZSCHDSC 404, Aëlos QMS 403C), operating under Ar
flow and using a heating rate of 10°C/min. Hydrogen absorption and desorption kinetic measurements were performed in a home-made Sievert volumetric apparatus.

### 3 Results

Figs. 1 (a), (b) and (e) show the morphology of the MgH₂ milled powder and Mg cold rolled foil. The magnesium hydride is constituted of agglomerates of very fine particles, most of them with diameters below 1 μm, and frequently reaching the nanometric scale. On the other hand, cold rolled or cold forged Mg assumes the form of thin foils of typical thickness of only 0.1 mm.
The effects of ageing (prolonged air-exposure) of the MgH$_2$ samples, in the as-received and milled conditions can be evaluated through the analysis of Figs. 1 (c) and (d). Fig. 1 (c) shows an increase in the hydrogen desorption range with the increase of ageing time, while Fig. 1 (d) illustrates the full conversion of the as-received MgH$_2$ to Mg(OH)$_2$ after long exposure to moisture present in air, since the mass spectrometry and TGA associates water release with the DSC endothermic peak presented by the aged sample. Water release is a result of the heating of magnesium hydroxide [4]. The activation behavior of the Mg sample after CR is presented in Fig. 1 (f). This kinetic measurement was performed after cold rolling in air and subsequent ageing of around 01 month. However, a good activation behavior is observed for the cold rolled sample.

The microstructural differences among the samples processed by HEBM and different SPD techniques are evidenced in Figs. 2 and 3. The XRD patterns of MgH$_2$ before and after HEBM are shown in Fig. 2 (a), while Fig. 2 (b) exhibits the XRD patterns of Mg in the as-received, MS and MS + CR. The mean crystallite size of MgH$_2$ was estimated by the Scherrer method as 37 nm. The Mg sample prepared by MS + CR present larger width XRD of peak than the as-received and MS condition. The MS + CR sample exhibits a high level of [002] fiber based texture, as indicated by the comparison of the relative intensities of the XRD relative intensities of the (002) and (101) peaks.
Figure 2. XRD patterns of (a) MgH$_2$ before and after HEBM and of (b) the Mg as-received and after MS or MS + CR. In this case, the diffracted intensity of each pattern was normalized considering the (101) planes as a reference.

Fig. 3 present TEM images of different Mg samples processed by SPD. The typical microstructure of the cold rolled sample is shown in Figs. 3 (a) and (b). In this case, coarser grains of several microns of diameter coexist with other grains and subgrains that are much smaller, most of them being submicrometric. The dislocation density is increased due to cold work, as illustrated by Fig. 3 (b). The microstructure obtained for the CF sample is similar to the obtained by CR (not shown here). The heterogeneous grain size obtained after CR (or CF) is related to the very initial grain size of the as-cast Mg ingot, of several millimeters. Mg samples with more refined and homogeneous microstructures were obtained by HPT, Fig. 3 (c), and by MS + CR, Fig. 3 (d). The intense straining provided by HPT and the small grain sizes of the MS sample (from 2 to 5 m) are responsible for the higher microstructural homogeneity in these samples.
Figure 3 (a) TEM micrograph (bright field) of Mg after CR. (b) Corresponding dark-field TEM image which was recorded using reflection from the first Mg ring from selected area electron diffraction pattern (SAEDP) (not shown here) showing details of a deformed grain. (c) STEM bright field of the samples prepared by HPT and (d) MS + CR.

The results of the H-absorption/desorption kinetic measurements for the ball milled MgH$_2$ and for the Mg processed by MS and MS + CR are presented in Fig. 4. An important detail about these measurements is the difference in the chosen temperature, being 300°C for the MgH$_2$ sample and 350°C for the Mg samples. After only 10 min, the ball milled sample has already absorbed more than 5 wt. % of H$_2$ as indicated in Fig. 4 (a); while the hydrogen desorption is much slower and takes around 3 h to reach the same capacity as shown in Fig. 4 (b). The combination of the MS and CR processes leads to a pronounced improvement in the H-absorption/desorption kinetics, as seen in Figs. 4 (c) and (d) respectively. For the MS + CR sample, after 1 hour, the absorbed capacity is around 4%, and continues to increase at longer times; desorption also occurs faster than for MS sample and the same capacity of 4 wt. % is achieved after 44 min.
Figure 4. Kinetic curves for the ball milled MgH₂: (a) absorption (300°C, 8 bar of H₂) and (b) desorption (300°C, 0.3 bar of H₂); similar results for the Mg after HPT, CR, MS and MS + CR, as indicated, after activation: (c) absorption (350°C, 20 bar of H₂) and (d) desorption (350°C, 0.3 bar of H₂).

4 Discussion

Bulk Mg samples with refined microstructures can be produced by SPD or SPD-like processing techniques, in contrast to the nanostructured powders that can be prepared by HEBM. Processing by SPD is much simpler than by HEBM, which can be performed in air, with much lower time and energy consumption. The brittle magnesium hydride suits well for HEBM, because it avoids excessive material losses during milling when compared to the ductile Mg, which sticks easily to the milling tools. However, MgH₂ has low air-resistance. In the microcrystalline condition, it reacts slowly with the moisture present in air to form Mg(OH)₂, Fig. 1 (d), and therefore losing its hydrogen storage functionality. After milling, its reactivity increases considerably, due to the intense microstructural refinement and also specific surface area, which favors better hydrogen storage properties, as illustrated in Figs. 4 (a) and (b), but also a much smaller air-resistance, Fig. 1 (c).

On the other hand, magnesium processed by SPD presents an elevated air-resistance, but this property enhancement is achieved at the expenses of a slow activation kinetics, Fig. 1 (f). The activation behaviour of the CR sample can be compared to the one exhibited by a similar sample processed by ECAP, in a previous work of our group [9]. In this case, no hydrogen absorption was obtained, unless the sample was submitted to a combination of ECAP with CR and HEBM. The thickness of the ECAPed bulk samples has shown to be a serious limiting aspect to hydrogen capacity and kinetics, as well as the limited grain refinement and introduction of defects, associated to the need of heating substantially the samples in order to achieve enough plasticity for processing. In some investigations, ECAP was combined to cold rolling and/or HEBM [9-12]. Skrypiuk et al. [11] and Krystian et al. [12] filed with a rasp ZK60 alloy samples prepared by ECAP and attractive hydrogen absorption and desorption kinetics were obtained. It shows that the microstructural refinement from SPD must be allied to the high surface area of the sample in order to increase the diffusion rate of hydrogen into the material. Therefore, CR and CF have advantages over ECAP in the production of hydrogen storage materials, since, contrarily to ECAP, CR and CF can be applied at room temperature, producing directly samples in the form of foils or flakes.
HPT was also applied for Mg [13, 20] or Mg alloys [15, 21] aiming better hydrogen storage properties, but in this case the main limitation is the production of large samples. Edalati et al. [20] studied the activation behavior of Mg samples after HPT and 90.8% of the theoretical capacity of magnesium was reached after 27.8 hours. In our case we have used a lower hydrogen pressure - 20 bar instead of 30 bar; higher temperature – 350°C instead of 150°C; and a smaller number of turns - 5 instead of 10. However, the hydrogen absorption capacity measured in our investigation (around 1.2 %) is higher than the obtained by Edalati et al, considering low activation times, e. g. 2 h, as shown in Fig. 4 (c). This is probably associated to the differences in the activation temperatures between the two studies.

Depending on the SPD processing conditions, a refined and homogeneous microstructure can be produced. For example, the use of a two step procedure, the first one involving rapid solidification, and the following, severe cold work, has shown to be promising for application, Figs. 4 (c) and (d), sample MS + CR. The effects of using a rapid solidification technique other than MS with lower cooling rates should be investigated and are under progress in our research group. The reduced grain and subgrain size, allied to a higher defect density, and intense [002] fiber type texture, Fig. 3 (b), and also to the reduced thickness of the sample, are associated to the high level of obtained hydrogen storage properties, which are comparable to the exhibited by the MgH$_2$ nanostructured powder, Fig. 4, keeping in mind the difference in the operation temperature (350 or 300°C).

Finally, it is important to mention that when SPD techniques, such as HPT, CR and CF, are applied to a MgH$_2$ instead of Mg, a much higher level of grain refinement is attained, reaching the nanoscale after only a few HPT turns or CR/CF passes [16-18]. This pronounced structural refinement provides enhanced kinetics of hydrogen absorption and desorption. SPD applied to MgH$_2$ can also result in a reasonably fine distribution of additives with positive effects on the hydrogen storage properties, the so-called ‘catalysts’ [14, 17, 18].

Conclusions

In this study, different SPD processing techniques were employed to produce bulk nanostructured Mg samples. The hydrogen absorption/desorption properties were compared to the ones observed for ball-milled MgH$_2$. In the best SPD processing conditions (melt spinning followed by cold rolling), the bulk samples present H-absorption/desorption kinetic properties that are comparable to milled powders, even if the temperatures involved are higher – 350°C compared to 300°C. Cold work during SPD results in a very refined microstructure, and superior hydrogen storage properties can be obtained with control of the deformation texture and smaller sample thickness. Additional advantages associated to the processing by SPD, as the enhanced air-resistance of the samples and their much more simple preparation make these processing routes competitive for the production of Mg-based materials for hydrogen storage. In a comparison among different SPD techniques, cold rolling and cold forging stand out as the processes with higher potential for industrial application, considering the level of the attained hydrogen storage properties, its simplicity and low cost.

Acknowledgements

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**Supplementary data**

**Table 1** Patent search expression for SPD processes used in the Derwent Innovations Index database.

| #   | Expression                                      |
|-----|-------------------------------------------------|
| #1  | ts=(severe-plastic-deformation)                 |
| #2  | ts=(angular-press OR angular-pressing) AND ts=(duct OR channel) |
| #3  | ts=(angular-extrusion OR angular-extruding OR angular-extruder) AND ts=(duct OR billet OR propert* OR channel-angular OR equal-channel* OR equichannel* OR diameter-angular) AND ip=(c22f* OR b21* OR b22f*) |
| #4  | ts=(high-pressure-torsion)                      |
| #5  | ts=(accumulat*-roll-bond*)                     |
| #6  | ts=(asymmetr*-roll*) AND ip=(c22c* OR c22f* OR b21* OR c21d* OR b22f*) |
| #7  | #1 OR #2 OR #3 OR #4 OR #5 OR #6            |