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Synthesis of nanocrystalline hydrogen storage materials

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Abstract

In this paper, we present a new and powerful method to directly synthesize nanocrystalline metal hydrides from elementary components. This method consists of milling at high temperature under hydrogen with the addition of graphite to facilitate the first hydrogenation. We found that a synergetic effect is achieved and that it is possible to reach full hydrogenation in a very short time. This technique was tested on magnesium, which is known to be a material hard to activate. We found that full hydrogenation was realized after only about 1 h. This represents an order of magnitude reduction in processing time compared to any other methods known in the art.

Keywords: Reactive milling; Activation; Nanocomposite; Metal hydrides

1. Introduction

Synthesis of metal hydride by mechanical alloying and mechanical milling is a relatively new but well documented technique [1–5]. Usually, the milling is performed under an inert atmosphere (generally argon) and the hydrogenation is performed in a subsequent step. However, for cost reduction and ease of formation, milling under hydrogen (reactive milling) could be an attractive alternative. Reactive milling has been investigated in numerous systems such as magnesium-based systems and systems with group IV and V transition metals [6–10]. In this paper, we will confine our discussion to the synthesis of magnesium hydride by reactive milling and describe a new reactive milling technique which drastically improves the hydride formation yield.

Reactive milling of magnesium has been intensively studied by a number of researchers. Without catalyst, the formation of magnesium hydride by reactive milling is quite slow. For example, Gennari et al. synthesized magnesium hydride by milling for 50 h under a hydrogen pressure of 0.5 MPa [11]. However, even for such a long milling time, only 50% of the magnesium was hydrided. Various catalysts have been used to speed up the reaction. Tessier and Akiba showed that a concentration of nickel as low as 1 at.% has a beneficial effect on formation kinetics of magnesium hydride during milling and on decomposition of this hydride [12]. However, the maximum yield of magnesium hydride was only 40 wt.% after 10 h of milling [13]. Bobet et al. reported the formation of 35 wt.% of magnesium hydride when milling under 1.1 MPa of hydrogen for 5 h without using any catalyst [14]. When Co (10 wt.%) was added as a catalyst, the yield of magnesium hydride went up to 71 wt.% for 10 h milling [15]. The hydrogenation showed a two-step process: Nucleation and diffusion [16]. Because reactive milling could be associated to nucleation [17], the activation process was suppressed in the ball-milled materials. For short milling time under hydrogen atmosphere, a hydride layer was formed on every magnesium particle. This layer acted as a protection against oxidation. For longer milling time, decrepitation occurred which resulted in ultra-fine powder [15]. The in-situ hydrogenation during ball milling was probably too slow to entirely cover every particle with a hydride layer. Therefore, the protection against oxidation was not as effective in the long milling time samples thus reducing the hydrogenation kinetics. The authors concluded that a short milling time is the most suitable route for producing a hydride with fast hydrogenation kinetics [17].

Wang et al. used the alloy $ZrFe_{1.4}Cr_{0.6}$ (40 wt.%) as a catalyst in reactive milling of magnesium under hydrogen pressure [18,19]. They found that the decomposition reaction of the nanostructured magnesium hydride was nucleation and growth controlled for transformation frac-

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tion less than 0.1. For higher transformation fraction the decomposition reaction was a diffusion-controlled growth mechanism [18]. Diffusion of hydrogen was accelerated by the uniform distribution of $ZrFe_{1.4}Cr_{0.6}$ on the surface and in the bulk [19]. However, the high proportion of catalyst makes that system unsuitable for practical applications.

Following the report of Klassen et al. [20] that the hydrogen sorption kinetics are improved by milling MgH_2 with metal oxides, Bobet et al. [21] tried to synthesize magnesium hydride by mechanically grinding Mg powder mixed with 10 wt.% of oxides (Cr_2O_3, Al_2O_3 and CeO_2) under a hydrogen pressure of about 11 bar. After 2 h of milling, the largest transformation fraction was given by the Mg+10 wt.% Cr_2O_3 mixture where 21.5% of the magnesium was hydrided.

Chen and Williams [9] used a vertical planetary mill with an initial hydrogen pressure of about 240 kPa to synthesize pure metal hydrides. They could synthesize titanium hydride in 5.5 h but it took 47.5 h to produce magnesium hydride. This is another proof that magnesium hydride is particularly hard to synthesize.

For the synthesis of magnesium-based intermetallics, the beneficial effect of milling at elevated temperature has recently been demonstrated [22,23]. At high temperature, thermal activation of diffusing species is greater and the reaction barrier energy is thus easier to overcome. Interdiffusion of atoms is also facilitated and leads to reduced reaction times. Previous experiments on the Mg–Ni system indicated that milling at elevated temperature did not impair the reduction of crystallite size and produce intermetallics with a high yield in a short time [23].

It is well known that usually, the first few hydrogenations of metal hydrides should be performed under drastic temperature and pressure conditions in a process called activation. In a recent investigation, Bouaricha et al. showed that ball milling of hydrogen absorbing materials with graphite for a short period resulted in a drastic improvement of the activation characteristics of the hydride [24,25]. It was shown that for magnesium, the activation time could be reduced from days to 1 h. Other C-based materials were tested and it was found that the most important characteristic is the 2D structure [25].

We present here a new method which consists of milling at high temperature under hydrogen pressure and with the presence of graphite additive. By combining these three techniques a synergetic effect is achieved and synthesis of metal hydride is quickly completed.

2. Experimental details

Magnesium turnings, made by cutting a magnesium ingot on a lathe without oil, were used for all experiments except for milling with cobalt addition where magnesium powder (Alfa, −325 mesh, 99.8%) was employed. The additives V (Alpha, granules, 99.7%), graphite (Aldrich, flake), Perylene (Alpha, 99.9%) and cobalt (Cerac, −100 +200 mesh, 99.8%) were mixed with magnesium in an argon-filled glove box and put in a hardened steel crucible. Milling was carried out in a specially designed apparatus where the crucible could be heated to the desired temperature and a hydrogen pressure could be continually applied during the milling process. The ball to powder weight ratio was 10:1 except for perylene addition where the ratio was 30:1. X-ray diffraction was performed on a Siemens D-500 diffractometer with Cu Kα radiation. Phase abundance, crystallite size and strain were determined from Rietveld analysis of the X-ray diffraction patterns using the FULLPROF software [26]. The hydrogen storage properties of the materials were evaluated by using an automatic Sieverts apparatus and we used commercial magnesium hydride (95 wt.% MgH_2, 5 wt.% Mg) from Th. Goldschmidt AG for comparison.

3. Results and discussion

3.1. Effect of graphite addition

The effect of each parameter on the synthesis of magnesium hydride has been investigated. To verify the importance of graphite addition, two samples of magnesium powder with and without graphite have been milled at 573 K under 4 bar of hydrogen pressure during 1 h. As seen in Fig. 1, only a small amount of magnesium hydride is synthesized when there is no graphite. However, when graphite is added, the transformation to magnesium hydride is complete. Therefore, a minimal amount of graphite has to be added in order to have synergetic effect.

3.2. Effect of catalyst

It has been shown in a series of papers that the nanocomposite Mg–V possesses excellent hydrogen sorp-

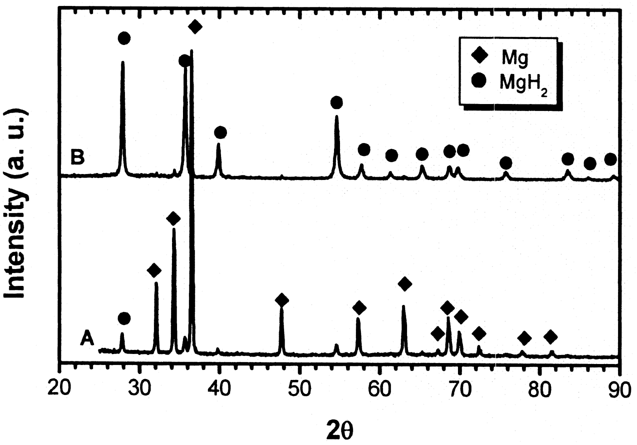

Fig. 1. X-ray powder diffraction pattern of ball-milled magnesium powder at 573 K under 4 bar of hydrogen during 1 h. (a) Without graphite, (b) with small addition of graphite.

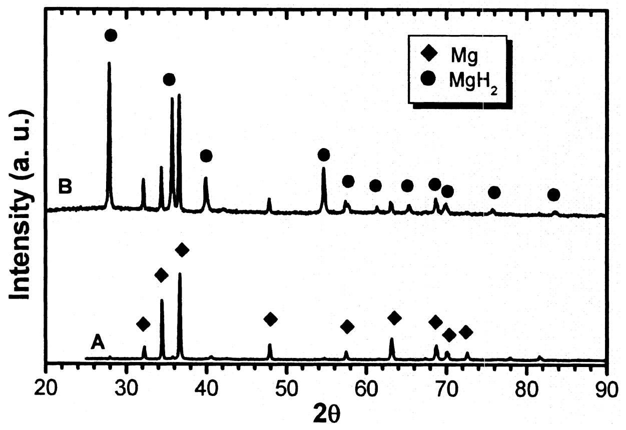

Fig. 2. X-ray powder diffraction pattern of ball-milled magnesium at 573 K under 4 bar of hydrogen. (a) With addition of 5 at.% V, 1 h milling, (b) with addition of 5 at.% V+graphite, milled for 30 min.

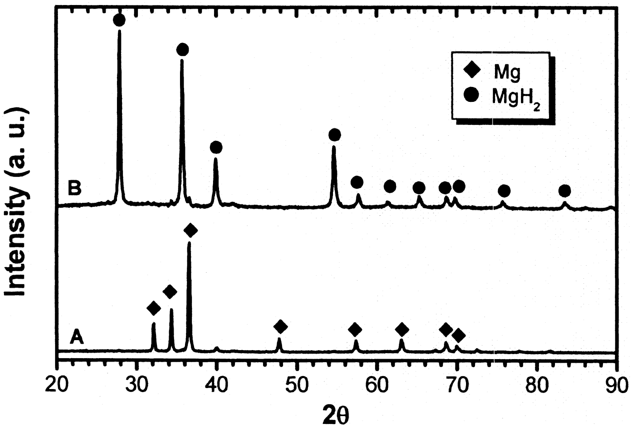

Fig. 3. X-ray powder diffraction pattern of ball-milled Mg+5 at.% V+graphite under 4 bar of hydrogen during 1 h. (a) T=295 K, (b) T=573 K.

tion properties [27–30]. We, therefore, investigated the effect of vanadium addition on the synthesis efficiency. Fig. 2 shows the effect of adding vanadium compared to the effect of pure graphite. When only vanadium is added, practically no magnesium hydride is synthesized after 1 h milling at 573 K under 4 bar of hydrogen. On the other hand, the combination of vanadium (5 at.%) and graphite makes the reactive milling more efficient and after only 30 min of milling, 64 wt.% of magnesium hydride is synthesized as determined by Rietveld analysis of the pattern 2b. From Rietveld analysis it was also determined that the crystallite size and strain are respectively 66±3 nm and 0.37±0.09%.

3.3. Effect of milling temperature

The effect of milling temperature for the system Mg+5 at.% V+graphite under 4 bar of hydrogen is shown in Fig. 3. When the mixture is milled at room temperature, no reaction takes place and only nanocrystalline magnesium is produced. When the temperature is raised to 573 K, an almost complete synthesis of magnesium hydride is observed. Even at such a high temperature, the milled material still has a nanocrystalline structure. By Rietveld refinement, of the diffraction of Fig. 3b it was determined that for the Mg+5 at.% V+graphite milled at 573 K, the crystallite size and strain are respectively 40±1 nm and 0.70±0.06%. Compared to the results of the 30 min milled sample, this means that further milling resulted in a decrease of crystallite size and an increase of strain. Therefore, even at high temperature, milling produced nanocrystalline materials very efficiently.

3.4. Effect of other additives

It has been shown previously that other carboneous compounds could be as effective as graphite for improving activation in magnesium-based compounds [25]. In the present study, we investigated the effect of perylene which, like graphite, has a planar structure. The mixture Mg+5 at.% V+perylene was tested. Because the melting point of perylene is 550 K, the milling was performed at 523 K for 2 h. The diffraction pattern of Fig. 4a shows that after the milling the magnesium is fully hydrided. Moreover, the metastable phase γ-MgH_2 was synthesized. It is known that by milling magnesium hydride (β-MgH_2) at room temperature the metastable phase γ-MgH_2 could be synthesized [31,32]. However, in the present case, the metastable phase was directly formed from pure magnesium. The fact that the γ phase was synthesized in the perylene milling and not in the others is due to the longer milling time. A sample of Mg+5 at.% V+graphite milled at 573 K for 2 h under 4 bar of hydrogen pressure also contained the metastable phase γ-MgH_2.

We also tested the effect of Co catalyst by milling

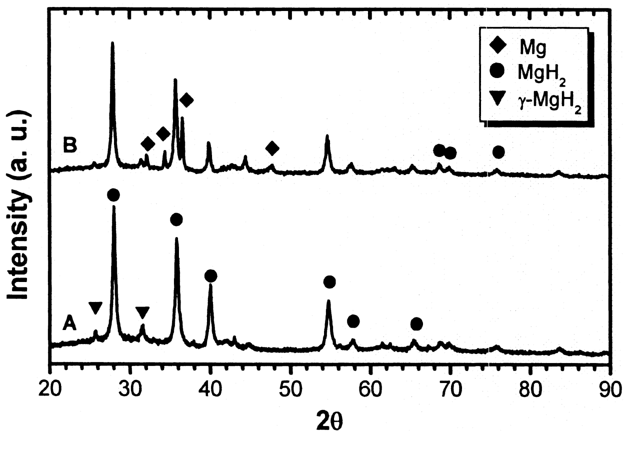

Fig. 4. X-ray powder diffraction pattern of Mg powder milled for 2 h. (a) At 523 K under 10 bar of hydrogen with addition of 5 at.% V+perylene, (b) at 573 K under 4 bar of hydrogen with addition of 10 at.% Co.

magnesium powder (−325 mesh) with 10 at.% of Co and without graphite for 2 h at 573 K under 4 bar of hydrogen. The diffraction pattern of the milled powder is shown in Fig. 4b. The proportion of magnesium hydride is quite high and was measured to be 85 wt.% from Rietveld analysis. In comparison, Bobet et al. showed that magnesium with 4 at.% Co milled at room temperature under 11 bar of hydrogen needs a milling time of 20 h to achieve a proportion of 82 wt.% of MgH_2 [16,17]. However, it should be mentioned that they use a smaller proportion of Co of 4 at.% (10 wt.%) instead of 10 at.% in the present case.

3.5. Hydrogen sorption properties

In order to understand the hydrogen sorption properties of magnesium hydride synthesized by our technique, we ball-milled Mg+graphite under 4 bar of hydrogen at 563 K for 5 h. This sample does not have any catalyst such as V or Co. Therefore, the effect of reactive milling at elevated temperature with graphite will not be masked by any catalyst. The pressure–composition isotherm at 623 K is shown in Fig. 5. Compared to commercial magnesium hydride (Th. Goldschmidt), it can be seen that the hydrogen capacity is slightly higher and closer to the theoretical value of 7.6 wt.%. The hysteresis is much smaller than in the case of commercial MgH_2. The reason for this behavior is the much faster kinetics as shown in Fig. 6. As seen from Fig. 6A, the most drastic difference between commercial MgH_2 and the Mg+graphite is for the dehydrogenation kinetics which is more than one order of magnitude slower in the case of the commercial product. The difference is particularly evident for the incubation time which is almost nonexistent for the Mg+graphite sample and is more than 1200 s for the commercial hydride. A strong improvement of the kinetics could also be seen for the hydrogenation (Fig. 6B). Preliminary tests indicated that graphite addition has little impact on hydrogen sorption kinetics in second and further absorption/desorption cycles. Therefore, the action of graphite seems to be limited to reduction of the activation time. More tests have to be done to confirm this observation.

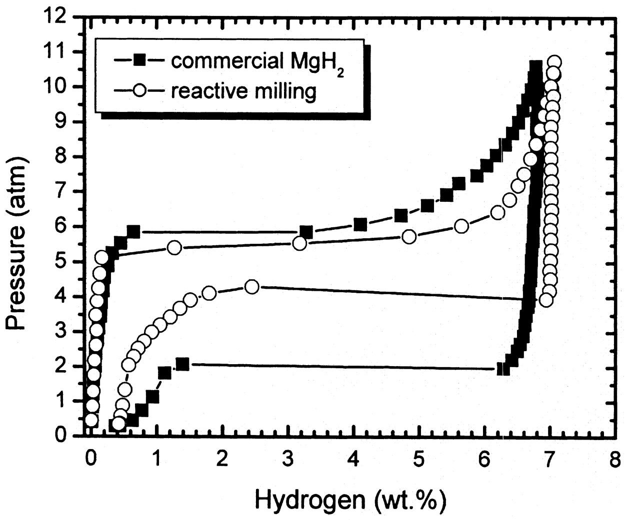

Fig. 5. Pressure–composition isotherm at 623 K of commercial magnesium hydride (Th. Goldschmidt) and of Mg+graphite ball-milled under 4 bar of hydrogen at 563 K during 5 h.

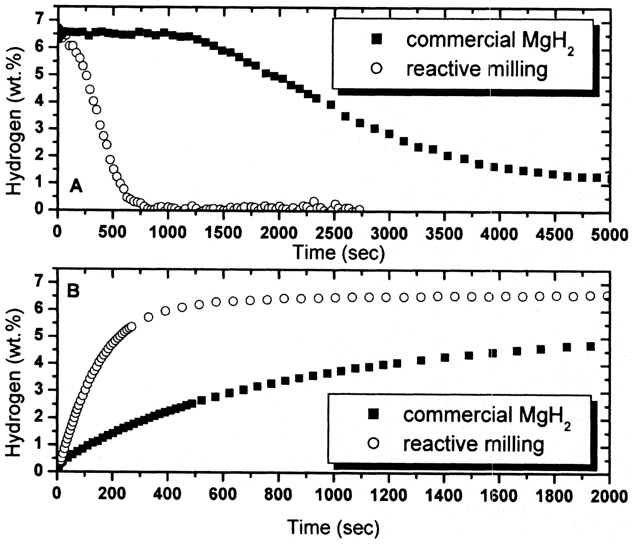

Fig. 6. Hydrogen sorption kinetics at 623 K of commercial magnesium hydride (Th. Goldschmidt) and of Mg+graphite ball-milled under 4 bar of hydrogen at 563 K during 5 h. (A) Desorption under 0.07 bar of hydrogen, (B) Absorption under 10 bar of hydrogen.

4. Conclusion

It was shown that rapid synthesis of metal hydride could be achieved by milling at elevated temperature under hydrogen pressure by adding graphite. A mixture of Mg+5 at.% V+graphite could be hydrided in 1 h of milling at 573 K under a hydrogen pressure of 4 bar. Variations of the different parameters clearly show a synergetic effect between temperature, graphite additive and hydrogen pressure. The synthesized magnesium hydride has been shown to have better hydrogen sorption properties than commercially available magnesium hydride.

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