Study of hydrogen absorption kinetics of Mg_2Ni -based powders produced by high-injected shock power mechanical alloying and subsequent annealing

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Abstract Mg_2Ni -based compounds were prepared using a high-energy milling technique, with a planetary ball mill, and subsequent annealing at 350 °C. X-ray diffraction analyses revealed that Mg_2Ni phase was obtained after 10 milling hours, in addition to Ni phase. Increasing the ball-milling duration from 10 to 17 h causes a decrease in the crystal size of particles from 93 to 76 nm. However, the subsequent annealing of all Mg_2Ni -based materials highly increases their crystallite sizes with calculated values in the range of 261–235 nm. In the same way, X-ray diffraction patterns of annealed compounds show the presence of highly crystallized Mg_2Ni phases. The particle size of $\text{Mg}_2\text{Ni}/\text{Ni}$ particles is estimated at 25 μm after 10 milling hours and drops to 5 μm at longer times. The scanning electron microscopy images of $\text{Mg}_2\text{Ni}/\text{Ni}$ particles demonstrated a drastic increase of their sizes up to 100 μm upon annealing. The hydrogenation reactivity and kinetic of $\text{Mg}_2\text{Ni}/\text{Ni}$ were both characterized by solid–gas reactions. The hydrogen absorption capacity value was about 3.5 H/f.u for milled and annealed $\text{Mg}_2\text{Ni}/\text{Ni}$ compound. The highest hydrogen absorption kinetic was obtained during the first 5 h of absorption time, where 95 % of the maximum absorption capacity was reached.

Keywords Mg_2Ni -based compounds · Mechanical alloying · X-ray diffraction · Hydrogen absorption kinetic · Annealing treatment

Introduction

Ni-metal hydrides (Ni-MH) are extensively studied as secondary batteries. Their applications include portable equipments and hydrogen fuel cell transportations. Among the materials investigated as possible Ni-MH negative electrode, Mg-based alloys exhibit promising performances [1–4]. Furthermore, the intermetallic Mg_2Ni compound received a great attention for the reversible hydrogen storage [5]. Mg_2Ni combines with hydrogen to form Mg_2NiH_4 hydride and highly improves the hydrogenation kinetic of magnesium [6]. Concerning synthesis processes of materials, melting is the conventional technique to prepare Mg_2Ni [7]. However, the large difference in melting points and vapor pressures between Mg and Ni make difficult the formation of high quality Mg_2Ni [7]. These drawbacks could be avoided by using the mechanical alloying (MA) process since the reaction between Mg and Ni occurs easily and reliably in the solid state [8–10]. Moreover, the MA process leads to the formation of surface defects and favors the formation of nanocrystalline materials. Commonly, amorphous phases are obtained from the MA of Mg and Ni, and may act as precursors for the formation of the crystalline Mg_2Ni phase. Such properties are required for the improvement of the hydrogenation kinetic and the absorption capacity [11]. Combining ball-milling with a heat-treatment step generally increases the yield of the synthesis reaction [12–14]. Spassov et al. [15, 16] showed that Mg_2Ni -based alloys subjected to an annealing step after the ball-milling procedure consist in homogeneously nanocrystalline particles. On the other hand, Rojas et al. [17] succeeded in reducing the long milling time (14 h), needed for the transformation of Ni and Mg into Mg_2Ni , to a shorter time (5 h) by a subsequent annealing at 673 K for 1 h. We have previously reported

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that the heat-treatment of ball-milled Mg_2Ni materials leads to a high absorption capacity of 3.5 wt% [8].

In this work, Mg_2Ni -based powders were prepared by mechanical alloying and subsequent annealing at 350 °C for 24 h. This temperature induces relevant microstructural modifications in the milled phase and enhances the hydrogen absorption/desorption properties. The control of the synthesis parameters plays an important role in increasing the equilibrium pressure and reducing the activation time of the hydrogen absorption reaction. The present paper presents an investigation of the hydrogenation kinetics of numerous Mg_2Ni -based powders obtained by varying the cumulated energy of milling. Series of Mg_2Ni phases were prepared and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analyses before being tested for the hydrogen storage.

Experimental section

A mixture of elemental Mg (VWR, 99.8 %) and Ni (VWR, 99.9 %), with an atomic ratio of 2:1, was sealed into a stainless steel vial (50 cm³ in volume) with 5 stainless steel balls (15 mm in diameter and 13.6 g in mass) in a glove box filled with purified argon gas. The ball-to-powder weight ratio was equal to 68:1. The MA experiments were performed at room temperature using a Retsh PM400 planetary ball miller. The disc rotation speed and the vial rotation speed were equal to 250 and 500 rpm, respectively. These milling conditions correspond to kinetic shock energy of 0.63 J/hit, shock frequency of 45.6 Hz, and injected shock power of 5.75 W/g.

The crystallographic characterization of synthesized powders was carried out by XRD using a (θ - 2θ) Panalytical XPERT PRO MPD diffractometer operating with Cu K α radiation ($\lambda = 0.15406$ nm). The powder morphology of the samples was characterized with a FEI Quanta 200 environmental scanning electron microscope. Thermogravimetric measurements were based on the differential scanning calorimetry (DSC) technique using a Setaram 131 instrument. The analyses were realized at a heating rate of 20 °C/min, under nitrogen gas atmosphere. Prior to the hydrogen absorption measurements, the sample was pulverized mechanically, by a metallographic hammer and an agate mortar, into a powder of 63 μm in size. Hydrogenations of synthesized compounds were performed using solid-gas reactions. The hydrogen absorption capacity was measured with a home-made Sievert's apparatus at a pressure of 11 bars and a temperature of 280 °C.

Results and discussion

Structural characterization

XRD patterns of mechanically alloyed powders are shown as a function of the alloying time in Fig. 1. After 10 h of milling, diffraction peaks relative to Mg_2Ni phase (JCPDS 01-75-1249) are observed at 2θ (hkl) = 20° (003), 23° (102), 37° (112), 40° (200), 45° (203), 72° (220) and 86° (226). At this stage of milling, the pattern indicates the coexistence of elemental Ni and Mg_2Ni phases. The presence of Ni is evidenced by diffraction peaks located at 2θ (hkl) = 44° (111), 52° (200) and 78° (220). Surprisingly, peaks relative to elemental Mg are not observed in any pattern. The absence of Mg peaks contrasts with previous studies, where elemental Mg and Ni still present in composites milled during 10 h [18–20], this behavior could be explained by the distinct shock powers injected during the mechanical alloying. In fact, in the same kinetic conditions (Ω_{disc} is the disc rotation speed, ω_{vial} is the vial rotation speed, R_{disc} is the disc radii, r_{vial} is the vial radii and r_{ball} is the ball radii), the injected shock power increases by increasing the ball number and weight, or by reducing the material weight. For these reasons, the injected shock power increases by increasing the ball-to-powder weight ratio (BPR). The injected shock power in this study corresponds to a BPR of 68:1. Such a value is more important than the ones considered elsewhere by Gennari et al. [18] (BPR = 42:1) and Ebrahimi-Purkani et al. [19] (BPR = 20:1). In our previous works [21, 22], we reported that the structure of the stationary state was only a function of the injected shock power. Nevertheless, we reported that the amount of intermediary phases depends on the cumulated energy of milling (E_{cum}), defined by the following equation [5, 6]:

$$E_{\text{cum}} = P_{\text{inj}} \times \Delta t \quad (1)$$

where E_{cum} is expressed in [Wh/g], P_{inj} is the injected shock power expressed in [W/g] and Δt is the alloying duration expressed in [h]. Consequently, the increase of the injected shock power allows the formation of the same intermediary states at lesser alloying durations.

In the present work, the absence of Mg diffraction peaks and the presence of remaining Ni suggest that amorphous Mg is confined in the $\text{Mg}_2\text{Ni}/\text{Ni}$ composite [18]. From 10 to 15 h of milling, i.e. cumulated energy from 57 to 86 Wh/g, the increase in the peak intensity of Mg_2Ni (203) simultaneously occur with a decrease in the peak intensity of Ni (111) (Fig. 1b). After 17 h of milling, the cumulated energy is about 98 Wh/g. At this stage, the diffraction line

Fig. 1 XRD patterns of mechanically alloyed (A, B) and annealed (C) Mg_2Ni powders. Milling durations are 10 h (a), 12 h (b), 13 h (c), 15 h (d) and 17 h (e)

of Ni (200) disappears, while the intensity ratio of Ni (111)/ Mg_2Ni (203) diminishes. These observations suggest a progressive formation of Mg_2Ni phase accompanied by a loss of residual Ni in the composite. On the other hand, the increase of milling time results in broadening of peaks. Two factors may explain such a behavior: (i) the decrease of the crystallite size and, in a lesser extent, (ii) the increase of the lattice strains [23]. The average crystallite size of Mg_2Ni powders were calculated from the corresponding (003) peak [8], using the following Debye-Scherrer equation [24]. The corresponding values are presented in Table 1 as a function of the milling time:

$$D_{003} = 0.89\lambda/\beta \cos(\theta) \quad (2)$$

where D_{003} is the crystallite size of Mg_2Ni , λ is the wavelength of the X-radiation, β is the full-width at half maximum (FWHM) of the peak and θ is the diffraction angle corresponding to (003) peak. Instrumental broadening and lattice distortion contributions were subtracted to values of peak broadening. Table 1 shows a continuous decrease of the crystallite size from 93 to 76 nm when the milling time varies from 10 to 17 h. The crystallite sizes estimated for as-prepared powder are higher than values reported in the literature [15, 18, 19, 25].

The heat-treatment of Mg_2Ni powders was carried out at 350 °C for 24 h under vacuum. The resulting powders were characterized by XRD as shown in Fig. 1c. Independently on the milling duration, annealed powders show similar patterns reflecting a similar structural rearrangement upon annealing. The heat-treatment leads to sharper peaks, the disappearance of Ni diffraction peaks and a pure and highly crystalline Mg_2Ni phase. The evaluation of the crystallite size for annealed powders indicates a steep increase of all D_{003} values upon annealing (Table 1) and demonstrates that heat-treating particles enhance their agglomeration.

SEM characterization

SEM micrographs of Mg_2Ni powders mechanically alloyed during 10 and 12 h are shown in Fig. 2. The powder obtained after 10 h of MA shows an irregular shape of porous particles with an average size of 25 μm (Fig. 2a). As milling progresses, powder particles are fractured and their size becomes 5–6 μm , as displayed in Fig. 2b and Table 1. During the mechanical alloying, the elemental powder is blended, cold worked, welded and fragmented repeatedly. After a long period of milling, fracturing

Table 1 Average crystallite size (based on XRD patterns) and particle size (measured by SEM technique) of Mg_2Ni -based powders

Milling time (h)	10	12	13	15	17
Cumulated energy of milling (E_{cum} , Wh/g)	57	70	75	86	98
Crystallite size of MA powders (nm)	93	87	86	79	76
Crystallite size of annealed powders (nm)	261	248	236	214	235
Particle size of as MA powders (μm)	25	5	6	6	5
Particle size of annealed powders (μm)	100	100	100	100	100

Annealing temperature: 350 °C, annealing duration: 24 h

Fig. 2 SEM micrographs (secondaries electrons mode) of Mg_2Ni powders prepared by mechanical alloying during **a** 10 h, **b** 12 h and **a'** 10 h with subsequent annealing at 350 °C for 24 h

becomes the predominant event because of the brittle nature of Mg_2Ni materials [19]. Further mechanical alloying from 12 to 17 h slightly affects the powder morphology (Table 1). On the other hand, Fig. 2a' shows that subsequent annealing of Mg_2Ni -based powders leads to a substantial increase of their particle size up to 100 μm . The same value was obtained for the whole series of milled and annealed Mg_2Ni powders (Table 1). These observations are in a good agreement with the XRD results. The heat-treatment promotes the diffusion and the coalescence of Mg_2Ni particles during the temperature increase. Thermodynamically, the particle size extends and converges to a value corresponding to the lowest free energy of Mg_2Ni composite. During the growth of particles, the volume energy decreases, while the surface energy increases [26].

Thermogravimetric investigation

Figure 3 shows the DSC curves of mechanically alloyed and annealed products. During the temperature increase, the composite formed upon 10 h of milling time exhibits two exothermic peaks located at 132 and 220 °C (Fig. 3a). Both peaks were assigned elsewhere to the crystallization of amorphous Mg_2Ni [17, 20]. In the present case, the first peak is assigned to the conversion of amorphous Mg_2Ni to crystalline Mg_2Ni , while the second one is attributed to the formation of highly crystallized Mg_2Ni from residual Ni and amorphous Mg [17, 20]. The same phenomena are considered for the composite milled during 12 h since two thermal events are observed at 132 and 200 °C (Fig. 3b). It should be noticed that the second peak shifts to lower temperatures. When the milling time is increased up to 13 h (Fig. 3d), the DSC curve shows the presence of three exothermic peaks. Thermal events located at 132 and

200 °C are similar to those observed for compounds milled during 10 and 12 h and, therefore, correspond to the same reactions. However, the new peak appearing at 280 °C is associated to a further formation of Mg_2Ni compound [27, 28]. This is thermodynamically favorable when the overall energy is increased by either increasing the milling time or through a thermal activation. For milling durations of 15 and 17 h, the peak located at 200 °C diminishes and only peaks located at 132 and 280 °C still present (Fig. 3f, g). XRD data demonstrated that increasing the milling time leads to Mg_2Ni -rich phase (Fig. 1). The fraction of residual Ni that is transformed during the DSC scan becomes lower since it was already been transformed into Mg_2Ni during the milling process. For this reason, the absence of the

Fig. 3 DSC curves of Mg_2Ni prepared by mechanical alloying during 10 h (**a**), 12 h (**b**), 13 h (**c**, **d**), 15 h (**e**, **f**) and 17 h (**g**), and subsequent annealing at 350 °C for 24 h (**c**, **e**)

second exothermic peak is associated with residual precursors being mechanically transformed into Mg_2Ni .

DSC curves of powders milled during 13 and 15 h and heat-treated at 350 °C for 24 h are shown in Fig. 3c, e. They are characterized by the absence of any thermal events. Curves of all annealed powders present a similar shape (data not shown). This is due to the formation of a highly crystalline Mg_2Ni phase following the heat-

treatment (Fig. 1c) and elucidates the role of the amorphous precursors in the Mg–Ni system.

Hydrogen storage properties

Figure 4 shows the evolution of the capacity during the hydrogen absorption for different ball-milled and annealed Mg_2Ni -based materials. Independently on the milling

Fig. 4 Evolution of the hydrogen absorption capacity during time for ball-milled Mg_2Ni powders before (*full lozenges*) and after (*open squares*) annealing at 350 °C for 24 h. Milling durations are 10 h (a), 12 h (b), 13 h (c), 15 h (d) and 17 h (e). The hydrogen absorption was performed at a pressure of 11 bars H_2 and a temperature of 280 °C

duration, the absorption capacity of Mg_2Ni expands significantly after 25 h of absorption time. For a longer time, the capacity value fairly increases and reaches a plateau. Nearly 90 % of the maximum capacity is reached after an absorption time of 25 h for all Mg_2Ni powders. This behavior reflects a fast kinetic of the hydrogen absorption reaction in the beginning of the absorption process. The maximum capacity values obtained with heat-treated and unheated Mg_2Ni -based powders are presented in Table 2. For all samples, experimental capacities are lower than the theoretical value expected for crystalline Mg_2Ni , i.e. 4 H/f.u. This is mainly due to the heterogeneous chemical composition of prepared composites including crystallized and amorphous Mg_2Ni , together with elemental Ni (Fig. 1). It was already demonstrated that amorphous Mg_2Ni exhibits lower hydrogen absorption capacity than crystallized Mg_2Ni [18]. Moreover, hydrogen atoms are poorly absorbed by the Ni phase in the present conditions. For these reasons, the hydrogen absorption capacity displayed by

Table 2 Maximum absorption capacity obtained for ball-milled Mg_2Ni -based powders before and after annealing

Milling time (h)	Maximum capacity (H/f.u.)	
	Before annealing	After annealing
10	3.02	3.49
12	3.11	3.48
13	3.19	3.46
15	3.21	3.48
17	3.28	3.46

The hydrogen absorption was performed at a pressure of 11 bars H_2 and a temperature of 280 °C

Annealing temperature: 350 °C, annealing duration: 24 h

as-prepared powders is mainly related to Mg_2Ni crystalline phase. Table 2 indicates that the absorption capacity increases by increasing the milling time for unheated compounds. This is explained by the decrease in the amount of residual Ni and the simultaneous formation of Mg_2Ni phase during the mechanical alloying (Fig. 1b).

On the other hand, annealing Mg_2Ni -based compounds enhances the capacity values for all prepared powders (Fig. 4). The absorption capacities of annealed samples vary with time following the same shape than unheated compounds. Again, the capacity value rises during the first 25 h and then stabilizes. The influence of the heat-treatment on the capacity values is indicated in Table 2. Annealed powders exhibit nearly the same absorption capacity with an average value of 3.47 ± 0.01 H/f.u. This similarity derives from the formation of comparable Mg_2Ni microstructures (Fig. 1c) and morphologies upon heat-treating powders. The increase in the capacity value observed upon annealing powders is caused by the transformation of the amorphous Mg_2Ni phase into a highly crystallized one, as evidenced by XRD characterizations (Fig. 1). In the same way, the annealing step promotes further conversion of residual Ni and amorphous Mg into Mg_2Ni . The latter phase is characterized by an absorption capacity higher than the ones of Ni and Mg. However, experimental capacities of annealed products are still lower than theoretical values (Table 2). Westlake et al. [29] reported that the radius of octahedral sites must be larger than 0.4 Å in order to accommodate hydrogen atoms. In the same way, Switendick et al. [30] demonstrated that tetrahedral sites separated by a distance lower than 2.1 Å are unable to absorb hydrogen. Thus, the catalytic activity of as-prepared Mg_2Ni samples may be limited by the narrow size of some unoccupied tetrahedral and octahedral sites.

Fig. 5 Evolution of the hydrogen absorption capacity with time for the first, second and third cycles of Mg_2Ni powder ball-milled during 10 h before (a) and after subsequent annealing at 350 °C for 24 h (b).

The hydrogen absorption was performed at a pressure of 11 bars H_2 and a temperature of 280 °C. The absorption cycles were performed successively without any desorption step

Figure 5 focuses on the evolution of the hydrogen absorption capacity during the first 20 h of absorption time. This experiment is designated as the first absorption cycle and was consecutively repeated two times, without any hydrogen desorption step. Curves are presented for Mg_2Ni -based powders milled during 10 h before and after their heat-treatment. During the first cycle, Mg_2Ni -based composites quickly absorbs 3.05 H/f.u at 5.5 h, which constitutes 96 % of the maximum capacity obtained at the end of this cycle, i.e. 3.17 H/f.u (Fig. 5a). After 5.5 h, the amount of absorbed hydrogen increases weakly, reflecting a slower kinetic of the absorption mechanism. For the second and third cycles, the absorption kinetic is significantly slow as the amount of absorbed hydrogen is too small: 0.070 and 0.067 H/f.u in the second and third cycle, respectively (Fig. 5a). During the first cycle, unoccupied sites of Mg_2Ni microstructure are able to accommodate and absorb hydrogen atoms easily. For further cycles, the hydrogen absorption only occurs inside highly energetic sites and only a small amount of hydrogen may be absorbed. In the case of annealed Mg_2Ni powders (Fig. 5b), most hydrogen is also absorbed during the first cycle. Figure 5b shows that 3.22 H/f.u is absorbed after 5.5 h, which constitutes 85 % of the maximum capacity (3.5 H/f.u). The amounts of absorbed hydrogen in heat-treated powders are 0.29 H/f.u (second cycle) and 0.043 H/f.u (third cycle) and constitute 7.4 and 1.1 % of the maximum absorption capacity, respectively.

Conclusions

Mechanical Alloying of Mg_2Ni -based alloys were performed using a high injected shock power mill. The formation of $\text{Mg}_2\text{Ni}/\text{Ni}$ compound was obtained after only 10 h milling, which corresponds to a cumulated energy of 57 Wh/g. The as-prepared composite also contains Mg - Ni amorphous phase and residual Ni . When the cumulated energy increases from 57 to 98 Wh/g, less residual Ni and higher Mg_2Ni contents are obtained. Consequently, an enhancement of the hydrogen absorption capacity was observed from 3.02 to 3.28 H/f.u upon the increase in the cumulated energy of milling. The combination of mechanical alloying and subsequent annealing at 350 °C for 24 h was able to improve the hydrogen absorption capacity and the hydrogenation kinetics. Independently on the preparation conditions of $\text{Mg}_2\text{Ni}/\text{Ni}$ powders, nearly 95 % of the hydrogen absorption capacity was reached after 5 h of absorption time. For longer absorption durations, the hydrogenation kinetics becomes very slow due to a drastic decrease of unoccupied sites, available to absorb hydrogen atoms, inside Mg_2Ni lattice.

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