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Hydriding/dehydriding of $Mg_{87}Ni_3Al_3Mm_7$ (Mm = La, Ce-rich mischmetal) alloy produced by mechanical milling

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Abstract

Nanocrystalline $Mg_{87}Ni_3Al_3Mm_7$ hydrides were produced by reactive mechanical milling (RMM) under hydrogen atmosphere. Milling first under argon, and then under hydrogen atmosphere was also carried out in order to study the effect of the gas atmosphere on the microstructure of the products of milling as well as on their hydriding properties. In both cases, the main product of the milling process turned out to be MgH_2 of the type β - MgH_2 . When the milling was carried out entirely under hydrogen atmosphere the amount of MgH_2 (~34 wt.%) was slightly larger than that resulted from milling under argon followed by milling under hydrogen atmosphere. X-ray diffraction studies revealed that the main product of the milling process is a nanocrystalline material with an average crystallite size of about 10–15 nm. The presence of a highly disordered (amorphous) phase was revealed as well. The first dehydriding reaction of the alloys (after RMM) was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). These studies allowed to determine the temperature and enthalpy of desorption (T_{des} , ΔH_{des}) as well as the amount of hydrogen released during heating. The T_{des} as well as the enthalpy of dehydriding of the alloys obtained by milling in different atmospheres were found not to differ significantly. The as-milled nanocrystalline materials were annealed to relieve the strain resulted from the milling and improve the material's crystallinity. Heat treatment at 350 °C for 1 h reduced the amount of the disordered phase in the sample milled only under hydrogen atmosphere. PCT analysis reveals an equilibrium pressure of about 2.5 atm for the alloy milled under Ar and hydrogen and about 2 atm for the alloy milled only under hydrogen. Both equilibrium pressures are higher than that found with pure Mg, indicating some thermodynamic destabilization of the hydride as a result of the alloying. Hydrogen-absorption kinetics was also studied at isothermal conditions. The hydrogen-absorption process in both nanocrystalline materials was found to be very fast most likely due to the alloying and fine particle size. The rate of H-absorption in the sample milled under argon and hydrogen was found to be higher than that in the sample obtained by milling only under hydrogen atmosphere.

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1. Introduction

Pure magnesium and magnesium-rich alloys have shown good promise as hydrogen storage materials. To fully utilize their good potential, the hydrogen-sorption kinetics needs to be improved at temperatures below 200–250 °C. Alloying magnesium with transition metals and rare-earth elements is one of the approaches employed to enhance the reaction ther-

modynamics and hydrogen-sorption kinetics [1–5]. Reducing the particle and grain size of the alloys by mechanical milling and adding catalysts have also been used successfully to improve the hydriding kinetics [5–10]. Our recent studies [5,10] on the hydriding/dehydriding behavior of Mg-rich alloys ($Mg_{87}(Ni,Al,Ti,Mm)_{13}$) showed a highly enhanced H-sorption kinetics at 300 and 250 °C compared to ball-milled pure nanocrystalline Mg. $Mg_{87}Ni_3Al_3M_7$ (M = Ti, Mn, Ce, La) alloys showed substantially decreased hydrogen-desorption temperature and higher equilibrium pressure of hydrogen absorption compared to pure nanocrystalline Mg

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[10]. This effect has been associated with thermodynamic destabilization of the hydride as a result of the alloying. Improved H-sorption behavior was also observed in melt-spun amorphous and nanocrystalline Mg-rich alloys (e.g. $\text{Mg}_{87}\text{Ni}_{12}\text{Y}_1$, $\text{Mg}_{83}\text{Ni}_{17}$) [11,12]. The H-sorption kinetics has been found to be influenced by the formation of solid solutions as well. Formation of supersaturated solid solutions of some transition (e.g. Zn, Cd, Al) and non-transition (In, Li, Ag, Sn) elements in the Mg phase as a result of mechanical milling was reported recently [13].

The present work aims at studying the hydriding/dehydriding properties of two magnesium-based alloys with the same composition ($\text{Mg}_{87}\text{Ni}_3\text{Al}_3\text{Mm}_7$) produced by mechanical milling under different atmospheres. One by reactive mechanical milling under hydrogen atmosphere (denoted later as Mg/H) and another by milling under argon, and then under hydrogen atmosphere (sample Mg/ArH). Thermodynamic and kinetic characteristics of the hydriding process with both alloys are reported here.

2. Experimental

High purity powders of magnesium, nickel, aluminum and La, Ce-rich mischmetal (Mm) were used as starting materials. The ball milling was performed with a planetary ball mill (Fritsch P5). The velocity of rotation was 300 rpm and the ball to powder mass ratio (B/P) was maintained 15/1. The milling was done once in hydrogen atmosphere (5 atm) (reactive mechanical milling, RMM) and a second time in argon, and then in hydrogen atmosphere again at 5 atm. At regular periods of time, some amount of the product of the milling process was taken out of the mill and subject to morphological, structural and thermal analyses.

The morphology and the microstructure were studied by scanning electron microscopy (JEOL 5510 SEM) and X-ray diffraction (XRD, X'Pert diffractometer) using Cu $K\alpha$ radiation. The thermal properties of the as-milled alloys were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) in argon, using Perkin-Elmer TGS-2 and Mettler differential scanning calorimeter.

Pressure-composition isotherms (PCI) were measured by Sieverts-type apparatus, using conventional volumetric method, at different temperatures.

3. Results and discussion

Results from SEM analysis are shown in Fig. 1. As can be seen in the figure powders obtained after 16 h RMM under hydrogen show particles with sizes ranging from 1 to 50 μm (Fig. 1a). All larger particles are indeed agglomerates of considerably smaller ones ($<1\ \mu\text{m}$), as the more detailed SEM picture (Fig. 1b) shows. Although noticeable difference in the morphology of the samples milled under different gas

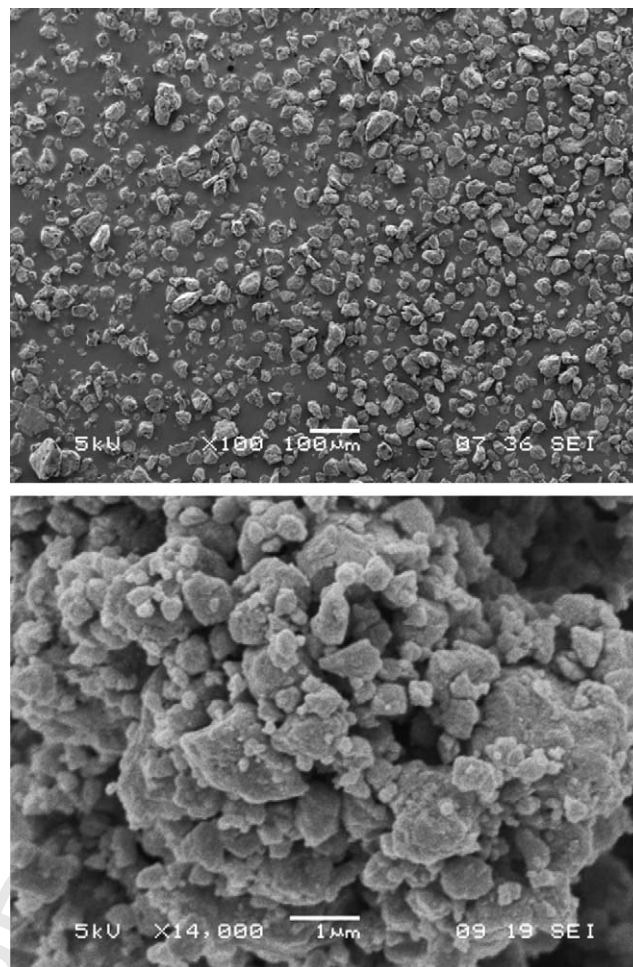


Fig. 1. SEM photographs of the as-milled material (a) and of an agglomerate (b).

atmosphere was not observed, the average particle size of the powder milled under hydrogen only is slightly smaller.

Results from X-ray diffraction experiments are shown in Fig. 2. As can be seen in the figure, the reactive mechanical milling of Mg (87 at.%)–Al (3 at.%)–Ni (3 at.%)–Mm (7 at.%) under hydrogen changes not only the microstructure but the phase composition of the starting mixture as well. Both alloys exhibit a similar phase composition: a predominant $\beta\text{-MgH}_2$ phase and traces of pure Mg and Ni. Some traces of Ce and La hydrides (CeH_x , LaH_x) and Mg–La phases could be also detected. Aluminum, which was used as additive is not seen and one may safely assume that it is dissolved into Mg [10]. A full profile fitting analysis based on the Rietveld method was carried out and the grain size and the phase content of the main phases were determined. The alloys milled for 16 h reveal nanocrystalline microstructure, with an average crystallite size of about 10 nm and about 34 wt.% MgH_2 for the alloy milled only in hydrogen and slightly less (~ 30 wt.%) for the alloy milled first 8 h under Ar, and then 8 h under hydrogen. The crystallite size does not change during subsequent milling for both alloys. The annealed alloys (350°C , 1 h) show coarser microstructure (~ 15 nm

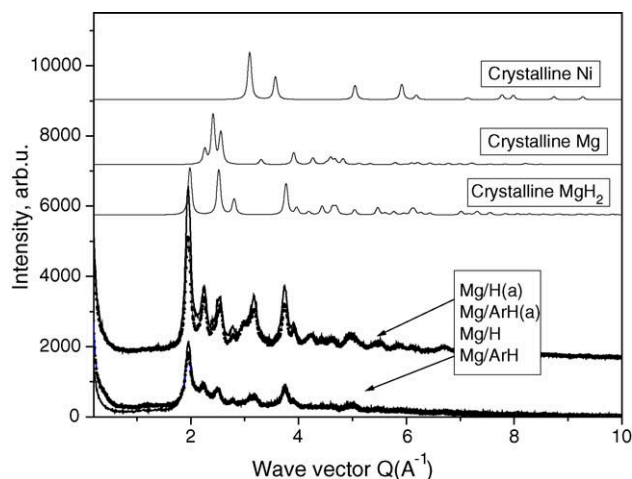


Fig. 2. XRD patterns for samples resulting from milling of a mixture of Mg (87 at.%)–Al (3 at.%)–Ni (3 at.%)–Mm (7 at.%) for 16 h under hydrogen atmosphere (Mg/H, thin line) and first under argon, and then hydrogen atmosphere (Mg/ArH, thick line). XRD patterns for the same samples annealed at 350 °C are shown as well (Mg/H(a) and Mg/ArH(a)). Theoretical powder diffraction patterns for several crystalline materials of the Mg, rare-earth, hydrogen and Ni family are shown in the upper part of the plot.

average crystallite size) compared to the as-milled material (Fig. 2).

Thermogravimetric (TG) analysis of powders milled for 16 h showed a total hydrogen amount of about 2.5 wt.%, thus confirming the findings of XRD quantitative analysis both indicating the formation of a hydride phase as a result of RMM. In a recent study [10], it was found that the amount of hydride phase depends on the time of milling and reaches a value of approximately 35 wt.% after 15 h of milling, which amounts to ~2.5 wt.% hydrogen absorbed. It has been also detected that further milling at such conditions leads to a little increase in the amount of hydride phase formed [10].

TG and DSC studies showed that the temperature of the hydride (MgH₂) decomposition is close to 230 °C, which is substantially lower than that reported with polycrystalline (400 °C) and ball-milled nanocrystalline MgH₂ (300 °C). The temperature of desorption, T_{des} , was found not to depend on the particular gas atmosphere. DSC studies revealed an enthalpy of dehydrogenating of about 70 kJ/mol H₂ for the alloy milled under hydrogen, which is slightly lower than the value for pure MgH₂ (75 kJ/mol H₂). The substantially lowered temperature of hydride decomposition is likely due to the combined effect of alloying and reduced particle and grain size of the powders.

Pressure-composition isotherms (PCT diagrams) at 300 °C for the hydriding/dehydrogenating of the Mg₈₇Ni₃Al₃Mm₇ alloys are presented in Fig. 3. Plateau regions, corresponding to the α -Mg(H) and β -MgH₂ coexistence, are observed with both alloys. The equilibrium pressure of H-absorption for the material milled first under Ar, and then under H (Mg/ArH) is higher ($p_{eq} \approx 2.5$ atm) than that for the alloy milled only under hydrogen (Mg/H). Both alloys reveal higher equilibrium pressures ($p_{eq} \approx 2$ –2.5 atm) than

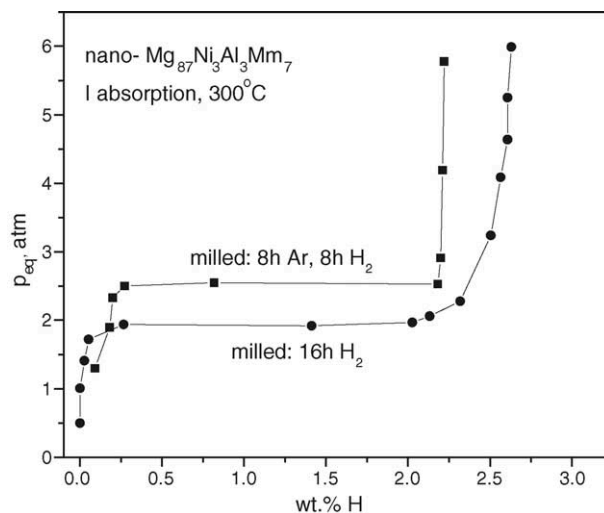


Fig. 3. PCI of hydriding at 300 °C: (■) Mg₈₇Ni₃Al₃Mm₇ (Mg/ArH) and (●) Mg₈₇Ni₃Al₃Mm₇ (Mg/H).

those reported with nanocrystalline Mg (1–1.5 atm) [2] at the same temperature of 300 °C. The increased equilibrium pressures are likely due to the alloying effect (formation of solid solution of Al and partially Ni in Mg). Similar findings were reported in our recent study of Mg₈₇Ni₃Al₃M₇ (M = Ti, Mn, Ce, La) alloys [10] and in a study of Liang [13] on mechanically alloyed Mg with transition as well as non-transition elements. The present results indicate a stronger thermodynamic destabilization of the hydride (MgH₂) for the alloy milled first under Ar. For comparison, the plateau pressure for nanocrystalline Mg₂Ni is around 2–2.5 atm [2], which is comparable to those observed with our Mg-based alloys. The difference in p_{eq} for samples Mg/H and Mg/ArH is not large (about 0.5 atm), but it is reproducible. The slightly higher p_{eq} with the alloy obtained in Ar is likely due to a better alloying. The alloying effect is not so strong with the sample milled just in hydrogen (Mg/H), likely due to the formation of the thermodynamically more stable MgH₂ phase. It is important to be mentioned that after cycling p_{eq} of Mg/ArH remains higher than that of sample Mg/H. This means that the solid solution does not completely decompose during cycling. The result is in agreement with the very recent findings of Liang [13].

The amount of hydride phases formed by RMM, obtained from the first dehydrogenating reaction (cycle) during a PCT analysis, is close to that determined by TG analyses. The second and third hydrogen-absorption/desorption cycles show an increase in the amount of the hydride; it reaches about 4.5 wt.% during the third cycle. After continuous cycling, the capacity decrease is not substantial showing that the hydriding process is reversible.

The plateau pressures of dehydrogenating of both alloys are about 1–1.5 atm. The PCT curves show some hysteresis during cycling (hydriding/dehydrogenating), which is similar for both alloys. This is usually ascribed to mechanical stress between the metal and the hydride phases or to kinetic constraints

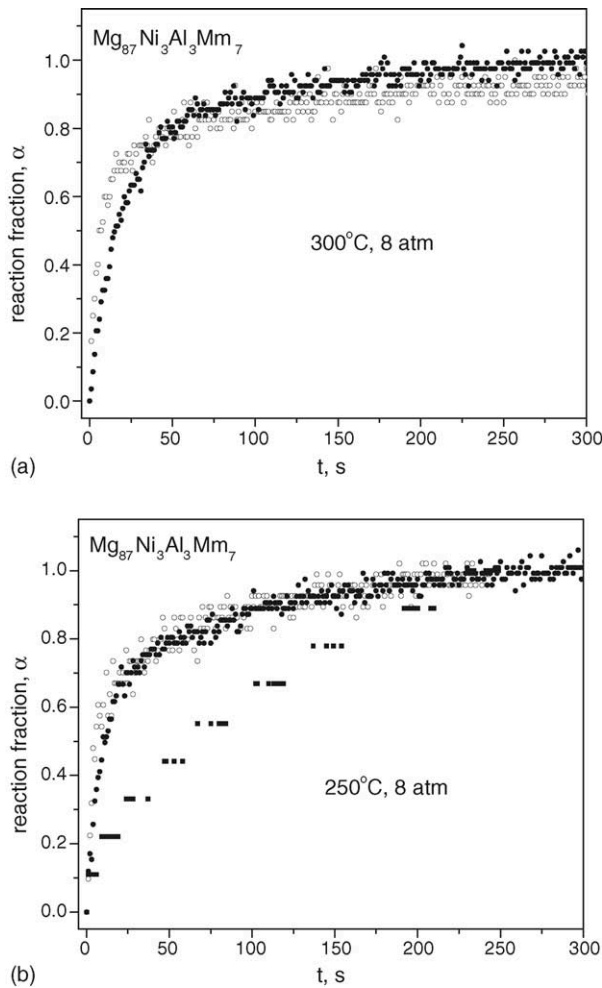


Fig. 4. Isothermal kinetics of hydrogen absorption at 300 °C (a) and 250 °C (b) ((○) Mg/ArH, (●) Mg/H, (■) Mg/H(a), where Mg/H(a) is the sample milled under hydrogen, and then annealed at 350 °C for 1 h).

during the measurement. The latter are due to the low driving force of the hydriding/dehydriding processes in the plateau regions [2]. The annealed alloys (with coarser microstructure, ~ 15 nm) do not show essential difference in p_{eq} .

The hydrogen-absorption kinetics was measured at different temperatures and pressures. Absorption kinetics curves at 8 atm and 300 °C are presented in Fig. 4. $Mg_{87}Al_3Ni_3Mm_7$ alloy (Mg/ArH) shows hydrogen-absorption rate that is higher than that of Mg/H alloy. The two rates are 0.27 and 0.14 wt.% H/s, respectively. The absorption kinetics does not change noticeably with the hydrogen gas pressure in the range 5–10 atm, indicating that the process is not diffusion controlled. In this pressure range and at temperatures as high as 300 °C the driving force $\{(P - P_{eq})/P_{eq}\}$ changes from 1 to 4. The rate of H-absorption depends slightly on the temperature in the temperature range of 250–300 °C, as the data in Fig. 4 show. The absorption rate at 250 °C is even somewhat higher than that at 300 °C (Fig. 4b). This is due to the higher thermodynamic driving force of the absorption reaction at low temperatures. For comparison, the H-absorption rate for

ball-milled nanocrystalline MgH_2 at 8.4 atm and 300 °C is in the range 0.030–0.035 wt.% H/s [8]. Addition of small amounts of metal oxides during milling leads to about 10 times increase of the H-absorption kinetics [9]. Our recent study revealed a significantly improved H-absorption kinetics (~ 0.25 wt.% H/s) for the ball-milled $Mg_{87}Al_3Ni_3Ti_7$ alloy as well [10]. The notable enhancement of the absorption kinetics is likely due to the very small particle size of the alloys.

The hydrogen-absorption kinetics changes with the microstructure coarsening of the alloys as shown in Fig. 4b. Annealing of the alloys at 350 °C for 1 h results in decrease of the H-absorption kinetics.

4. Conclusion

Nanocrystalline $Mg_{87}Ni_3Al_3Mm_7H_x$ powders were produced by reactive mechanical milling under hydrogen atmosphere as well as in a sequence of argon and hydrogen atmosphere. Both regimes of milling result in the formation of MgH_2 phase. Its amount is slightly larger when the milling was done entirely in hydrogen atmosphere. The ball-milled powders consist of grains (1–50 μm), which incorporate much smaller particles ($< 1 \mu m$). An average nanograin size of about 10–15 nm and a presence of disorder intergrain phase for both as-milled alloys were detected. The temperature of hydrogen desorption of the alloys is substantially lower than that of pure nanocrystalline MgH_2 . The enthalpy of dehydriding (~ 70 kJ/mol H_2) is similar for both alloys. PCT analysis reveals an equilibrium pressure of about 2.5 atm for the alloy milled first under Ar, and then under hydrogen atmosphere. This equilibrium pressure is higher by about 0.5 atm than that observed with the alloy prepared under hydrogen atmosphere only. The result indicates a stronger thermodynamic destabilization of the hydride as a result of the alloying during the milling under argon. The hydrogen-absorption kinetics in the alloy milled both under argon and hydrogen is markedly faster compared to that in the alloy milled under hydrogen atmosphere only.

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