Hydrogen Storage Properties of Nanocrystalline Mg_2Ni Based Alloys Prepared by Ball-Milling

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Nanocrystalline hydrides are a new class of material in which outstanding hydrogen sorption may be obtained by proper engineering of the microstructure and surface. The nanocrystalline Mg_2Ni alloy is a promising hydrogen storage material. In the present work, nanocrystalline Mg_2Ni alloy powders with grain size of about 50 nm were prepared by high-energy ball-milling, and its phase, crystal structure and hydrogen storage properties were investigated by X-ray diffraction analysis, transmission electron microscopy and pressure-composition isotherms, respectively. The hydrogen storage characteristics of Mg_2Ni are also presented. Nanocrystalline Mg_2Ni can readily absorb hydrogen at temperature lower than 523 K. The reversible hydrogen capacity is up to 3.5 wt.%.

Keywords: Mg_2Ni, nanocrystalline, mechanical alloying, ball-milling, hydrogen storage

1. Introduction

Many metallic materials are known to form hydrides reversibly. Intermetallic Mg_2Ni with its high hydrogen capacity (up to 3.6 wt.%) is the prime candidates among hydrogen storage systems [1–5]. However, Mg_2Ni cannot absorb hydrogen under normal conditions (i.e. room temperature and atmospheric pressure), and the ability of hydrogenation appears in temperature range from 523–623 K with hydrogen pressure of 1.5–5 MPa. Moreover, even if Mg_2Ni is heated more than 523 K, it also needs to be activated before hydrogenation. The activation process usually involves a heating process at a high temperature (598 K) under a high hydrogen pressure (2 MPa). The activation process has to be carried out several times to obtain reproducible hydrogen absorption/desorption characteristics. Improvement of the hydrogenation conditions of Mg_2Ni is therefore essential to produce a suitable material for practical hydrogen storage [6–8].

The mechanical alloying (MA) may give various homogeneous composite particles. Since 1970, the MA process via the ball-milling (BM) technique has been used to prepare several dispersion-strengthened alloy powders. The application of the MA process has been expanded recently to produce several hydrogen storage metals using a method called the reactive ball-milling.

Metal hydrides are usually prepared by passing a flow of reactive hydrogen over the metallic material under high pressure and at temperatures usually above room temperature. In our study, the single-phase Mg_2NiH_4 alloy powders with grain size about 50nm has been synthesized by milling an equiatomic mixture of elemental Mg and Ni powders under hydrogen atmosphere. Mg_2Ni alloy powder has been followed by X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the values of enthalpy and entropy changes for hydrogen absorption and desorption were evaluated from the pressure-composition isotherms on van't Hoff equation.

2. Experimental

In order to produce Mg_2Ni, a mixture of magnesium (99.95%, 150 mesh) and nickel (99.95%, 250 mesh), purified hydrogen and argon gas (H_2O and O_2, less than 20 ppm) has been used. The mixed powders were charged and sealed in a cylindrical stainless steel shell together with stainless steel rods in a laboratory high-energy mill SPEX 8000 (from SPEX Industries). The rod-to-powder weight ratio was controlled to be about 20 to 1.The inlet of the shell was connected to a rotary pump and evacuated for about 4 Pa. After evacuation, a flow of hydrogen gas was passed into the rod mill through a bellows pipe. Once the rod mill was filled with hydrogen at 0.25 MPa, the inlet of the vial was closed and the reactive rod-milling (RRM) process was carried out at ambient temperature by mounting the rod mill on a rotator at the rate of 2.0 s^{-1}. The RRM was stopped at selected intervals and a small amount of the rod-milled powder was taken out under argon atmosphere in a glove box.

3. Results and discussion

Mg_2Ni is difficult to prepare by conventional metallurgy because of the great difference in melting

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temperature and vapor pressures of Mg and Ni. Mechanical alloying by ball-milling requires no melt process of the elements and yields the compound through a solid-state reaction. Although this ball-milling is quite a common technique, published results on ball-milled Mg and Ni powders have not yet been shown to produce single-phase [2,5].

Under the ball-milling conditions (high-energy mill and high ball-to-powder mass ratio) in the present work, Mg_2Ni alloy powder was formed directly. The ball-milling parameters were as follows: The ratio of rod and metallic powder was 20 to 1, rotational speed of ball-milling per minute was 0.2 s^{-1} and processing control reagent is stearic acid.

Fig. 1 shows the X-ray diffraction patterns of Mg_2Ni after mechanically ball-milling for 2 h and 50 h under hydrogen atmosphere. Fig. 1 (a) shows an intermediate stage of mechanical alloying reaction (after 2 h of ball-milling), and this diffraction pattern includes the peaks of the Mg_2Ni compound, Mg and Ni. After milling for 50 h, the diffraction peaks of Mg_2NiH_4 become broader and none of the peaks corresponding to MgH_2 and NiH_2 are seen. It is worth noting that the broadness of these peaks can be attributed to the formation of Mg_2NiH_4 solid solution powder, as shown in Fig. 1 (b). We should emphasize that this solid solution phase has not changed to any other phase, even after milling for as long as 50 hours.

The size of nanocrystalline Mg_2Ni alloy was calculated by Scherrer formula as follows:

$$D = K\lambda/\beta_{1/2}\cos\theta, \quad (1)$$

where D is the size of nanocrystalline, K is Scherrer constant (0.89), λ is the wavelength of CuKα X-rays (0.15405 nm), $\beta_{1/2}$ is the width of half-height for diffraction peak (rad). Those of (101) and (105) of common Mg_2Ni alloy are 0.3062° and 0.2879°, respectively. In our work, those of (101) and (105) of nanocrystalline Mg_2Ni alloy were 0.3204° and 0.2950°, respectively. The size of nanocrystalline Mg_2Ni alloy was evaluated from XRD patterns to be about 50 nm.

Detailed TEM analyses were performed in order to understand the change in the fine structure of mechanically alloyed Mg_2NiH_4 particles during above-mentioned stages of milling (Fig. 2). The powder have large grains of about 50 nm diameter and the selected-area diffraction patterns (SADPs) taken at the center of this micrograph shows sharp rings coexisting with spot patterns of nanocrystalline Mg_2Ni alloy powder in Fig. 2 (c).

Figs. 3 and 4 show pressure-composition isotherms of nanocrystalline Mg_2Ni prepared with 50 h of ball-milling. The absorption/desorption temperature was in a range from 473 K to 623 K, and the nanocrystalline Mg_2Ni-H_2 system has obvious and wide plateau region. Reversible hydrogen capacity amounts to 3.5 wt.% within the

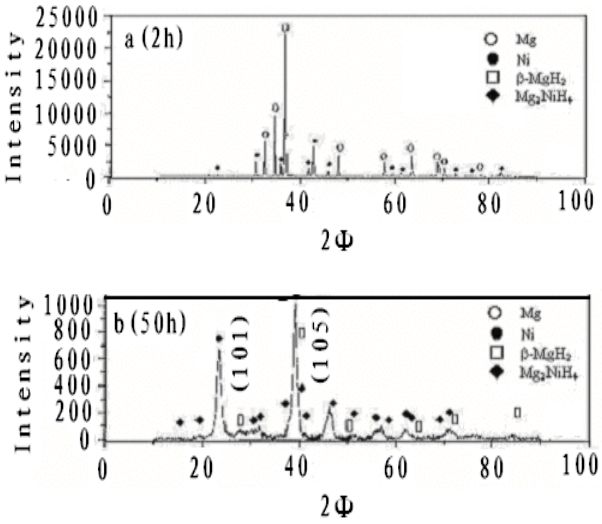

Fig. 1 XRD patterns of Mg-Ni alloys prepared by ball-milling for 2 h and 50 h.

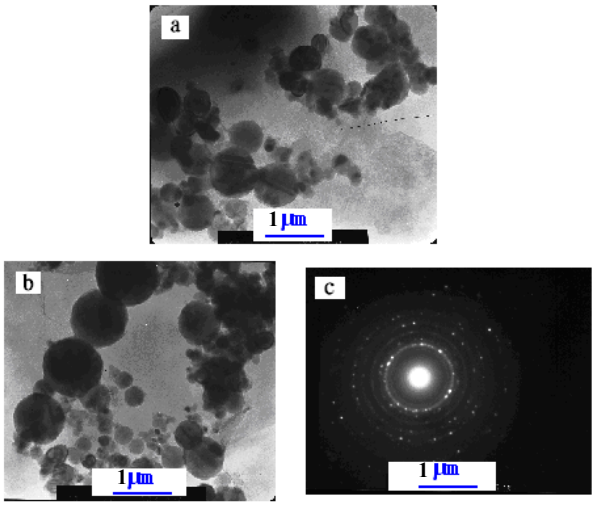

Fig. 2 TEM images of Mg-Ni alloys prepared by ball-milling under different conditions (a-2h, 120 K; b-50h, 150 K; c-electron diffraction pattern n (50h)).

applied hydrogenation time, and the capacity agreed with the literature [5]. The amount of absorbed hydrogen is usually 3.0–3.45 wt.% in the reversible hydrogenation cycles as reported in [5, 6]. The hydrogenation of the high-temperature phase of Mg_2NiH_4 is apparently much easier than for the low-temperature phase. The low-temperature phase of Mg_2NiH_4 is very difficult to obtain by the direct hydrogenation under moderate pressure conditions. The plateau pressures difference between absorption and desorption at the same temperature was observed (Fig. 5). The phenomenon was referred to hysteresis (its represents by hysteresis factor H_f), H_f increases with temperature. The hysteresis originates duo to the presence of transformation strains during both hydride formation and decomposition.

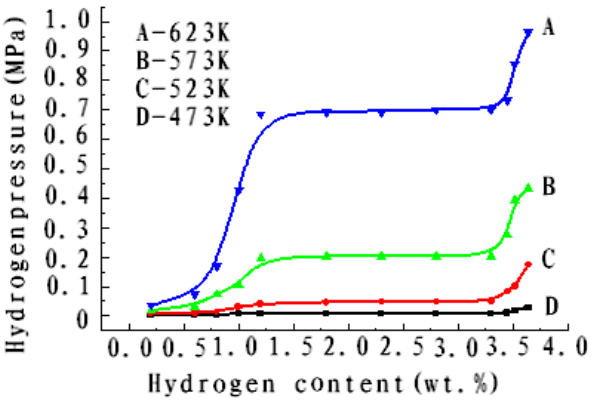

Fig. 3 Pressure-composition isotherms of hydrogen absorption for nanocrystalline Mg_2Ni alloy.

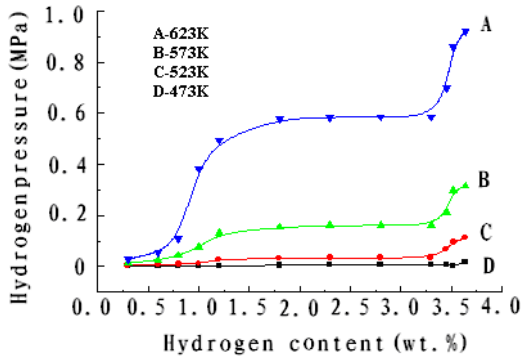

Fig. 4 Pressure-composition isotherms of hydrogen desorption for nanocrystalline Mg_2Ni alloy.

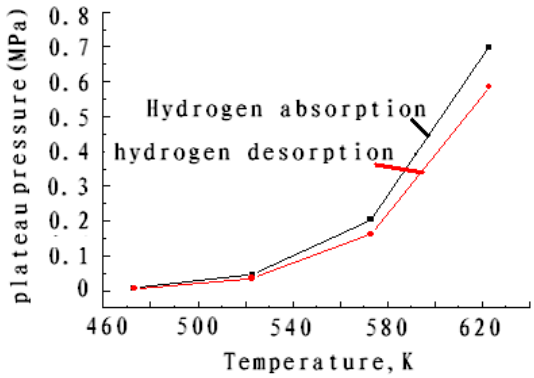

Fig. 5 The relationship between plateau pressure and temperature for nanocrystalline Mg_2Ni alloy.

According to van't Hoff equation, the relationship between temperature and hydrogen equilibrium pressure can be expressed as

$$\log(P_{H_2}) = \frac{-\Delta H^{\Theta}}{RT} + \frac{\Delta S^{\Theta}}{R}, \quad (1)$$

where ΔH^{Θ} is the standard enthalpy changes ($J \cdot mol^{-1}$) of hydriding reaction, ΔS^{Θ} is the standard entropy changes ($J \cdot mol^{-1} \cdot K^{-1}$) of the reaction, R is the gas constant, T is the given measurement temperature, and P_{H2} is the equilibrium hydrogen pressure.

The van't Hoff plots of the nanocrystalline Mg_2Ni alloy ($\log(P_{H2})$ versus $1/T$) were shown in Fig. 6. The best–fitting equations for ΔH^{Θ} and ΔS^{Θ} are given by hydrogen absorption process:

$$\log(P / 0.1\ \text{MPa}) = -3843/T + 7.012, \quad (2)$$

and by hydrogen desorption process:

$$\log(P / 0.1\ \text{MPa}) = -3992/T + 7.173. \quad (3)$$

The values of enthalpy and entropy changes for hydrogen absorption are $-73.58\ kJ \cdot mol^{-1}$ and $-134.26\ J \cdot mol^{-1} \cdot K^{-1}$, and those for hydrogen desorption are $76.44\ kJ \cdot mol^{-1}$ and $137.34\ J \cdot mol^{-1} \cdot K^{-1}$, respectively. The results agreed well with the literature [8].

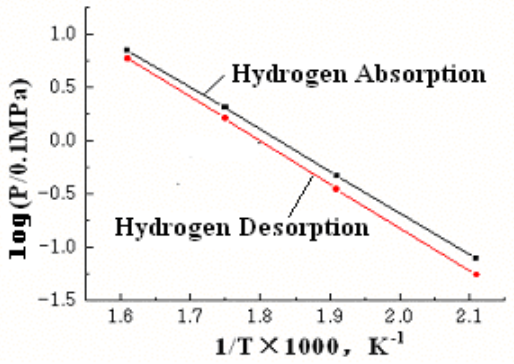

Fig. 6 Temperature dependence of plateau for nanocrystalline Mg_2Ni alloy.

Hydrogen absorption properties for ball-milled nanocrystalline Mg_2Ni alloy were better than those for conventional Mg_2Ni alloy. The as-produced powder readily absorbs hydrogen with no activation, and the final hydrogen content was found to be about 3.5 wt.% after the first hydrogenation cycle at 573 K (Fig. 7). In successive cycles, the absorption kinetics of Mg_2Ni prepared was reproducible and about four times faster than that of conventional Mg_2Ni. The results imply that the nanocrystalline Mg_2Ni alloys would be a promising hydrogen storage material.

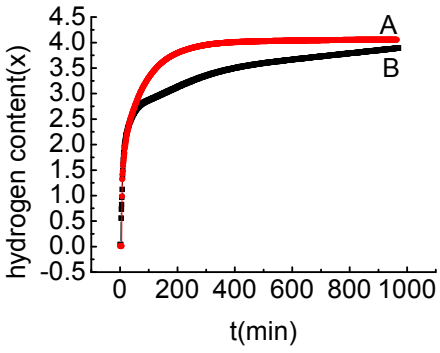

Fig.7 Absorption rate of hydrogen at 573K A-nanocrystalline Mg_2Ni alloy (50h) and B- conventional Mg_2Ni alloy

4. Conclusions

The Mg_2Ni alloys were prepared by ball-milling, which was composed of nanoparticles with grain size of about 50 nm. The structures and the hydriding behavior of Mg_2Ni prepared were studied. The absorption and desorption thermodynamic properties of Mg_2Ni alloys were improved by a ball-milling method. The reversible hydrogen capacity was found to be to 3.5 wt.%. The values of the enthalpy and the entropy for hydrogen absorption are −73.58 $kJ \cdot mol^{-1}$ and −134.26 $J \cdot mol^{-1} \cdot K^{-1}$, and those for hydrogen desorption are 76.44 $kJ \cdot mol^{-1}$ and 137.34 $J \cdot mol^{-1} \cdot K^{-1}$, respectively. The nanocrystalline Mg_2Ni alloy will be a promising hydrogen storage material for hydrogen energy and fuel cell systems.

References:

[1] L. Zaluski et al., J. Alloys Compd., **217**, 245 (1995).
[2] S. Orimo et al., J. Alloys Compd., **232**, L16 (1996).
[3] L. E. A. Berlouis et al., J. Alloys Compd., **305**, 82 (2000).
[4] L. Zaluski et al., J. Alloys Compd., **70**, 253 (1997).
[5] S. Orimo et al., J. Alloys Compd., **217**, 287 (1995).
[6] S. Orimo et al., J. Alloys Compd., **253**, 94 (1997).
[7] H. Imamura et al., J. Alloys Compd., **386**, 211 (2005).
[8] P. Selvam et. al, Int. J. Hydrogen Energy, **11**,169 (1986).