ELSEVIER

Journal of Alloys and Compounds 404–406 (2005) 716–719

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Catalytic effect of Ni nano-particle and Nb oxide on H-desorption properties in MgH_2 prepared by ball milling

N. Hanada[a,*], T. Ichikawa[a,b], H. Fujii[a,b]

[a] *Graduate School of Advanced Sciences of Matter, Hiroshima University, 1-3-1 Kagamiyama,*
Higashi-Hiroshima 739-8530, Japan
[b] *Natural Science Center for Basic Research and Development, Hiroshima University,*
1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

Received 31 May 2004; received in revised form 2 December 2004; accepted 9 December 2004

Abstract

We examined the catalytic effect of Ni nano-particle and Nb oxide on hydrogen desorption (HD) properties in MgH_2 prepared by mechanical ball milling under a hydrogen gas atmosphere of 1 MPa. The MgH_2 composite with 2 mol% Ni nano-particle prepared by milling for a short time of 15 min at 200 rpm desorbed a large amount of hydrogen (∼6.5 wt.%) in the temperature range from 150 to 250 °C at heating rate of 5 °C/min. On the other hand, the MgH_2 composite with 1 mol% Nb_2O_5 prepared by milling for a long time of 20 h at 400 rpm desorbed ∼6.0 wt.% H_2 in the temperature range from 200 to 250 °C at heating rate of 5 °C/min. After second hydrogen absorption/desorption cycles at 200 °C, the HD properties of the Ni-catalyzed MgH_2 composite became worse than those before cycling, while the Nb_2O_5-catalyzed composite showed better HD properties than those before cycling.

Keywords: Hydrogen storage material; High energy ball milling; X-ray diffraction; Thermal analysis

---

1. Introduction

Magnesium hydride MgH_2 is one of the most attractive hydrogen storage materials because it is directly formed from the reaction of Mg metal with gaseous hydrogen and reaches a high hydrogen capacity (∼7.6 wt.%). However, the reaction is too slow for practical use and needs higher temperature than 300 °C for progress of the hydrogen absorption and desorption reactions [1–3].

Recently the hydrogen storage (H-storage) properties of the composites composed of Mg or MgH_2 catalyzed by a small amount of transition metals or metal oxides have been intensively studied to improve the hydriding/dehydriding kinetics without reducing its high hydrogen capacity [4–9]. Zaluska et al. have studied H-storage properties of Mg composites prepared by ball milling Mg with 1 wt.% transition metals (Pd and Fe), in which ∼5 wt.% of hydrogen was absorbed at 300 °C within 10 min under a H_2-gas pressure of 1 MPa [4]. Their TEM observation indicated that the catalyst with several tens nanometer size is uniformly distributed on the metal surface, suggesting that the reaction kinetics could be sufficiently improved by doping small amounts of such catalysts. Recently, Kanoya et al. have investigated H-storage properties of the composite prepared by ball milling Mg with small amounts of nanometer sized transition metals (Ni and Fe) as catalyst [5]. The results indicated that 7.49 wt.% of hydrogen was absorbed at 300 °C by mechanically milling the mixture of Mg–0.33Ni–0.17Fe (at.%) for 15 min. On the other hand, Oelerich et al. have reported the catalytic effect of cheap metal oxides (Nb_2O_5, Fe_3O_4, V_2O_5, Mn_2O_3, Cr_2O_3, TiO_2, Sc_2O_3, Al_2O_3, CuO and SiO_2) on hydrogen desorption (HD) properties in MgH_2 [6–9]. The MgH_2 composite with 0.2 mol% Nb_2O_5 prepared by ball milling for 100 h showed the best HD properties among all the composites with metal oxides: ∼7 wt.% of hydrogen was

---

* Corresponding author. Tel.: +81 82 424 5744; fax: +81 82 424 7486.
E-mail address: hanadan@hiroshima-u.ac.jp (N. Hanada).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.166

absorbed within 60 s and desorbed within 130 s at 300 °C [9]. However, the role of metal oxide catalysis on H-desorption properties has not been clarified yet.

In this work, we examined the catalytic effect of Ni nanoparticle and micron sized Nb_2O_5 on the HD properties in MgH_2 prepared by ball milling under a hydrogen gas atmosphere of 1 MPa at room temperature.

2. Experimental procedures

MgH_2 powder (the purity is 90 wt.%, with several micron sizes, the rests of 9 and 1 wt.% are respectively no reacted Mg and MgO) was purchased from Sigma–Aldrich. The dry catalyst metals Ni with diameter of several tens of nanometers were from Shinku-Yakin, and Nb_2O_5 (99.5%, mesoporous, 32 Å pore) was from Sigma–Aldrich. The mixture of 300 mg MgH_2 and 1∼2 mol% Ni or Nb_2O_5 were put into a Cr steel pot (3×10^{-5} m^3 in volume) together with 20 steel balls (7 mm in diameter). The mass ratio of sample to ball is 1:100. Then, the inside of the pot was degassed below 1×10^{-4} Pa for 12 h. After introducing high-purity hydrogen (7N) of 1.0 MPa, the mixed sample was mechanically milled for 15 min to 20 h at the revolution speed of 200–400 rpm using a planetary ball milling apparatus (Fritsch P7). All the samples were always handled in a glovebox filled with purified argon Ar so as to minimize the oxidation on the samples.

The structural properties were examined by X-ray diffraction measurement (Rigaku RINT2000) using a Cu Kα radiation. The dehydriding properties of the products were examined by a thermal desorption mass spectroscopy (TDMS) (Anelva M-QA200TS) equipped with thermogravimetry (TG) at a heating rate of 5 °C/min. This equipment was specially designed and built up for using it inside the glove box filled with purified argon, which permitted simultaneous measurements of TG and TDMS without exposing the samples to air at all.

3. Results and discussion

3.1. Catalytic effect of nanoparticle Ni

Fig. 1 shows the thermal desorption mass spectra (TDMS) of hydrogen (H_2) for the MgH_2 composite with 1 mol% Ni nano-particle prepared by ball milling for 15 min to 2 h. The MgH_2 composite milled for 2 h has a hydrogen desorption peak around 260 °C, which are much lower than that of pure MgH_2 milled for 2 h (370 °C). Thus, we notice that a small amount of Ni nano-particle doping has a significant catalytic effect on the HD properties in MgH_2. To improve the milling condition, we decreased the milling time from 2 h to 15 min at 400 rpm for 1 mol% Ni-doped MgH_2 composite. As shown in Fig. 1, the milling for 1 h leads to a decrease of the onset temperature to about 150 °C, while the milling for 15 min leads to the further decrease in the peak temperature to about 210 °C. So, we see short time milling brings the better HD properties. However, the TDMS profile widely broadens in the temperature range from 150 to 300 °C. Then, we changed the milling revolution speed and the amount of Ni nano-particle as catalyst under a milling time 15 min to obtain much better milling conditions. As a result of this procedure, the MgH_2 composite with 2 mol% Ni at 200 rpm showed the most superior HD profile in the TDMS curves among all composites examined in this work. The product desorbs a large amount of hydrogen (∼6.5 wt.%) in the temperature from 150 to 250 °C at a heating rate of 5 °C/min. From these results, it is concluded that the short milling time and slow milling revolution speed brings better HD properties for Ni^{nano}-catalyzed MgH_2 composite.

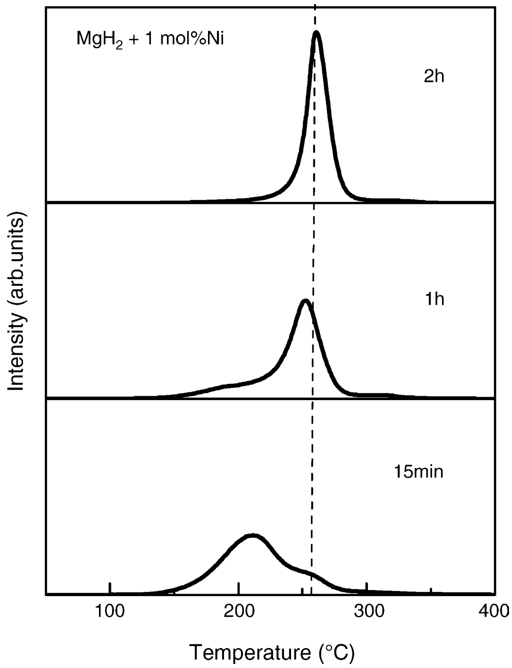

Fig. 1. Thermal desorption mass spectra of hydrogen from the MgH_2 composite with 1 mol% Ni by milling for 15 min, 1 h, and 2 h at 400 rpm under a hydrogen gas atmosphere of 1 MPa.

Next, we examined the cyclic properties of hydriding/dehydriding reactions for the MgH_2 composite with 2 mol% Ni prepared by milling for 15 min at 200 rpm under H_2 gas atmosphere of 1 MPa. The durability was tested through the following cyclic processes: the dehydrogenation was performed by holding the sample at 150 °C (corresponding to the onset temperature of dehydrogenation) and at 200 °C (corresponding to the peak temperature of dehydrogenation) for 12 h under high vacuum, and then the hydrogenation was performed under a pure hydrogen gas of 3 MPa at 150 and 200 °C for 12 h, respectively. After completing those hydrogen absorption/desorption cycles, we examined the HD spectra by the TG–TDMS measurement. The results obtained are shown in Fig. 2. The HD properties after the second cycle at 200 °C are worse than those after second cycle at 150 °C regarding the hydrogen desorption temperature.

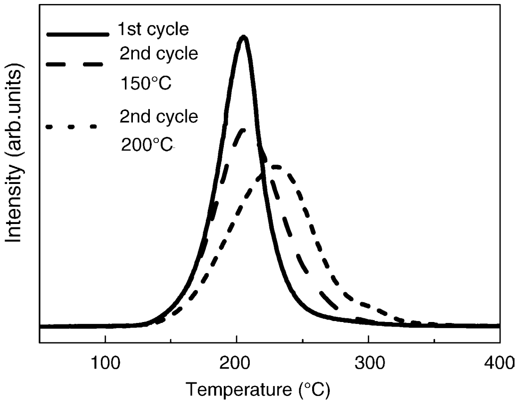

Fig. 2. Thermal desorption mass spectra of hydrogen for the 2 mol% Ni-catalyzed MgH_2 composite prepared by milling for 15 min at 200 rpm. The solid line is the product after milling for 15 min at 200 rpm, the dashed line for the sample after the second hydriding/dehydriding cycle at 150 °C and the dotted line for the sample after second cycle at 200 °C, respectively.

Then, we examined the XRD profile of the composite after dehydrogenation at 200 °C, which indicated the existence of Mg_2Ni phase in addition to Mg and Ni metal phases [10]. It seems that catalytic effect of Mg_2 Ni on hydrogen desorption of MgH_2 is weaker than Ni-metal, so that the existence of Mg_2Ni in the $MgH_2 + Ni$ composite makes the dehydrogenation properties worse.

3.2. Catalytic effect of metal oxide

Fig. 3 shows the TDMS for H_2 for the MgH_2 composite with 1 mol% Nb_2O_5 prepared by ball milling for 15 min to 2 h at 400 rpm under a H_2 gas atmosphere of 1 MPa. The composite milled for 15 min has two hydrogen desorption peaks around 230 and 270 °C, which are much lower than that for pure MgH_2 milled for 15 min (370 °C). This indicates that Nb_2O_5 is one of the good catalysts for improving the HD properties in MgH_2. To improve the milling condition, we increased the milling time up to 20 h from 15 min for the Nb_2O_5 doped composite. After 2 h milling, the HD peak at high temperature becomes much weaker as is shown in Fig. 3. Furthermore, the milling for 20 h leads to a single HD peak around 230 °C, possessing a large amount of hydrogen (∼6.0 wt.%). This result indicates that the HD properties of the Nb_2O_5-catalyzed composite are improved with increasing milling time in contrast to the behavior of the Ni-catalyzed composite.

As is evident from Fig. 4(a), the composite of MgH_2 and 1 mol% Nb_2O_5 milled for 20 h shows the existence of β-MgH_2 in the XRD profiles, but there is no trace of Nb_2O_5. This indicates that Nb_2O_5 disperses on the surface of MgH_2 in the nanometer scale by ball milling and acts as a good catalyst. The XRD profile after heat treatment up to 450 °C in Fig. 4(b) indicates the existence of Mg and MgO. In addition, the intensity of the 2 0 0 peak corresponding to MgO is larger than that corresponding to pure MgH_2 milled for 20 h in Fig. 4(c). Therefore, it seems likely that Nb_2O_5 dispersed in nanometer scale is reduced by Mg to form metallic Nb and MgO during ball milling or heat treatment as follows:

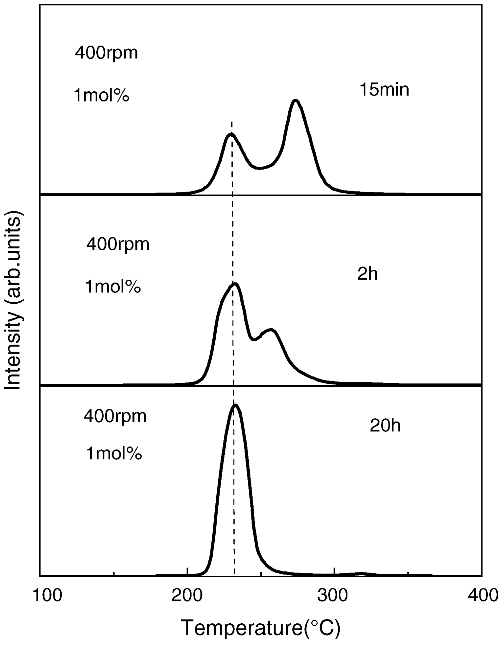

Fig. 3. Thermal desorption mass spectra of hydrogen from the MgH_2 composite with 1 mol% Nb_2O_5 prepared by milling for 15 min, 2 h, and 20 h at 400 rpm under a H_2 gas atmosphere of 1 MPa.

$$\tfrac{1}{2}Nb_2O_5 + \tfrac{5}{2}Mg \rightarrow Nb + \tfrac{5}{2}MgO,$$

$$\Delta H = -554.5\,\mathrm{kJ/mol\,Nb}.$$

Since the standard enthalpy change of this reaction is negative large value, this reduction reaction should be possible to

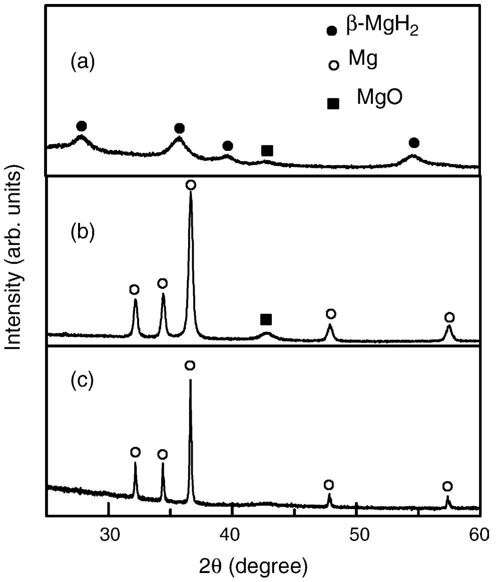

Fig. 4. X-ray diffraction profiles for (a) the 1 mol% Nb_2O_5-catalyzed MgH_2 composite prepared by milling for 20 h, (b) the composite after heat treatment up to 450 °C, (c) the pure MgH_2 by milling for 20 h after heat treatment up to 470 °C.

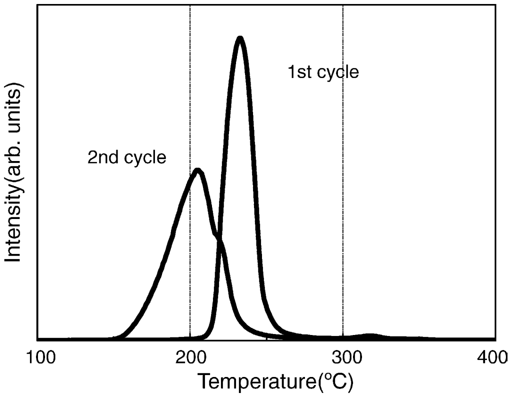

Fig. 5. Thermal desorption mass spectra of hydrogen for the 1 mol% Nb_2O_5-catalyzed MgH_2 composite prepared by milling for 20 h (first cycle) and the sample after second dehydriding/hydriding cycle at 200 °C (second cycle).

proceed during ball milling or heat treatment. Consequently, the metallic Nb dispersed in nanometer scale could act as an excellent catalyst for hydrogen desorption in MgH_2.

Next, we examined the cyclic properties of hydriding/dehydriding reactions at 200 °C for the composite of MgH_2 with 1 mol%Nb_2O_5 milled for 20 h according to the same cyclic processes as the MgH_2 composite with Ni nanoparticle. As is shown in Fig. 5, the dehydrogenation properties after the second cycle at 200 °C is better than that after the 1st cycle regarding the HD properties. This suggests that Nb_2O_5 is reduced by Mg to form metallic Nb during dehydriding/hydriding cycle at 200 °C, leading to the HD of ~6 wt.% in the temperature range from 150 to 250 °C. This result indicates that Nb is the best catalyst we have studied so far.

4. Conclusion

We investigated the hydrogen desorption (HD) properties of the MgH_2 composite doped with Ni nano-particle and Nb oxide prepared by ball milling method. The MgH_2 composite with 2 mol% Ni nano-particle prepared by ball milling for 15 min at 200 rpm showed good HD properties: a large amount of hydrogen (~6.5 wt.%) was desorbed in the temperature range from 150 to 250 °C under heating rate of 5 °C/min. However, HD properties of this composite became worse by repeating the dehydriding/hydriding cycles at 200 °C. This degradation at 200 °C may be due to the fact that Mg_2Ni alloy is formed in the product after the dehydrogenation at 200 °C, which is a worse catalyst for recombination of H atoms into H_2 molecule on the surface of MgH_2 and vice versa.

On the other hand, the MgH_2composite with 1 mol% Nb_2O_5 metal oxide prepared by ball milling for 20 h at 400 rpm shows superior HD properties, in which a large amount of hydrogen (~6.0 wt.%) is desorbed in the temperature range from 200 to 250 °C at a heating rate of 5 °C/min. Further, this composite after dehydriding/hydriding cycles at 200 °C showed better HD properties than those before cycling. This could suggest that Nb_2O_5 dispersing in nanometer scale is reduced by Mg to form metal Nb and MgO during ball milling or heat treatment, acting as a good catalyst for improving the HD properties in MgH_2.

Acknowledgements

This work was supported by a Grant-in-Aid for COE Research (No. 13CE2002) of the Ministry of Education, Sciences and Culture of Japan, and the New Energy and Industrial Technology Development Organization (NEDO), Japan.

References

[1] D.L. Cummings, G.J. Powers, Ind. Eng. Chem. Process. Des. Dev. 13 (2) (1974) 182.
[2] J.F. Stampfer Jr., C.E. Holley Jr., J.F. Stuttle, J. Am. Chem. Soc. 82 (1960) 3504.
[3] B. Vigeholm, J. Kjoller, B. Larsen, J. Less-Common Met. 74 (1980) 341.
[4] A. Zaluska, L. Zaluski, J.O. Ström Olsen, J. Alloys Compd. 288 (1999) 217.
[5] L. Kanoya, M. Hosoe, T. Suzuki, Honda R&D Tech. Rev. 14 (2002) 91.
[6] W. Oelerich, T. Klassen, R. Bormann, J. Alloys Compd. 315 (2001) 237.
[7] W. Oelerich, T. Klassen, R. Bormann, Adv. Eng. Mater. 3 (2001) 487.
[8] Z. Dehouche, T. Klassen, W. Oelerich, J. Goyette, T.K. Bose, R. Schulz, J. Alloys Compd. 347 (2002) 319.
[9] Gagik Barkhordarian, Thomas Klassen, Rüdiger Bormann, Scripta Materialia 49 (2003) 213.
[10] Nobuko Hanada, Takayuki Ichikawa, Hironobu Fujii, J. Phys. Chem. B 109 (2005) 7188.