Journal of Alloys and Compounds 446–447 (2007) 138–141

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Hydrogen storage Mg_2Ni alloy produced by induction field activated combustion synthesis

Yasuhiro Kodera[a,*], Natsuki Yamasaki[a], Takeshi Yamamoto[a], Takashi Kawasaki[a], Manshi Ohyanagi[a], Zuhair A. Munir[b]

[a] *Department of Materials Chemistry, Innovative Materials and Processing Research Center, Ryukoku University, Ohtsu 520-2134, Japan*

[b] *Facility for Advanced Combustion Synthesis (FACS), Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA*

Received 7 October 2006; received in revised form 17 April 2007; accepted 17 April 2007

Available online 21 April 2007

Abstract

It is difficult to obtain pure Mg_2Ni alloy by conventional melting method because of the large difference in vapor pressure and melting point between Mg and Ni. However, Mg_2Ni with high purity and fine properties as a hydrogen storage material was successfully synthesized from elemental Mg and Ni powders by Induction Field Activated Combustion Synthesis (IFACS). The IFACSed Mg_2Ni showed convenient hydrogen properties as same as the reference. The effect of Mechanical Grinding (MG) on the hydrogen storage behavior in Mg_2Ni is also described. The MG process developed the applicability of Mg_2Ni as a hydrogen storage material by decreasing the absorption pressures and enhancing the reaction kinetics.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Hydrogen absorbing materials; X-ray diffraction

---

1. Introduction

Mg and Mg-based alloys are some of the potentially important hydrogen storage materials owing to their high hydrogen storage capacity and relatively low environmental impact. Pure Mg is an attractive material for hydrogen storage because of its high hydrogen absorbing capacity (7.6 wt%). On the other hand, the stable ionic Mg-H bonding (i.e., the formation energy for MgH_2 is -74.4 kJ/mol [1]) makes Mg difficult to desorb hydrogen. However, the Ni addition into pure Mg is known to be effective as a catalysis [2]. Since Reilly and Wiswall [3] found reversible hydrogenation reaction for Mg_2Ni compound, much effort has been made to improve the hydrogen absorption-desorption kinetics of Mg–Ni alloys.

There are still some difficulties in the synthesis of Mg_2Ni alloy because of the large differences in vapor pressure and melting point between Mg and Ni. Furthermore, it is difficult to obtain pure Mg_2Ni alloy by conventional melting method. The hydriding combustion synthesis with elemental Mg and Ni was successfully applied as an alternative process to synthesize full hydride of Mg_2Ni, Mg_2NiH_4 directly by Akiyama et al. [4]. Moreover, the hydrogen storage capacity reached 3.6 wt%, which is same as the theoretical value for Mg_2Ni. The hydriding combustion synthesis is a promising process; however, it has to be performed under pressured hydrogen atmosphere.

In this paper, the synthesis of pure Mg_2Ni from elemental Mg and Ni was carried out using Induction Field Activated Combustion Synthesis (IFACS) method. IFACS is the new processing method of combustion synthesis utilized an electromagnetic induction field. The formation energy of Mg_2Ni is $\Delta H = -40$ kJ/mol and is generally not enough to self-sustain the combustion reaction without any external heat support. Reactions which are weakly exothermic cannot be initiated or sustained. We, herein, applied the field-activated process arising from the use of induction [5–8] for the external heat support. The reactants sample is covered with a conductive carbon foil and is placed inside an induction coil. The induction current is generated in the foil as well as in the sample. Since the

---

[*] Corresponding author. Tel.: +81 775437464; fax: +81 775437714.
E-mail address: kodera@rnoc.fks.ryukoku.ac.jp (Y. Kodera).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.04.241

induction current is localized in a surface layer of the foil and the sample, ignition takes place in this region and is expected to propagate in an inward radial direction. After preparation of Mg_2Ni by IFACS, the specimen was mechanically milled to improve properties as hydrogen storage material.

2. Experimental details

High-purity powders of Mg and Ni were used. Both Mg and Ni powders were 99.9% pure and had average particle sizes of about 180 and 63 μm, respectively (Kojundo Chemical Laboratory, Inc., Japan). Powders of Mg and Ni were weighed out in mole ratios of Mg/Ni: 2/1 to give a composition of Mg_2Ni and were ball milled under dry condition with Si_3N_4 balls and vial for 1 h. After mixing, the reactants sample coated by MgO was covered with a conductive carbon foil (0.4 mm in thickness and 40 mm in diameter) and was placed inside an induction coil. The induction current (45–85 V, 100–170 A, 70 kHz) was generated both in the foil and sample to reach 500–1000 °C. The reactants sample was heated at 900 °C and held for 0–30 min. After induction heating, sample was thermal treated at 600 °C for 2.5 h using electrical furnace to complete formation of Mg_2Ni. To observe the effect of strain and crystallite size on hydriding/dehydriding properties of Mg_2Ni, Mechanical Grinding (MG) process for powders was performed using planetary ball milling (P5, Fritsch, Germany) with Si_3N_4 balls and vials (revolution: 300 rpm, weight ratio: powder/ball = 1/10).

The phase identification of powder samples was carried out using X-ray diffraction (XRD) analysis (Model: RINT2500, RIGAKU, Japan) with Cu Kα radiation operated at 200 mA and 40 kV. Strain and crystallite size of specimen were estimated using the Halder–Wagner method [9–11]. The determination of crystallite size and the lattice strain was carried out through the governing relationship:

$$\left(\frac{\beta^*}{d^*}\right)^2 = \frac{\beta^*}{Dd^{*2}} + (2\varepsilon)^2 \tag{1}$$

where β ($\beta^* = \beta\cos\theta/\lambda$, Å^{-1}) is the integral width in the lattice plane, λ is 1.5405 Å, D the crystallite size, ε the lattice strain, and d^* ($2\theta/\lambda$, Å^{-1}) is the reciprocal of the lattice distance. The strain and the crystallite size can be calculated from the intercept and the slope of the linear plot of $(\beta^*/d^*)^2$ versus $\beta^*/(d^*)^2$.

Pressure-composition isotherms (PC) and the kinetics of hydrogen sorption were measured by PCT-A04 (LESCA, Japan). Before measuring hydride/dehydride properties, the samples were heated at 350 °C under vacuum as a pretreatment process.

3. Results and discussion

Fig. 1 shows XRD patterns of specimens prepared by IFACS at various reaching temperatures, at which the induction current was stopped. When mixed powder was heated at 500 °C, the specimen still contained remaining of metallic Mg and Ni from green powder. Hence, the reaction between powders has not been taking place yet. As the temperature reached 600 °C, the reaction initialized and formed Mg_2Ni phase. Below 800 °C, the specimen contained remarkable amount of unreacted material (mainly Ni). Furthermore, even if the synthesizing temperature was increased from 800 to 900 °C, the unreacted Mg still existed. From the comparison between specimens treated at 800 and 900 °C (Fig. 1), it was observed that the latter contained slightly less unreacted metal. When the temperature reached above 1000 °C, the unreacted metals seemed to be no longer existing in the product; however, the peaks corresponding to $MgNi_2$ were observed after all.

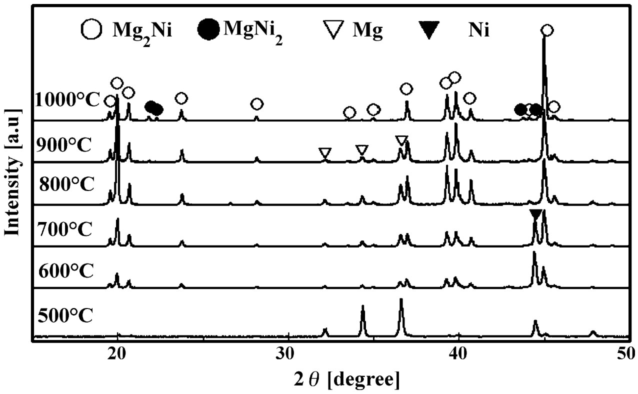

Fig. 1. X-ray diffraction patterns of specimen prepared by IFACS at various reaching temperature for 0 min.

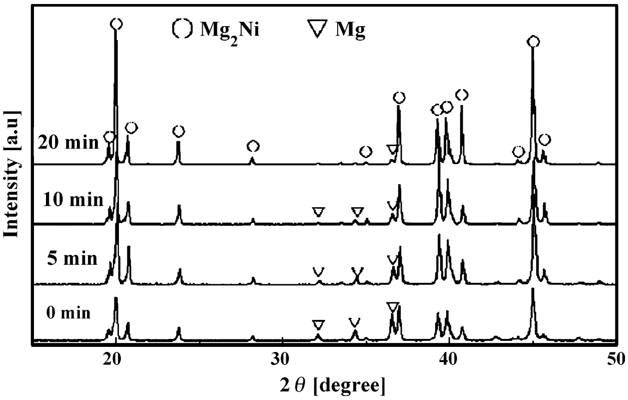

Fig. 2. The effect of holding time on specimen prepared by IFACS at 900 °C for 0–20 min.

Fig. 2 shows the effect of holding time on product phase prepared by IFACS at 900 °C for 0–20 min. In order to have further reaction, the induction heating was kept for 0–20 min. The unreacted Ni was not detected on the specimen held for 0 min, whereas the amount of unreacted Mg decreased with holding time and became negligible on the sample held for 20 min.

Fig. 3 shows the comparison between commercial Mg_2Ni powder with 99.9% purity and thermal treated specimen prepared by IFACS. The IFACSed sample was thermal treated at 600 °C for 2.5 h using electrical furnace. The commercial

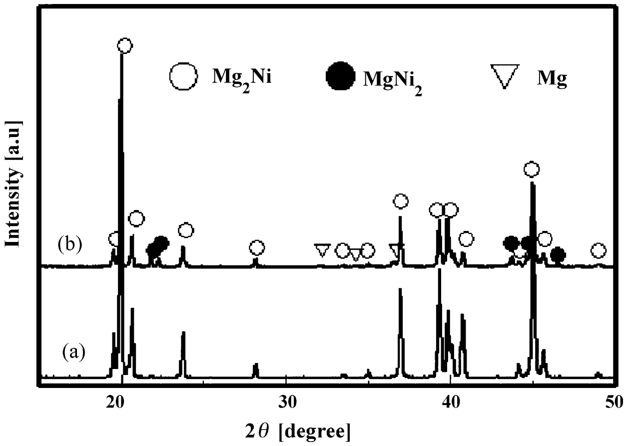

Fig. 3. The comparison between (a) thermal treated specimen prepared by IFACS at 900 °C for 20 min and (b) commercial Mg_2Ni powder with 99.9% purity.

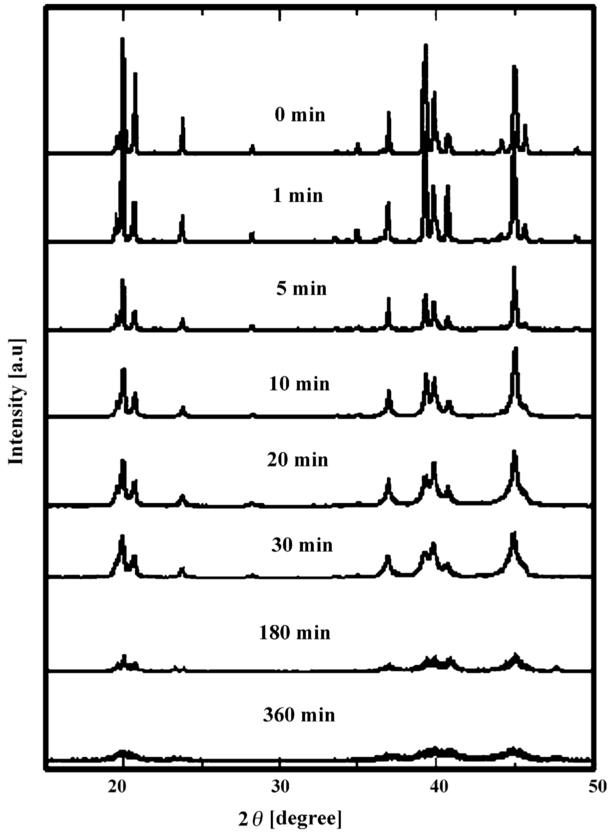

Fig. 4. XRD patterns of Mg_2Ni pulverized for 0–360 min by planetary ball milling.

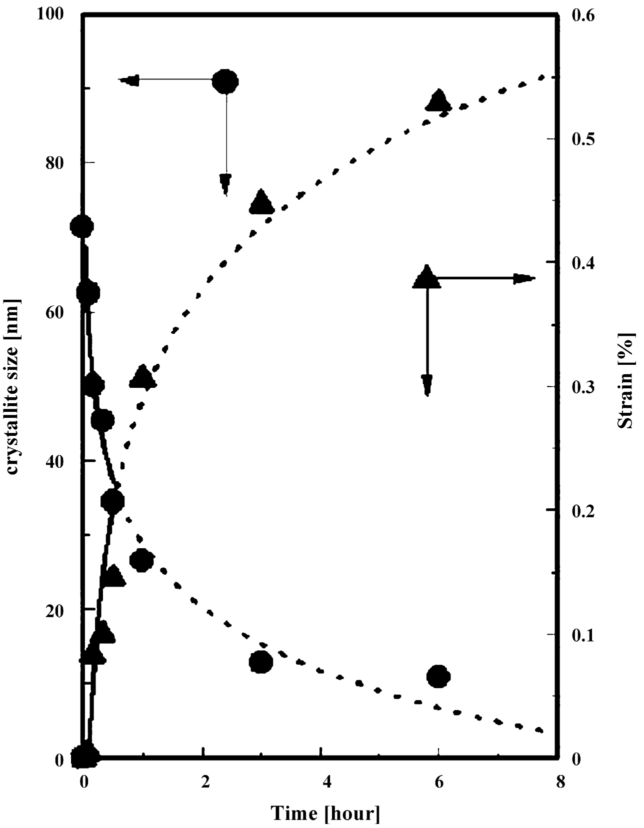

Fig. 5. The dependence of the crystallite size and strain on MG time.

powder contained small amount of unreacted Mg and $MgNi_2$. However, Fig. 3 reveals only one phase of Mg_2Ni existed in the product of IFACS, which suggested that it has higher purity than the commercial one. Hence, Mg_2Ni with high purity was synthesized successfully using IFACS.

The maximum hydrogen storage capacity of Mg_2Ni prepared by IFACS was 3.5% at 350 °C, which coincided with the theoretical value of 3.6%. Absorption and desorption curves on PC measurement showed good agreement with reference data [12]. Unusual activation process, such as acid or base cleaning, was not required before PC measurement, which suggested that there was only negligible amount of inactive phase on the surface of IFACSed Mg_2Ni grains. From the result of XRD analysis on the hydrogenated specimen, only Mg_2NiH_4 phase was identified. Due to the large differences in vapor pressure and melting point between Mg and Ni, the synthesis of Mg_2Ni is generally difficult. However, these results suggest that IFACS method is effective for preparing Mg_2Ni as the hydrogen storage material.

To further develop the applicability of IFACSed Mg_2Ni as hydrogen storage material, the properties such as hydrogenation/dehydrogenation kinetics should be improved. Fig. 4 shows XRD patterns of sample pulverized for 0–360 min by planetary ball milling. All peaks weakened and got wider as grinding time was increased. At and above 180 min, the peaks became broad and weak, significantly. These data suggested that the structure like crystallite size and strain of Mg_2Ni could be changed during MG.

Fig. 5 shows the dependence of crystallite size and strain on the grinding time. To clarify the structural change in the MG process, the crystallite size and strain were estimated using Halder–Wagner method. Estimated value of strain increased with MG time. Balls collided with powder, then strain was introduced into the lattice, and they broke down the grain causing crystallite size to decrease. Above 180 min of MG time, the specimen might have partial or dominant amorphous structure and unattractive property as hydrogen storage material (i.e., hydrogen storage capacity) due to the extremely low crystallinity, which was suggested from the results of XRD analysis.

Fig. 6 shows the hydrogen storage capacity of Mg_2Ni after MG. Hydrogen storage capacity slightly increased by MG. However, the decreasing of hydrogen storage capacity on MGed specimen for 10 min and more was observed, which could be caused by excess MG declining H site on the crystal structure. Fig. 7 shows the absorption kinetics at 350 °C. Absorption kinetics of Mg_2Ni well agreed with reference before MG process [12]. When MG was performed for 10 min, the specimen showed quicker reaction than the ones carried out for shorter times. Recently, Hanada et al. reported the effect of milling on hydrogen storage properties of MgH_2 system, and showed the role of decreasing crystallite size and introducing lattice strain on the properties [13]. Smaller particles and crystallite size (also larger specific surface area) caused by MG lead to the increase in hydrogen molecule diffusion length and hydrogen absorption sites. Therefore, absorption kinetics of IFACSed Mg_2Ni was enhanced by MG in this study.

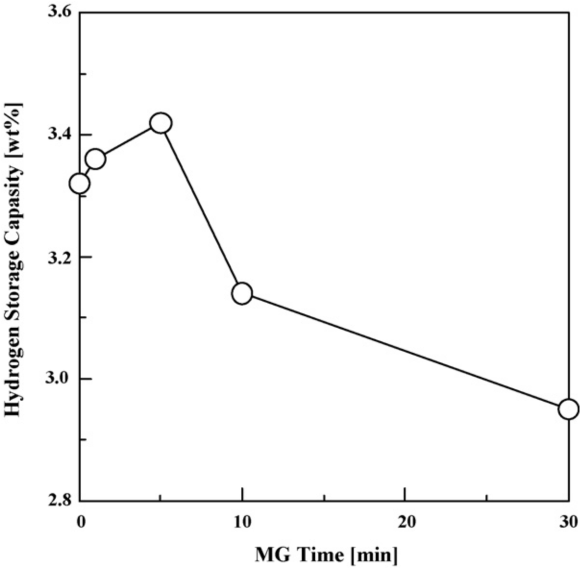

Fig. 6. Hydrogen storage capacity of specimen after MG process for 1–30 min.

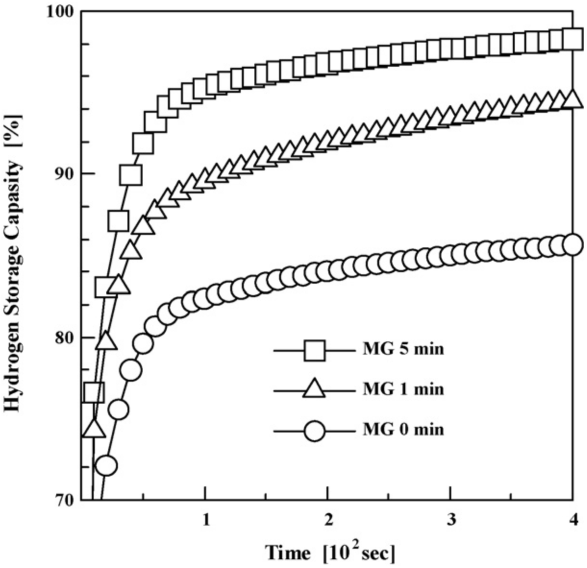

Fig. 7. Absorption kinetics of specimen after MG process for 1–30 min. Y-axis values were calculated based on maximum hydrogen storage capacity from PCT data.

4. Conclusions

Pure Mg_2Ni was successfully synthesized from elemental Mg and Ni powder by IFACS. IFACS is the new processing method of combustion synthesis utilized an electromagnetic induction field. The maximum hydrogen storage capacity of the specimen was 3.5% at 350 °C. Only Mg_2NiH_4 phase was identified after the hydrogenation process. Those results suggested that IFACS method is effective for preparing Mg_2Ni as the hydrogen storage material. During MG process, strain and crystallite size of Mg_2Ni increased and decreased, respectively, with milling time. MG process enhanced the absorption kinetics of IFACSed Mg_2Ni.

Acknowledgements

The authors acknowledge the partial support of this work by grant based on High-tech Research Center Program for private Universities from the Japan Ministry of Education, Culture, Sport, Science and Technology (MO), and by the Army Research Office, ARO (ZAM).

References

[1] R. Wiswall, in: G. Alefeld, J. Volkel (Eds.), Hydrogen in Metals, vol. 29, Springer-Verlag, 1978, p. 209.
[2] B. Bogdanovic, B. Spliethoff, Int. J. Hydrogen Energy 12 (1987) 863.
[3] J.J. Reilly, R.H. Wiswall, Inorg. Chem. 7 (1968) 2254.
[4] T. Akiyama, H. Isogai, J. Yagi, Int. J. SHS 4 (1995) 69.
[5] M. Ohyanagi, I. Shimazoe, T. Hiwatashi, T. Tsujikami, M. Koizumi, E.A. Levashov, Z.A. Munir, Ceramics Transaction, Functionally Graded Materials 2000, vol. 114, 2001, p. 259.
[6] M. Shibuya, M. Kawata, M. Ohyanagi, Z.A. Munir, J. Am. Ceram. Soc. 85 (2003) 706.
[7] M. Ohyanagi, T. Hiwatashi, M. Koizumi, Z.A. Munir, Proceedings of the 1st Russia–Jpn. Workshop Self-Propag. High-Temp. Synth., 1998, p. 65.
[8] D. Kata, M. Ohyanagi, Z.A. Munir, J. Mater. Res. 15 (2000) 2514.
[9] N.C. Halder, N.C.J. Wagner, Acta Crystallogr. 20 (1966) 312.
[10] V. Gauthier, F. Bernard, E. Gaffet, Z.A. Munir, J.P. Larpin, Synthesis of nanocrystalline $NbAl_3$ by mechanical and field activation, Intermetallics 9 (2001) 571.
[11] J.W. Lee, Z.A. Munir, M. Shibuya, M. Ohyanagi, J. Am. Ceram. Soc. 84 (2001) 1209.
[12] I. Saita, L. Li, K. Saito, T. Akiyama, J. Alloys Compd. 356/357 (2003) 490.
[13] N. Hanada, T. Ichikawa, S. Orimo, H. Fujii, J. Alloys Compd. 366 (2004) 269.