ELSEVIER

Journal of Alloys and Compounds 356–357 (2003) 490–493

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Hydriding combustion synthesis of Mg_2NiH_4

Itoko Saita[a], Liquan Li[b], Katsushi Saito[c], Tomohiro Akiyama[a],*

[a] *Department of Chemical Engineering, Osaka Prefecture University, Sakai 599-8531, Japan*
[b] *College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, PR China*
[c] *Toyota Motor Corporation, Toyota 471-8572, Japan*

Received 1 June 2002; received in revised form 21 January 2003; accepted 30 January 2003

Abstract

Hydriding combustion synthesis (HCS) can produce full hydrides of alloys simply and in a short time. The conventional process based on ingot metallurgy (IM) cannot produce magnesium-based alloy easily with the desired composition and the cast product needs a long activation process for the practical use of hydrogen storage. The purpose of this study was to investigate the various hydrogen storage properties of HCSed Mg_2NiH_4 in comparison to the cast Mg_2Ni. The results suggest that the HCSed Mg_2NiH_4 has some advantages over the IM product.

Keywords: Hydrogen storage; Intermetallics; Chemical synthesis; X-ray diffraction; Scanning electron microscopy

1. Introduction

Magnesium-based alloys are most important hydrogen storage materials because magnesium and its alloys potentially have a high hydrogen storage capacity. In particular, Mg_2Ni is well known due to absorbing hydrogen 3.6 mass% and its high hydrogenation kinetics. However, the conventional process based on ingot metallurgy (IM) cannot produce magnesium-based alloy easily with the desired composition [1–3] and the cast product needs a long activation process for the practical use of hydrogen storage.

Hydriding combustion synthesis (HCS) has been proposed as an alternative process to produce a full-hydride of Mg_2Ni, Mg_2NiH_4, directly without any activation treatment [4]. Some reports [5–7] also demonstrated the attractive advantages of the HCS product—high purity, high hydrogenation kinetics and high hydrogen storage capacity without any activation process.

In spite of these attractive points, systematic comparative analysis between the HCS product and the IM product has not been carried out. Therefore, in this study, Mg_2NiH_4 produced based on HCS was analyzed systematically and comparatively with Mg_2Ni produced based on IM. Pressure–composition–temperature (PCT), hydrogenation rate at various temperatures, X-ray diffraction (XRD), and scanning electron microscopy (SEM) analysis were the tests used.

2. Experimental

The sample of Mg_2NiH_4 was prepared based on HCS as in a previous study [4]. Commercially available magnesium and nickel powders (purity; 99.9 mass%, particle size; 180 μm pass and purity 99.9 mass%, particle size; 2–3 μm, respectively) were well-mixed in a 2:1 molar ratio by an ultrasonic homogenizer in acetone for 3.6 ks. After complete drying, 10 g of the powder mixture was used directly for the following HCS procedure.

The powder mixture sample was heated to 873 K at a heating rate of 0.12 K/s, then held for 3.6 ks. After the holding period, the sample was naturally cooled down to room temperature. Whole heat treatment was conducted under 4 MPa hydrogen in a reactor, which was developed specially for HCS [8].

---

*Corresponding author. Tel./fax: +81-72-254-9303/9911.
E-mail address: takiyama@chemeng.osakafu-u.ac.jp (T. Akiyama).

0925-8388/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0925-8388(03)00230-5

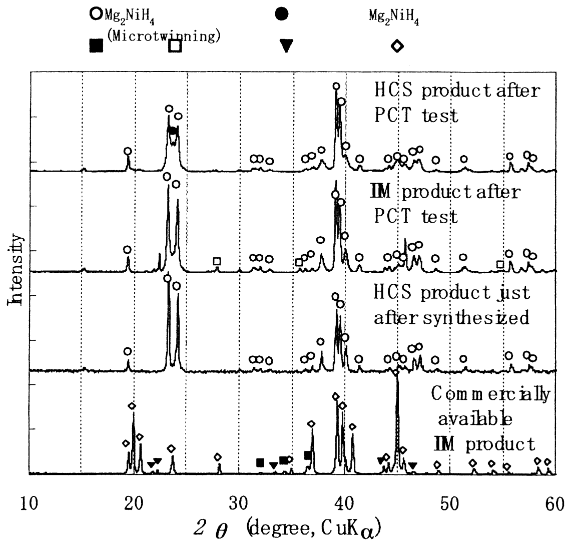

Fig. 1. XRD patterns of the IM product, the HCS product just after synthesis, and those samples after PCT tests. The HCS product showed microtwinning peak at $2\theta = 23.7°$ after the PCT test.

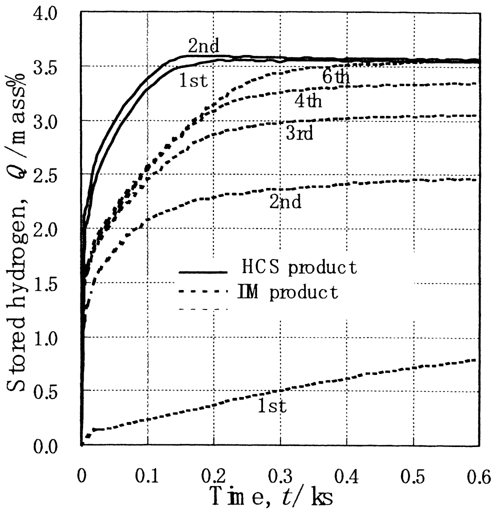

Fig. 2. Effect of cycling on hydrogenation curves of the HCS and IM products at 603 K.

The sample (used as HCS product in this study) and commercially available Mg_2Ni (99.9 mass% purity), cast product based on IM (IM product), were analyzed by means of XRD, SEM and PCT analysis without any special treatment. The cast Mg_2Ni was physically crushed to be <5 mm particle sizes. All PCT measurements were conducted based on Sieverts' method, after vacuuming the samples for 2 h at 603 K by a rotary pump.

3. Results and discussion

The XRD pattern of the HCS product just after synthesis clearly reveals only one phase of Mg_2NiH_4 (Fig. 1). This result accentuates that the HCS process produced very high purity Mg_2NiH_4 successfully; in contrast, commercially available IM product showed the undesired peaks of Mg and $MgNi_2$.

Fig. 2 shows the hydrogenation curves of the HCS and IM products at 603 K. The initial activity of the HCS product was pretty good: the hydrogen storage capacity reached as much as the theoretical value of Mg_2Ni, 3.6 mass%, and the hydrogenation rate was large. In contrast, the IM product showed less activity at the 1st cycle and showed an activation period. Initial activity of hydrogen storage material depends on its particle size, thus, the longer activation time for IM product seems reasonable because its particle size was nominally much larger than that of the HCS product (Fig. 3A and C). However, the IM

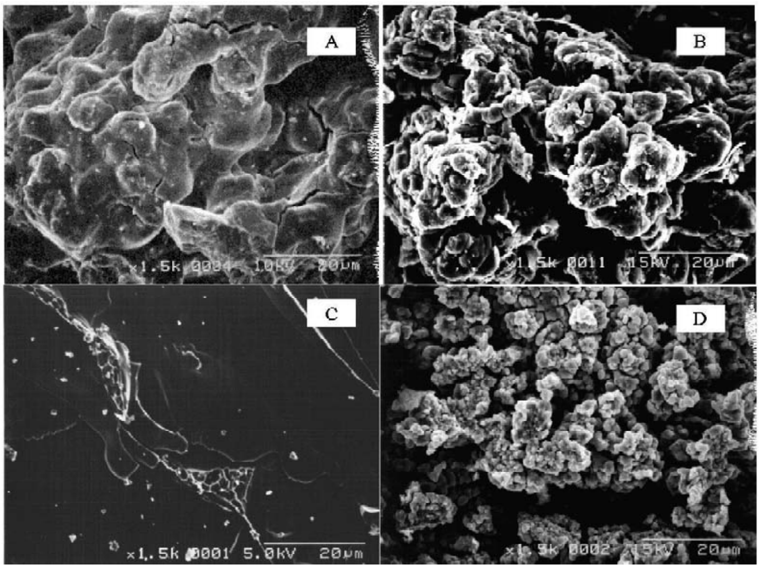

Fig. 3. SEM observations of HCS product just after synthesis (A), IM product (C), and those samples after PCT tests (B and D, respectively).

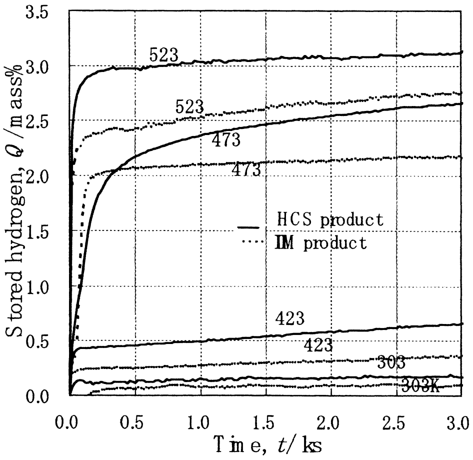

Fig. 4. Hydriding curves of the HCS and IM products at 303, 423, 473 and 523 K. Both products were the same sample used in hydrogenation at 603 K (Fig. 2).

product did not catch up with the hydrogenation rate of the HCS product (6th cycle) even though it had smaller particles than the HCS product (Fig. 3B and D).

SEM observation gives more information. The particle size of HCS product had not changed dramatically as the IM product had. To explain that result, the HCS product was expected to have smaller grains because pulverisation is induced due to grain expansion during the hydrogenation.

Fig. 4 shows the hydrogenation curves of HCS and IM products at various temperatures. The hydrogenation rate and hydrogen storage capacity of the HCS product were much larger than that of the IM product at every temperature. Especially at lower temperatures, 423 and 303 K, the HCS product absorbed hydrogen twice as much as the IM product. This result also suggests the high hydriding activity of the HCS product.

Fig. 5 shows PCT curves of the HCS and IM products at 603 K. The most significant point is that, in the area under 2.0 mass% of stored hydrogen, the PCT curve of the HCS product was sloping roundly and its plateau pressure was not clear. It was obviously different from the IM one. The curve of the HCS product over 2.0 mass% and that of IM product conformed to previous results, about 0.7 MPa of equilibrium pressure in the dehydrogenation period [9,10]. The final hydrogen storage capacity of the IM product was over the theoretical value of Mg_2Ni, 3.6 mass%, and reached 3.7 mass%. This might be caused by excess magnesium contained in the IM product

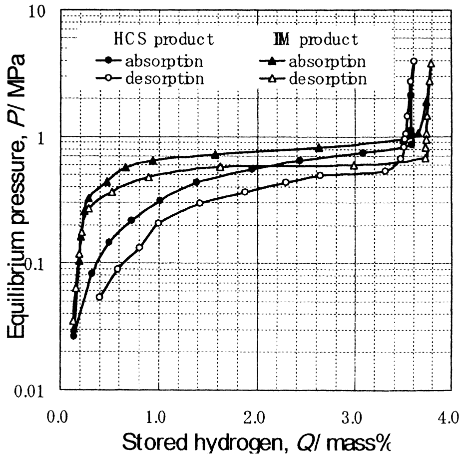

Fig. 5. PCT curves of the HCS and IM products at 603 K.

After the PCT test, the HCS product had mainly one phase of Mg_2NiH_4; however, around $2\theta=23.7°$, a characteristic peak was clearly visible. According to Zolliker et al., the peak is due to microtwinning [11]. Blomqvist et al. reported that such microtwinning happens when excess magnesium is avoided [12]. In this study, the HCS product of Mg_2NiH_4 did not contain excess magnesium, thus, the microtwinning peak might appear.

4. Conclusions

HCS successfully produced pure Mg_2NiH_4. No impurity phase was observed in the XRD pattern. Such high purity should affect microtwinning, which is dependent on excess magnesium. In contrast, the IM product showed impurity peaks of Mg and $MgNi_2$ and, after the PCT measurement, showed no peaks of microtwinning.

The hydrogenation property of the HCS product was clearly different from the IM product. The hydrogenation kinetics of the HCS product was so large from the initial hydrogenation that the IM product could not catch up even after 6th times activation. The hydrogen storage capacity of the HCS product was also larger than the IM product at various temperatures. The SEM observations indicated that the differences between hydrogenation properties of two products were not caused by the difference in their particle sizes. The microtwinning shown in HCS product after PCT test was expected as the cause.

Acknowledgements

The authors would like to express their great thanks to Taiatsu Techno Corporation for cooperation in development of the new version of the synthesis reactor used in this study. This work was supported by Grant-in-Aid for Scientific Research (B, no. 14350402) by Japan Society for the Promotion of Science (JSPS). This research was also supported by 21st Century, COE program, 24403, E-1 from the Ministry of Education, Culture, Sports, Science and Technology.

References

[1] M.Y. Song, M. Pezat, B. Darriet, P. Hagenmuller, J. Less-Common Met. 103 (1984) 145.

[2] J.S. Han, J.-Y. Lee, J. Less-Common Met. 131 (1987) 109.
[3] S. Ono, Y. Ishido, E. Akiba, K. Jindo, Y. Sawada, I. Kitagawa, T. Kakutani, Int. J. Hydrogen Energy 11 (1986) 381.
[4] T. Akiyama, H. Isogai, J. Yagi, J. Alloys Comp. 252 (1997) L1–L4.
[5] S. Nagashima, T. Akiyama, J. Yagi, J. Japan Inst. Metals 63 (12) (1999) 1555–1560.
[6] L. Li, T. Akiyama, T. Kabutomori, J. Yagi, J. Alloys Comp. 287 (1999) 98–103.
[7] T. Akiyama, H. Isogai, J. Yagi, Int. J. SHS 7 (1998) 2.
[8] I. Saita, L. Li, K. Saito, T. Akiyama, Mater. Trans. 43 (25) (2002) 1100–1104.
[9] A. Seiler, L. Schlapbach, Th. Von Waldkirch, D. Shaltiel, F. Stucki, J. Less-Common Met. 73 (1980) 193.
[10] J.J. Reilly, R.H. Wiswall Jr., Inorg. Chem. 7 (1968) 2254.
[11] P. Zolliker, K. Yvon, C. Baerlocher, J. Less-Common Met. 115 (1986) 65.
[12] H. Blomqvist, E. Rönnebro, D. Noréus, T. Kuji, J. Alloys Comp. 330 (2002) 268.