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Intermediate products during the hydriding combustion synthesis of Mg₂NiH₄

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Abstract

Magnesium-based hydrogen storage alloy is one of the most attractive mediums, as a hydrogen storage tank for a fuel cell. However, the practical application is still limited because of its poor hydriding and dehydriding kinetics and relatively high reaction temperature. To overcome such problems, the hydriding combustion synthesis (HCS) was established in 1997, as one of the most effective production methods. The understanding of these microstructures is strongly related to the improvement of the reaction property. However, up to now, little efforts have been made as to the microstructures of final product and intermediate products. Therefore, the purpose of this paper is to prepare intermediate products at several stages during the HCS of Mg_2NiH_4 , and to study their microstructures by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM) for the first time. Interestingly, the results revealed that: (1) the intermediate product generated at lower temperature than 800 K caused the unique particle morphology of final product of Mg_2NiH_4 ; (2) severe thermal corrosion, cotton-like material, was also observed on the surface of intermediate products at 705 K, which became enhanced with increasing temperature; (3) after the dehydriding reaction of MgH₂ at 750 K, a large amount of the Mg₂Ni phase existed in the intermediate product; (4) hydrogen present during the heating period makes the product to have smaller size. Further investigation on the mechanism of the gas–solid reaction deserves attention, because lowering of the synthesis temperature by as much as 100° is very attractive and significant for industrializing this process. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Magnesium-based alloy is potentially most important hydrogen storage materials from the points of lightweight, high specific storage capacity, abundant raw materials and low environmental impact; for example, magnesium-based hydrogen storage alloy is one of the most attractive mediums, as a hydrogen storage tank for fuel cells in transportations. Nevertheless, the practical application of magnesium-based alloys has been still limited unfortunately because of their poor hydriding, dehydriding kinetics and high reaction temperature (623–673 K). Many papers have been published to overcome these problems, most of which addressing new production methods. One of the well-known examples is mechanical alloying or ball milling. The results reported that, by means of mechanical alloying, the hydriding and dehydriding properties at lower temperature than 573 K can be much improved due to the physical control of the microstructures of the yield product, such as the generation of nanocrystalline alloys, a large number of grain boundaries and highly disordered interface phase [1–4]. Another effort of a new production method of magnesium-based alloys is a newly developed process called hydriding combustion synthesis (HCS) [5].

HCS has been proposed since 1997 and regarded recently as an innovative processing and fabrication to produce hydrogen storage alloys, especially for magnesium-based alloys [6,7]. By means of the HCS, magnesium-based hydrogen storage alloys can be prepared at 873 K below the melting point of magnesium and the product was really active, which was obtained by only one step combining the synthesis of the alloys and the hydrogenation of the alloys without any activation process [8–12]. It has been recognized widely as a highly promising technology offering many benefits

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such as short processing time, high product purity, low energy requirement and so on [13–15].

The reaction mechanism of HCS of Mg₂NiH₄ from the compact of a magnesium and nickel mixture at 2.0 MPa hydrogen was studied based on systematic experiments [16]. The interesting results were that as much as seven reactions were detected from the peaks of heat flow in a differential scanning calorimeter (DSC) curve and from X-ray diffraction (XRD) analysis. That is, (1) Mg + H₂ \rightarrow MgH₂, with a wide temperature range from about 520-660 K; (2) $MgH_2 \rightarrow Mg + H_2$, between 675 and 700 K; (3) 2Mg + Ni \rightarrow Mg₂Ni (L), an eutectic reaction in the Mg–Ni system at 790 K; (4) $2Mg + Ni \rightarrow Mg_2Ni$, an exothermal reaction of the combustion synthesis; (5) Mg₂Ni + 0.15H₂ \rightarrow Ng₂NiH_{0.3}, a solid solution reaction during the cooling period; (6) Mg₂Ni + H₂ \rightarrow Mg₂NiH₄ (HT), between 645 and 600 K, and (7) Mg₂NiH₄ (HT) \rightarrow Mg₂NiH₄ (LT), initiating at 510 K.

The most recent study revealed the reason why the product catches hydrogen quickly, in which the kinetics of the product of HCSed Mg2NiH4 was microscopically studied in comparison to the commercially available product of Mg₂Ni based on ingot metallurgy (IM) [17]. The results showed that the HCSed product was fully charged by hydrogen in the form of Mg₂NiH₄ just after being synthesized and had a very large reaction rate without any activation treatment; only 5 min for full charge. One of the most noteworthy results is the high activity of the product obtained; that is, it stored hydrogen even at room temperature. Moreover, observation by transmission electron microscopy (TEM) revealed the mechanism of this improved kinetics of the HCSed product. Many tree-like nano fissures emerged inside the HCSed product just after the first dehydrogenation; in contrast, the IM product has no such fissures even after three-times activation treatment.

Certainly, all attractive properties of the HCSed product is related to the microstructures of the product, as the similar phenomena reported on the mechanical alloying or ball milling of magnesium-based hydrogen storage alloys. Therefore, further improvement of the HCSed product properties depend clearly on the well understanding and control of the microstructures of the product. Not only the microstructure of the final product of HCS but also the microstructure of intermediate products in HCS process should be studied because there are seven reactions during HCS process and there must be a close correlation between the microstructure of intermediate products and final product. However, no efforts, up to now, have been made to investigate the intermediate products of HCS although such research work is very important to improve the properties of final product, leading to the industrization of this process. Therefore, the purpose of this paper is to prepare the intermediate products in the hydriding combustion synthesis of Mg₂NiH₄ first and then to study the microstructure of these intermediate products by means of XRD and scanning electron microscopy (SEM).

2. Experiment

The apparatus used in this study was the same as reported in [7]. The reactor is an Inconel tube with inside length of 520 mm and inner diameter of 70 mm. Three CA-type thermocouples were attached to three holes under the sample container of stainless steel through the sample frame. These thermocouples were used not only for measurement of the reactor temperature distribution but also for fixing the sample container on the same place, the middle of the tube, every time. The temperature distribution measured by the central thermocouple was used for sample temperature control with high accuracy. An accuracy within ± 1 K was confirmed by a thermocouple inserted into the sample in a preliminary test. As a result, a uniform temperature zone of $40 \text{ mm} \times 60 \text{ mm}$ was within ± 5 K. The atmosphere pressure inside of the reactor was also controlled precisely within ± 0.015 MPa. The samples of the HCS product were prepared from commercially available magnesium and nickel powders. The particle sizes of the magnesium, less than 180 µm, and nickel, 2-3 µm, were selected as the minimum sizes in commercial available chemicals for maximizing the contacting area between the particles. The powders, with 99.9 mass% in purity, were mixed well in 2:1 of Mg:Ni molar ratio by an ultrasonic homogenizer in acetone for 3.6 ks. After completely dried, 10 g of the powder mixture was used for the HCS directly. Generally, in the combustion synthesis, the powder mixture was usually compressed to increase the contacting area between the particles. However, an uncompressed powder mixture was used in this study for easy hydrogen penetration into the sample.

In order to synthesize intermediate products in the HCS of Mg₂NiH₄, three groups of samples were obtained at different stages according to Fig. 1, which is the DSC curve of hydriding combustion synthesis of Mg₂NiH₄ at 4.0 MPa of hydrogen pressure as reported in [9]. The samples of group H (High temperature) were obtained by heating the powder mixture up to 850 K after the combustion synthesis of Mg₂Ni. The samples of group L (Low temperature) were heated up to 705 K or about 750 K after the hydriding reaction of Mg and the dehydriding reaction of MgH₂, respectively, and the samples of group E (Eutectic temperature, 779 K) were obtained around 790 K near the eutectic temperature of the Mg-Ni system. Table 1 gives the synthesis conditions of all samples in this study. The obtained intermediate products were identified by XRD analysis and were carefully examined by SEM.

3. Results and discussion

Fig. 2 shows the XRD patterns of sample group H. Argon was used in heating and cooling periods for sample 1902. In contrast, hydrogen was used in heating and argon in cooling for sample 1901 and hydrogen was used in heating and cooling for sample 1701. Fig. 3 shows the SEM images of



Fig. 1. DSC curve of hydriding combustion synthesis of Mg₂NiH₄ at 4.0 MPa of hydrogen pressure.

Experimental conditions of intermediat	e products	synthesized	during the	e hydriding	combustion synth	nesis of Mg ₂ NiH ₄
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Group no.	Sample no.	Synthesis temperature (K)	Atmosphere in heating (MPa)	Atmosphere in cooling (MPa)	Comments
H (high)	1902	850	Ar, 0.1	Ar, 0.1	After combustion synthesis of Mg ₂ Ni
	1901	853	H ₂ , 4.0	Ar, 0.1	After combustion synthesis of Mg ₂ Ni
	1701	870	H ₂ , 4.0	H ₂ , 4.0	Final product of Mg ₂ NiH ₄
L (Low)	1702	705	H ₂ , 4.0	H ₂ , 4.0	After hydriding of Mg
	3001	750	Ar, 0.1	Ar, 0.1	After dehydriding of MgH ₂
	1803	757	H ₂ , 4.0	Ar, 0.1	After dehydriding of MgH ₂
E (Eutectic)	1801	794	H ₂ , 4.0	Ar, 0.1	Near eutectic point
	2202	795	Ar, 0.1	Ar, 0.1	Near eutectic point
Reference	1700	None	None	None	Raw material

these three samples. Comparing the XRD patterns of samples 1901 with that of 1902 as shown in Fig. 2, almost no differences existed and all showed a single phase of Mg_2Ni , except that the diffraction peaks of sample 1901 shifted to

Table 1

the left side slightly. However, if comparing the SEM images of the samples 1901 and 1902 as shown in Fig. 3, appreciable differences existed in their product morphology and the size of the product on the right hand side of the figure when



Fig. 2. XRD pattern of mixture powder 2Mg + Ni heated up to 850 and 870 K under different atmospheres by the process of hydriding combustion synthesis.



Fig. 3. SEM images $(1500 \times)$ of mixture powder 2Mg + Ni heated up to 850 and 870 K under different atmospheres by the process of hydriding combustion synthesis.

hydrogen was used in the heating period is obviously smaller than that on the left hand side when argon was used in the same period. The reason why a hydrogen atmosphere during heating reduced the particle size is not clear at present. The point here is that a hydrogen atmosphere during the heating period generates a small particle size, increasing the specific surface area as a result, although the phase identified by XRD of the product was the same (Mg₂Ni).

The XRD pattern of sample 1701 in Fig. 2 showed a very pure phase as the final product of the hydriding combustion synthesis of Mg_2NiH_4 . From the SEM image of sample 1701 in Fig. 3, one can recognize that the size became slightly larger in comparison to that in 1901 and a large number of cracks appeared on the particle surfaces and/or across the particles. The cracks must be from the expansion of the intermediate product of the combustion synthesis of Mg_2Ni during the hydriding reaction during the cooling period under hydrogen atmosphere, because there are no cracks in those particles when argon was used during cooling as shown in the SEM images of samples 1901 and 1902.

Some of the conclusions, which can be derived from Figs. 2 and 3, are: (1) Pure Mg_2Ni , as an intermediate product during the HCS of Mg_2NiH_4 , is obtainable from the powder mixture of magnesium and nickel by heating up to 850 K under argon or hydrogen. Moreover, pure Mg_2NiH_4 , as the final product of HCS, is generated at 4.0 MPa of hydrogen pressure during the cooling period as reported previously [18], (2) A hydrogen atmosphere during the heating

period does not affect the XRD pattern of the intermediate product of Mg₂Ni, but reduces the particle size. It should be beneficial for improving the kinetics of the hydrogen storage alloys due to an expansion of the surface area. (3) On the final product of HCS, some cracks in the particles of Mg₂NiH₄ were generated. The cracks are also useful to accelerate the hydriding and dehydriding of the hydrogen storage alloys at the initial stage.

Fig. 4 gives the XRD patterns of samples of group L. Sample 1702 was heated up to 705 K then kept there for half an hour and a hydrogen atmosphere was used during both heating and cooling. Our idea was to obtain the intermediate product of the metal hydride of MgH₂ based on the DSC curves in Fig. 1. Sample 1803 was heated up to 757 K, in which hydrogen and argon were used during heating and cooling, respectively. The heating temperature of 757 K was selected and argon atmosphere was used during cooling, because 757 K is just after the dehydriding reaction of MgH₂ as shown in Fig. 1. Therefore, the intermediate product was produced shortly after the dehydriding reaction. As a reference, sample 3001 was heated up to 750 K but argon was used during both heating and cooling. Fig. 5 shows the SEM images of the samples of group L. Here, the image of sample 1700 is from the original mixture of metal powder of magnesium and nickel.

The XRD pattern of sample 1702 in Fig. 4 shows that it was a mixture of three phases; these were MgH₂, unreacted Mg and Ni. This result indicated that the hydriding of Mg



Fig. 4. XRD pattern of mixture powder 2Mg + Ni heated up to 705 and 750 K under different atmosphere by the process of hydriding combustion synthesis.

was not completed even at 4.0 MPa pressure of hydrogen and at 705 K for about 30 min. Comparing the XRD patterns of sample 3001 with sample 1803, all consist of a mixture of three phases. These were Mg₂Ni, unreacted Mg and Ni, except the peak height of Mg and Ni was a little high in sample 1803 when hydrogen was used during heating. It seems that there is an effect of hydrogen on the synthesis of Mg₂Ni during heating. On other hand, the existence of Mg_2Ni just after the dehydriding reaction of MgH_2 in the samples 3001 and 1803 is not predicted from the knowledge of the reaction mechanism of the process reported in Ref. [16]. Actually, the amount of Mg_2Ni was not small but large from the relative XRD peak heights of these phases.

From the SEM images as shown in Fig. 5, two very interesting features of the morphologies of these intermediate products can be observed. One is the corrosion of the sur-



Fig. 5. SEM images ($500 \times$) of mixture powder 2Mg + Ni heated up to 705 and 750 K under different atmospheres by the process of hydriding combustion synthesis.

faces of the magnesium particles. This kind of corrosion can be called thermal corrosion because it was developed during increasing temperature. It is not difficult to observe the development of corrosion if comparing the SEM image of sample 1702, heated up to 705 K with that of sample 1700, the raw material of mixture powder and with that of sample 3001 or sample 1803 heated up to 750 K. Another feature of the morphology of these intermediate products is the growth of the particle size of the nickel. Again, it was developed with increasing temperature obviously and it occurred even at only 705 K if comparing the particle sizes, as indicated by the arrows, of sample 1702 with sample 1700 in Fig. 5.

Taking into account of the XRD results, that is a large amount of Mg₂Ni existed, as shown in Fig. 4 and the thermal corrosion of the particles of Mg mentioned above, it seems to be possible to understand that the growth of nickel particles was from the synthesis of Mg₂Ni, that is the magnesium was evaporated by thermal corrosion and transferred to the particles of nickel in gas phase, then the synthesis of Mg₂Ni by diffusion reaction, even though the temperature of 705 K and 750 K was much lower than 790 K, the eutectic temperature of Mg-Ni system as shown in Fig. 2. Because there was not much interface contact between the nickel particles and magnesium particles and the amount of Mg₂Ni was not small, as well as the temperatures of 705 and 750 K are very low, the synthesis mechanism such as gas-solid reaction must have played an important role in the process of hydriding combustion synthesis. A detailed investigation of this point is planned and the result will be in the near future. Since 750 K is lower than the usual temperature of HCS of Mg_2NiH_4 , that is 850 K by 100° it must be very attractive and significant to an industrialization of this process.

Fig. 6 shows the XRD patterns of intermediate products of samples 1801 and 2202 synthesized at 793 K near the eutectic point of the Mg–Ni system but before the combustion synthesis reaction of Mg₂Ni. Hydrogen during heating and argon during cooling were used for sample 1801. However, argon was used during heating and cooling for sample 2202. The XRD patterns showed that three phases, Mg₂Ni, Mg and Ni, existed in samples 1801 and 2202 and the main phase was Mg₂Ni. Although the diffraction peaks of Mg did not appear in the pattern of sample 2202, Mg did exist in sample 2202 considering the low diffraction sensitivity of a light metal and the fact that the peak of Ni appeared in the pattern. This result is similar to the observation that more magnesium remained when hydrogen was used than when argon was used during heating, as follows from the results of sample 3001 and sample 1803 in Fig. 4. Why the appearance of hydrogen retarded the synthesis reaction between magnesium and nickel needs to be further studied from the point of view of reaction kinetics and thermodynamics of our system.

Some shifts of the Mg₂Ni diffraction peaks to lower angles appeared again when hydrogen was used during heating. This can be seen by comparing the XRD patterns of samples 1801 and 2202 in Fig. 6. This kind of diffraction peak shifts comes from the expansion of the crystal lattice as mentioned previously. The expansion of the crystal lattice is due to the solid solution of hydrogen into the crystal lattice of Mg₂Ni because the hydrogen used during heating period is not easily completely removed from the furnace tube at high temperature, and remained in the argon atmosphere used during cooling.

Fig. 7 shows the SEM images of samples 1801 and 2202. The most obvious difference is the particle sizes. Here a particle is actually an aggregation of particles. We find again that the particle sizes are smaller when hydrogen used than when argon used during heating as discussed previously for samples 1901 and 1902 in Fig. 3. The result indicates that hydrogen strongly interfered in the particle size growth, and that such interference happened already below 800 K during heating. Since the particle sizes of sample 1801 was almost the same as that of sample 1901 and the particle sizes of sample 2202 was almost the same as that of sample 1902 as shown in Fig. 3 and Fig. 7, this result indicates that the intermediate products of the eutectic below 800 K already possessed the morphology characteristic of particles of the final product.

Based on the reaction mechanism of HCS of Mg_2NiH_4 , the purpose to use hydrogen in the process was only for the formation of the final product Mg_2NiH_4 during cooling, though it was also involved in the hydriding and dehydriding reactions of Mg and the hydriding reaction of Mg_2Ni . The results here, however, revealed that hydrogen also played



Fig. 6. XRD pattern of mixture powder 2Mg + Ni heated up to 795 K under different atmosphere by the process of hydriding combustion synthesis.



Fig. 7. SEM images $(1500 \times)$ of mixture powder 2Mg + Ni heated up to 795 K under different atmospheres by the process of hydriding combustion synthesis.

an important role in the morphology of the particles of the intermediate product during heating, which determined substantially the morphology of the particles of final product. This is possibly related to the hydriding and dehydriding reactions of magnesium before the eutectic reaction during heating. This role played by hydrogen in the morphology of particles remains to be further investigated.

4. Conclusion

Intermediate products at several stages during the hydriding combustion synthesis (HCS) of Mg_2NiH_4 were prepared and their microstructures were studied by means of XRD and SEM.

- (1) The intermediate product of eutectic composition at temperature lower than 800 K affected strongly the particle morphology of the final product of Mg_2NiH_4 obtained at temperature higher than 850 K by HCS.
- (2) Hydrogen during heating leads to the product smaller size. The hydrogen atmosphere would be quite effective for improving the kinetics due to large surface area in hydrogen storage alloys.
- (3) Severe thermal corrosion; cotton-like feature, was observed on the surface of the intermediate products of Mg obtained near 750 K. It was observed even on the intermediate product of MgH₂ obtained at 705 K.
- (4) A large amount of Mg₂Ni appeared in the intermediate product at 750 K just after the dehydriding reaction of MgH₂. From the observation of the particle size of nickel, the synthesis of Mg₂Ni happened even at only 705 K, which is much lower than 790 K, the eutectic temperature of Mg–Ni system.
- (5) Since no effective interface contact tightly between the particles of nickel and magnesium, gas-solid reaction must have played an important role before the temperature reached to 790 K in the HCS.

Further investigation of this mechanism is deserved because the lowering of synthesis temperature by 100° is attractive and significant.

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