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Journal of Alloys and Compounds 281 (1998) 175–180

Journal of ALLOYS AND COMPOUNDS

In situ X-ray diffraction study of the hydriding combustion synthesis of Mg_2NiH_4

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Received 6 July 1998; received in revised form 10 August 1998

Abstract

An in situ X-ray diffraction study of the hydriding combustion synthesis of Mg_2NiH_4 directly from the compact of magnesium and nickel mixture in a pressurized hydrogen atmosphere has been conducted. During two cycles of heating (hydriding) and cooling (dehydriding) in a temperature range from 300 to 823 K, the X-ray diffraction patterns were obtained in a pressure of 1.0 MPa at eleven points of the temperature. The obtained X-ray diffraction patterns reveal nine reactions existing in two cycles of heating and cooling. In the first cycle, (1) $Mg+H_2 \rightarrow MgH_2$, partially, (2) $MgH_2 \rightarrow Mg+H_2$, (3) $2Mg+Ni \rightarrow Mg_2Ni$, in the heating period, and (4) $Mg_2Ni+2H_2 \rightarrow Mg_2NiH_4$ (HT), partially, (5) Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT), in the cooling period. In the second cycle, (6) Mg_2NiH_4 (LT)$\rightarrow Mg_2NiH_4$ (HT), (7) Mg_2NiH_4 (HT)$\rightarrow Mg_2Ni+2H_2$, in the heating period, and (8) $Mg_2Ni+2H_2 \rightarrow Mg_2NiH_4$ (HT), partially, (9) Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT), in the cooling period. The X-ray diffraction intensity of Mg_2Ni after the second cycle of hydriding decreases to 1/6 times of that after the first cycle of hydriding. In contrast, the X-ray diffraction intensity of Mg_2NiH_4 after the second cycle of hydriding is six times of that after the first cycle of hydriding, although only one single phase of Mg_2Ni exists at 823 K before hydriding either the first cycle or the second cycle.

Keywords: Combustion synthesis; Hydriding; Hydrogen storage alloy; Magnesium nickel

1. Introduction

Magnesium–nickel alloys are potentially important hydrogen storage materials because of their lightweight, high specific hydrogen capacity, abundant raw materials, low environmental impact and numerous applications. For example, based on its high temperature characteristics of hydriding and dehydriding, it has been proposed as a heat-storage/transportation medium in ironworks [1]. In the conventional ingot process, however, it is essentially difficult to control the chemical composition of this alloy because magnesium evaporates easily due to its high vapor pressure [2]. Thus, a repeated remelting process with an additional supply of magnesium is needed to prepare Mg_2Ni alloy with a specific chemical composition and the alloy obtained by this method must be activated by over ten-times hydriding/dehydriding cycles after a crushing process to form Mg_2NiH_4 for practical use [3].

A new production method of magnesium nickel alloy of Mg_2Ni by combustion synthesis was investigated [4–6]. In this method, one end of a compact of well-mixed magnesium and nickel powders with 2:1 molar ratio is ignited, the compact gives pure Mg_2Ni quickly by means of an exothermic solid–solid reaction. Upon the method of combustion synthesis, a possibility of synthesizing magnesium nickel hydride directly from the compact of magnesium and nickel mixture in pressurized hydrogen by combustion synthesis was also proposed [7]. Furthermore, research on the experimental production of hydrogen storage alloy of Mg_2NiH_4 by *hydriding combustion synthesis* has been initiated very recently [8,9]. Therefore, the combustion synthesis process for the production of the hydrogen storage alloys is quite attractive, with many advantages such as short processing time, simple equipment, high product purity, low energy requirement and so on.

The effect of hydrogen pressure on the hydriding combustion synthesis of Mg_2NiH_4 in 0.5, 1.0, 2.0 and 4.0 MPa hydrogen was reported in Ref. [8]. It is observed that

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0925-8388/98/$ – see front matter
PII: S0925-8388(98)00797-X

there are four sharp peaks on the heat flow curves from differential scanning calorimeter (DSC) during the heating and cooling periods between room temperature and 850 K. Two peaks (1st and 2nd peak) are endothermic peaks and occur during the heating period. The other two peaks (3rd and 4th peak) are exothermic peaks and occur during the cooling period. The 2nd and 4th peaks always happen at fixed temperatures, but the 1st and 3rd peaks are movable with the hydrogen pressure. With increasing hydrogen pressure, the 1st and 3rd peaks move into a higher temperature range. These results indicate that the hydriding combustion synthesis of Mg_2NiH_4 is not such a simple reaction that it can be expressed by a single reaction formula, such as $2Mg+Ni+2H_2=Mg_2NiH_4$, but a complicated process, in which there are several endothermic and exothermic reactions with pressure dependence.

In order to understand the process of experimental production of magnesium nickel hydride (Mg_2NiH_4), a study of the reaction mechanism of the hydriding combustion synthesis of Mg_2NiH_4 was tried by means of DSC and X-ray diffraction (XRD) [9]. It was reported that, before the formation of Mg_2NiH_4, the Mg_2Ni was formed. The Mg_2NiH_4 was produced by hydriding of Mg_2Ni at high temperature to form a high temperature type of Mg_2NiH_4 (HT) at first, then a phase transformation from a high temperature type to a low temperature one of Mg_2NiH_4 (LT).

In previous research on the reaction mechanism of the hydriding combustion synthesis of Mg_2NiH_4, the samples used in analysis were obtained by stopping the process of synthesis [9]. That was done by means of quenching to room temperature and/or changing the atmospheres from 2.0 MPa hydrogen to 0.1 MPa argon. That is, this method is based on indirect measurement. To sophisticate our theory on the hydriding combustion synthesis, direct measurement of sample phase is needed. Therefore, in a present study, we conduct an in situ X-ray diffraction study of the hydriding combustion synthesis of Mg_2NiH_4. The X-ray diffraction patterns are obtained at eleven points of the temperature according to the heat flow curves from DSC during two cycles of heating and cooling in a temperature range between 300 and 823 K in 1.0 MPa hydrogen atmosphere.

2. Experimental

The samples were prepared from commercially available magnesium and nickel powders as in a previous study [7]. The powders of Mg and Ni, with 99.9 mass % in purity and -177 μm in particle size for Mg and 2–3 μm for Ni, were well-mixed in 2:1 molar ratio by an ultrasonic homogenizer in acetone. After completely drying in air, the well-mixed powder was compressed and formed into a cylinder with about 10 mm in diameter, 2.5 mm in height and 0.5 g in weight by a uniaxial single-acting press at 500 MPa.

A high temperature and high-pressure X-ray diffractometer (XRD) with rotating-target in 18 kW power was used in the experiment. The sample prepared above was thinned to about 1.2 mm in height to fit the sample holder. A hole of 0.5 mm in diameter and 2 mm in depth was drilled on the side of the cylinder for a thermocouple to measure the sample temperature. The sample sat in the sample holder by a thin film of Be fixed on the surface of the sample holder to avoid the shift of the sample during the measurement. Then, the sample holder was put into the sample platform which is also the heater controlling the sample temperature. The parameters of X-ray diffraction were Cu Kα; power: 50 kV, 150 mA; fixed-time mode: 0.05°, 0.5 s; divergence slit: 0.5°, scattering slit: 0.5° and receiving slit: 0.15 mm.

A hydrogen pressure of 1.0 MPa was used in the experiment. The sample was heated from room temperature to 823 K and held at 823 K for 30 min, then cooled down to 423 K in a rate of $0.1\ K\,s^{-1}$. With the same rate, the sample was heated again from 423 to 823 K and held at 823 K for 5 min, then cooled down to room temperature. X-ray diffraction patterns of the sample in the two cycles of heating and cooling were obtained at eleven points of the temperature. These eleven points of the sampling temperatures were selected based on the result of DSC experiment. In Fig. 1 the curve of heat flow vs. temperature from DSC of hydriding combustion synthesis of Mg_2NiH_4 is shown, which is in 1.0 MPa hydrogen atmosphere in the two cycles of heating and cooling between 300 and 850 K under a rate of $0.1\ K\,s^{-1}$. The peaks in Fig. 1 are numerated by the same order as in Ref. [9]. In Table 1 the sampling temperatures of the eleven points in the in situ X-ray diffraction experiment are given.

3. Results and discussion

3.1. First cycle

In Fig. 2 the in situ X-ray diffraction patterns of all the samples from sampling 1 to sampling 11 in the hydriding combustion synthesis of Mg_2NiH_4 in the two cycles of heating and cooling between 300 and 823 K in 1.0 MPa hydrogen are shown. This reveals phase transformation of the sample from the compact of magnesium and nickel mixture to metallic hydride. In order to show the diffraction lines clearly, all patterns are plotted in a normalized scale by the strongest line, respectively, as the normalization factor.

The pattern of sampling 1 is from the raw materials at room temperature. The X-ray diffraction lines from Mg and Ni appear clearly with the standard relative intensities in it, respectively. In the pattern of sampling 2 at 423 K, the diffraction lines of Mg and Ni appear again, but in the

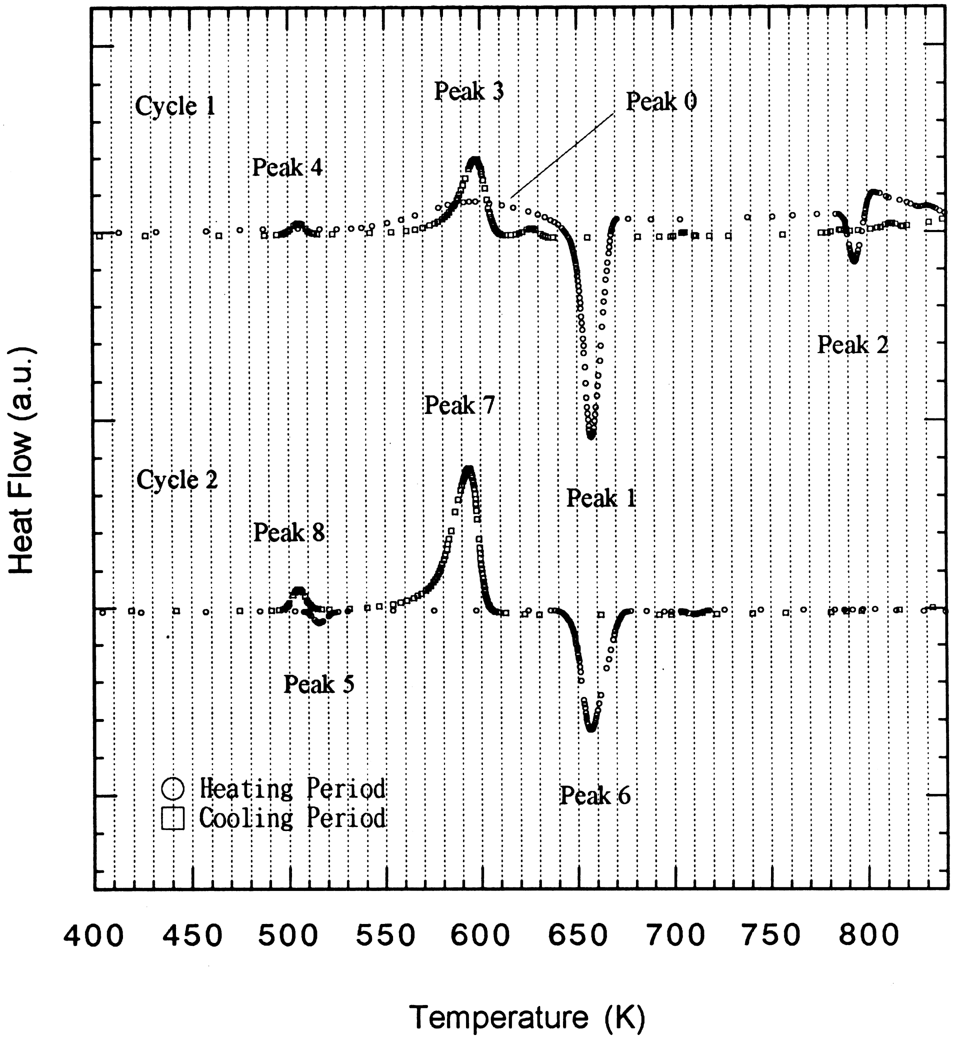

Fig. 1. Curve of heat flow vs. temperature from DSC of hydriding combustion synthesis of Mg_2NiH_4 in two cycles of heating and cooling between 300 and 850 K under a rate of 0.1 K s^{-1} in 1.0 MPa hydrogen atmosphere.

sampling 3 at 633 K, the diffraction lines of MgH_2 appear beside the diffraction lines of Mg and Ni. With the temperature increasing to 723 K, in the pattern of sampling 4, the diffraction lines of MgH_2 disappear and the diffraction lines of Mg_2Ni appear in a very low intensity.

Table 1
In situ X-ray diffraction sampling temperatures in hydriding combustion synthesis of Mg_2NiH_4 in two cycles of heating and cooling between 300 and 823 K in 1.0 MPa hydrogen atmosphere

Sampling No.	Temperature (K)	Comment
1	300	Raw material
2	423	Before peak 0
3	633	Before peak 1
4	723	Before peak 2
5	823	After peak 2
6	543	After peak 3
7	423	After peak 4
8	543	After peak 5
9	823	After peak 6
10	543	After peak 7
11	423	After peak 8

As shown in Fig. 1, the temperature of 633 K is after peak 0 but just before peak 1 and the 723 K is after peak 1. Therefore, the X-ray diffraction patterns of sampling 3 and 4 indicate clearly that peak 0 comes from the partially hydriding of $Mg+H_2 \rightarrow MgH_2$ and peak 1 is the dehydriding of $MgH_2 \rightarrow Mg+H_2$. It is worth noticing that the diffraction intensities of the strongest lines from Mg and Ni in patterns of sampling 2, 3 and 4 and to compare the relative heights of these lines in the pattern of sampling 4 with those in the patterns of sampling 2 and 3. As a result, we can find easily that the intensity of the strongest diffraction line from Mg is changed when the temperature is from 423 to 723 K. It means that the content of Mg undergo a process from decreasing to increasing. This is consistent with the result of the reaction of $Mg+H_2 \rightarrow MgH_2$ of peak 0, then, a reaction of $MgH_2 \rightarrow Mg+H_2$ of peak 1.

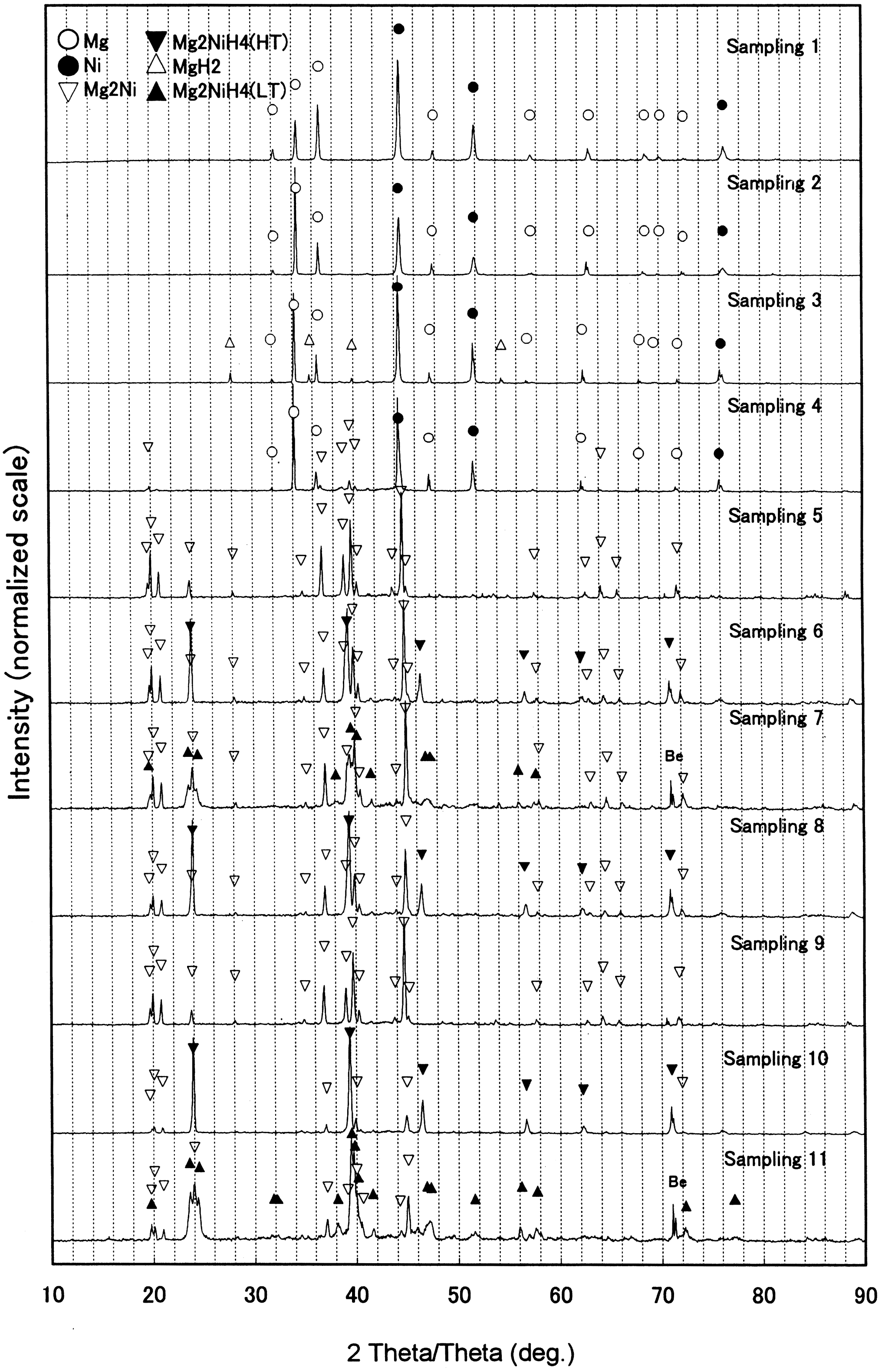

Fig. 2. In situ X-ray diffraction patterns in hydriding combustion synthesis of Mg_2NiH_4 in two cycles of heating and cooling between 300 and 850 K under a rate of 0.1 K s^{-1} in 1.0 MPa hydrogen atmosphere.

From the X-ray diffraction patterns of sampling 1, 2, 3 and 4, the effect of temperature on the lattice expansion of crystals is very evident. The X-ray diffraction lines of either Mg or Ni move to a lower 2-theta range regularly with the temperature increasing from 423 K to 723 K. These diffraction line shifts, resulting from temperature, introduce confusion in analyzing whether it is a Mg_2Ni or a $Mg_2NiH_{0.3}$ in our experiment, although we believe $Mg_2NiH_{0.3}$ is produced in the process. Because the distinguishable difference of the X-ray diffraction lines of Mg_2Ni from that of $Mg_2NiH_{0.3}$, practically, as reported in Ref. [9], is that the diffraction lines of $Mg_2NiH_{0.3}$ happen at a lower 2-theta range than that of Mg_2Ni. For this reason, we only labeled the Mg_2Ni in all X-ray diffraction patterns regardless of whether a Mg_2Ni or $Mg_2NiH_{0.3}$ in this research.

There are no distinguishable diffraction lines from Mg and Ni, except the diffraction lines of a single-phase of Mg_2Ni, appear in the pattern of sampling 5. This result is very significant. It presents one of the great advantages of the combustion synthesis in production of the hydrogen storage alloy of Mg_2Ni by contract with the conventional ingot process, which is a repeated remelting process with an additional supply of magnesium to produce Mg_2Ni alloy with a specific chemical composition.

With decreasing temperature from 823 to 543 K, a new phase of Mg_2NiH_4 (HT) appears in sampling 6. With further decreasing temperature to 423 K, the Mg_2NiH_4 (HT) disappears and the Mg_2NiH_4 (LT) appears in sampling 7. Since sampling 6 is after peak 3 and sampling 7 after peak 4, as given in Fig. 1 and Table 1, these results demonstrate that peak 3 is a hydriding reaction of $Mg_2Ni+H_2 \rightarrow Mg_2NiH_4$ (HT) and peak 4 a phase transformation of Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT). This result is agreeable to the results reported in Ref. [8]. That is, peak 3 involving gas reactions and peak 4 involving non-gas reactions, because peak 3 occurs at non-fixed temperatures and peak 4 does at fixed temperatures in different pressures of hydrogen. From the patterns of sampling 6 and 7, it is also obvious that the Mg_2Ni produced by the combustion synthesis is not hydrided to Mg_2NiH_4 completely.

3.2. Second cycle

The patterns of sampling 8, 9, 10 and 11 are obtained in the second cycle of heating and cooling. In the heating period, we can see that the low temperature form of Mg_2NiH_4 (LT) in sampling 7 is transformed to the high temperature form of Mg_2NiH_4 (HT) in sampling 8, and the Mg_2NiH_4 (HT) in sampling 8 is dehydrided to form Mg_2Ni fully in sampling 9. In the cooling period, on the contrary, the Mg_2Ni in sampling 9 absorbed hydrogen to form Mg_2NiH_4 (HT) partially in sampling 10, and the Mg_2NiH_4 (HT) in sampling 10 is transformed to Mg_2NiH_4 (LT) in sampling 11. Combining these results with Fig. 1 and Table 1, it is clear that peak 5 is a reaction of Mg_2NiH_4 (LT)$\rightarrow Mg_2NiH_4$ (HT); peak 6 is Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT); peak 7, Mg_2NiH_4 (LT)$\rightarrow Mg_2NiH_4$ (HT) and peak 8, Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT), respectively.

It is noticeable that, at 823 K after either the first heating period or the second heating period, only one single phase of Mg_2Ni exists in the sample and that the Mg_2Ni produced is not fully hydrided to form Mg_2NiH_4 even after the second cycle of cooling (hydriding). It is also noticeable that, however, the content of Mg_2NiH_4 in the sample of sampling 11 after the second cycle of hydriding is much more than that in the sample of sampling 7 after the first cycle of hydriding. This result gives some characteristics of hydriding and dehydriding of the product produced by hydriding combustion synthesis of Mg_2NiH_4.

We can give a pseudo-quantitative analysis about it by the ratio of the heights of these two diffraction lines in the patterns of sampling 6 and 10, both in the cooling periods. One is from Mg_2Ni occurring in the 2-theta range between 44 and 46° and the other is from Mg_2NiH_4 (HT) occurring between 46 and 48°. This ratio of the height of the diffraction line from Mg_2Ni to that from Mg_2NiH_4 is 3:1 in the pattern of sampling 6 in the first cycle and it is 1:2 in the pattern of sampling 10 in the second cycle. That is, the X-ray diffraction intensity of Mg_2Ni after the second cycle of hydriding is 1/6 times of that after the first cycle of hydriding. Conversely speaking, the X-ray diffraction intensity of Mg_2NiH_4 after the second cycle of hydriding is six times of that after the first cycle of hydriding. It is reasonable to expect this number will increase further in the following cycles of dehydriding and hydriding.

This result reveals some behavior of hydriding and dehydriding of the product in our experiment. It means that the hydriding activities of the products of sampling 5 and sampling 9 are different, although the same products of a single phase of Mg_2Ni were produced at 823 K after the period of heating either the first cycle or the second cycle. A study on the hydriding and dehydriding behaviors of product produced by hydriding combustion synthesis of Mg_2NiH_4 will be discussed in our next paper. In Table 2 all the results of the phase compositions of the eleven samples in this study are given.

4. Conclusion

Nine reactions are observed in two cycles of heating and cooling periods in hydriding combustion synthesis of Mg_2NiH_4 by in situ X-ray diffraction. In the first cycle, (1) $Mg+H_2 \rightarrow MgH_2$, partially, (2) $MgH_2 \rightarrow Mg+H_2$, (3) $2Mg+Ni \rightarrow Mg_2Ni$, in the heating period, and (4) $Mg_2Ni+2H_2 \rightarrow Mg_2NiH_4$ (HT), partially, (5) Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT), in the cooling period. In the second cycle, (6) Mg_2NiH_4 (LT)$\rightarrow Mg_2NiH_4$ (HT), (7) $MgNiH_4$ (HT)$\rightarrow Mg_2Ni+2H_2$, in the heating period, and (8) $Mg_2Ni+2H_2 \rightarrow Mg_2NiH_4$ (HT), partially, (9) Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT), in the cooling period.

The content of Mg_2NiH_4 in the sample after the second cycle of hydriding is much more than that in the sample after the first cycle of hydriding. The X-ray diffraction intensities of Mg_2Ni after the second cycle of hydriding is 1/6 of that after the first cycle of hydriding. Conversely,

Table 2
The phase compositions of eleven samples of in situ X-ray diffraction and the reactions in hydriding combustion synthesis of Mg_2NiH_4 in two cycles of heating and cooling between 300 and 823 K in 1.0 MPa hydrogen atmosphere

Sampling No.	Phase Compositions	Reactions
1	Mg, Ni	
2	Mg, Ni	
3	MgH_2, Mg, Ni	$Mg+H_2 \rightarrow MgH_2$
4	Mg_2Ni, Mg, Ni	$MgH_2 \rightarrow Mg+H_2$
5	Mg_2Ni	$2Mg+Ni \rightarrow Mg_2Ni$
6	Mg_2NiH_4 (HT), Mg_2Ni	$Mg_2Ni+2H_2 \rightarrow Mg_2NiH_4$ (HT)
7	Mg_2NiH_4 (LT), Mg_2Ni	Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT)
8	Mg_2NiH_4 (HT), Mg_2Ni	Mg_2NiH_4 (LT)$\rightarrow Mg_2NiH_4$ (HT)
9	Mg_2Ni	Mg_2NiH_4 (HT)$\rightarrow Mg_2Ni+2H_2$
10	Mg_2NiH_4 (HT), Mg_2Ni	$Mg_2Ni+2H_2 \rightarrow Mg_2NiH_4$ (HT)
11	Mg_2NiH_4 (LT), Mg_2Ni	Mg_2NiH_4 (HT)$\rightarrow Mg_2NiH_4$ (LT)

the X-ray diffraction intensities of Mg_2NiH_4 after the second cycle of hydriding are six times that after the first cycle of hydriding. The same products of a single phase of Mg_2Ni are produced after the first and the second periods of heating, however, the hydriding activities of the two products are very different.

Acknowledgements

This research was partially supported by the Ministry of Education, Science, and Culture, Japan (Grant No. B-09450276 and 10450282). The authors would like to thank Prof. R. Takahashi, Dr. X.H. Zhang (Institute for Advanced Materials Processing, Tohoku University) and Mr. K. Kubo (Muroran Research Laboratory, JSW) for their help in the experiment.

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