Effect of synthesis pressure on hydride phases in Mg–M systems (M = Mn, Y)

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Abstract

High-pressure synthesis of the hydrides in Mg–M (M = Mn, Y) systems and the influence of applied pressures during synthesis on present phases and their crystal structures have been studied. In Mg–Mn system, it was found that the crystal structure of Mg$_3$MnH$_y$ changed from hexagonal structure ($a = 0.47107(4)$ nm and $c = 1.0297(1)$ nm) to monoclinic structure ($a = 0.8819(8)$ nm, $b = 0.4658(4)$ nm, $c = 0.4678(5)$ nm and $\beta = 105.6(1)^\circ$) in a pressure range of 3–3.5 GPa. This crystal structural change was reversible with respect to pressure. The Mg$_3$MnH$_y$ synthesized under 5 GPa was stable up to around 620 K. From thermogravimetric and fusion extraction analyses, the hydrogen content was determined as Mg$_3$MnH$_{5.0-5.6}$. In Mg–Y system, the high-pressure hydride (MgY$_2$H$_y$) with yellowish color was synthesized at 1073 K for 2 h under 3 GPa or higher. This phase exhibited an FCC-type structure with a cell parameter of $a = 0.516$ nm. Its hydrogen content was determined to be about 3.7 mass%, corresponding to a chemical formula of MgY$_2$H$_{7.8}$. The hydride was partially dehydrogenated at around 600 K, and the amount of hydrogen partially desorbed was 1.4 mass%. The FCC-type structure was stable even after the partial dehydrogenation.

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1. Introduction

High-pressure synthesis is an effective technique to obtain new compounds. In metal–hydrogen systems, one can obtain further freedom for exploring new hydrides by using pressure as a processing parameter as well as compositions and temperatures. The high-pressure synthesis can be mainly classified into two groups according to the manner of generating pressures, that is, autoclave-type and anvil-type apparatuses. Many new Mg-based hydrides such as LaMg$_2$H$_7$ [1], CeMg$_2$H$_7$ [1] and Mg$_3$RuH$_6$ [2] have been prepared under the hydrogen pressure of around 10 MPa by using an autoclave-type apparatus utilizing compressed gases. On the other hand, Mg$_3$MnH$_7$ [3] and Eu$_2$MgH$_6$ [4] have been synthesized under a high pressure of GPa ranges by an anvil-type apparatus. In addition, Mg$_3$NiH$_{3.4}$ [5,6], Ca$_2$NiH$_4$ [7], (Ca$_{0.8}$Mg$_{0.2}$)$_2$NiH$_4$ [8–10] and MgCaH$_{1.95}$ [9,10] have been synthesized by using the anvil-type apparatus in our previous work.

Among a number of Mg-based hydrides prepared under a high pressure, Mg$_3$MnH$_7$ exhibits relatively high hydrogen concentration reaching to 5 mass%. This Mg$_3$MnH$_7$ compound with a hexagonal Mg$_3$ReH$_7$-type structure has been originally prepared by Bortz et al. under 2 GPa [3]. But, recently, it had been reported that the hydride with monoclinic structure was prepared under 6 GPa from powder mixture with the same nominal composition by Kyoi et al. [11,12]. This discrepancy implies that the crystal structure of Mg$_3$MnH$_y$ may depend on synthesis pressure or hydrogen content. In addition, for MgY$_2$H$_y$ with an FCC structure prepared under 5 GPa in our previous work [13,14], the effect of applied pressure on present phases remains unclear as well. Thus, the purposes of this study are to prepare the hydrides in Mg–M (M = Mn and Y) systems under various pressures, and clarify the influence of the applied pressure during synthesis on present phases and their crystal structures. The hydrogen content of the hydrides was also investigated.
2. Experimental procedures

The raw materials were MgH2 (90 mass%, major impurity was metallic Mg), Mn (99.9 mass%) and YH3 (99.9 mass%) powders. Powder mixtures were pressed into a pellet and put into a BN container, which is expected to work as electric insulator. The container was then put into a graphite tube heater, and placed into a pressure media made from a pyrophyllite. All the manipulations of sample preparation were conducted in a glove box filled with Ar gas. The high-pressure synthesis was carried out by using anvil-type apparatus. Samples were prepared at 1073 K for 2 h. To clarify the effect of pressure on present phases, pressure was varied from 2 to 5 GPa. The detailed processing schedules were described elsewhere [13]. Phase identification was carried out by X-ray diffractometry (XRD). Compositional analysis was performed by SEM–EDX. Thermal stability of the samples was measured by using differential scanning calorimeter (DSC) in Ar flow. The hydrogen content of hydrides was measured by means of a fusion extraction analysis using LECO and also estimated from a weight loss observed in a thermogravimetric analysis (TGA) equipped with thermal desorption spectroscopy (TDS).

3. Results and discussion

3.1. Mg–Mn–H system

Fig. 1 shows X-ray diffraction patterns of MgH2–x mol%Mn prepared at 1073 K for 2 h at 5 GPa. For the sample of MgH2–25 mol%Mn, the hydride of Mg3MnH7 with a monoclinic structure (a = 0.8819(8) nm, b = 0.4658(4) nm, c = 0.4678(5) nm and \( \beta = 105.6(1)^\circ \)) was observed, which have been prepared at 873 K under 6 GPa in Refs. [11,12]. As mentioned above, Mg3MnH7 with a hexagonal structure has been synthesized at 1073 K under 2 GPa by Bortz et al. Therefore, the crystal structure of the hydride must change from hexagonal to monoclinic at somewhere between 2 and 5 GPa. To clarify the boundary, applied pressures were varied.

Fig. 2 shows X-ray diffraction patterns of MgH2–25 mol%Mn samples prepared at 1073 K for 2 h under a high-pressure ranging from 2 to 5 GPa. As a result, the hexagonal phase with cell parameters of \( a = 0.47107(4) \) nm and \( c = 1.0297(1) \) nm was found to exist under less than 3 GPa, while the monoclinic phase appeared under 4 GPa or higher. The monoclinic phase was also prepared under 3.5 GPa. To clarify whether or not the transformation from the hexagonal structure to monoclinic one is reversible with change of pressure, the sample with a monoclinic structure prepared under 5 GPa was annealed under a lower pressure of 2 GPa for 2 h and the sample with a hexagonal prepared under 2 GPa was annealed under a higher pressure of 5 GPa for 2 h. Fig. 3 shows the X-ray diffraction patterns of (a) the sample prepared at 5 GPa and (b) one followed by annealing under 2 GPa for 2 h. The processing schedules were shown as an inset. As can be seen, the sample annealed under 2 GPa had the hexagonal structure. While, the sample annealed under 5 GPa after

![Fig. 1. X-ray diffraction patterns of MgH2–x mol%Mn prepared at 1073 K for 2 h under 5 GPa, where (a) x = 10, (b) x = 25, (c) x = 50, (d) x = 67 and (e) x = 80.](image)

![Fig. 2. X-ray diffraction patterns of MgH2–25 mol%Mn prepared at 1073 K for 2 h under the pressure of (a) 2 GPa, (b) 3 GPa, (c) 4 GPa and (d) 5 GPa.](image)
preparation at 2 GPa had the monoclinic structure as shown in Fig. 4. Therefore it can be concluded that the phase transformation existing between 3 and 3.5 GPa is reversible. And from this result, the hydrogen content of the monoclinic hydride can be estimated to be almost same as that of the hexagonal hydride. The hydrides exhibited orange-reddish color regardless of crystal structures. To further investigate the difference between the hexagonal and monoclinic phases, thermal stability was also evaluated by using DSC. Fig. 5 shows the DSC curves of (a) hexagonal and (b) monoclinic phases prepared at 1073 K for 2 h under 2 and 5 GPa, respectively. For the hexagonal phase, an endothermic peak with an onset of around 670 K was observed. On the other hand, for the monoclinic phase, the onset temperature decreased to around 620 K. This decrease in decomposition temperature by 50 K seems to be reasonable, given that the monoclinic phase was prepared under a higher pressure compared to the hexagonal phase. And, it can be noted that the hexagonal and monoclinic hydrides seem to have two endothermic peaks, indicating that hydrogen may occupy two different crystallographic sites.

The hydrogen content of the monoclinic Mg₃MnH₅ phase prepared under 4 GPa was investigated by TGA and LECO analyses. Fig. 6 shows the TG and TDS curves of Mg₃MnH₅. A significant weight loss starting from about 600 K due to hydrogen desorption was observed. From its weight loss, the amount of hydrogen was estimated to be 3.7 mass%. Moreover, from LECO analysis, it was estimated to be 4.2 mass%. From these analyses, the chemical formula of the monoclinic phase can be expressed as Mg₃MnH₅₋ₓ. This hydrogen content shows a good agreement with the value reported by Kyo [11,12]. On the other hand, for the hexagonal phase, which have been reportedly contained 5.2 mass%H, a weight loss of 3.5 mass% was observed in this work. As mention above,
the hydrogen content of the monoclinic hydride was almost same as that of the hexagonal hydride in this work.

3.2. Mg–Y–H system

In this system, a high-pressure hydride of MgY \(_2\)H\(_y\) with an FCC-type structure has been prepared at 1073 K under 5 GPa as shown in Fig. 7 [13]. Even though YH\(_2\) and Y\(_2\)O\(_3\) also exhibit the FCC-type structure, a cell parameter of MgY\(_2\)H\(_y\) (\(a = 0.516 \text{ nm}\)) was a little smaller than those of YH\(_2\) and Y\(_2\)O\(_3\). Moreover, the FCC-type phase appeared as a single phase only when the nominal composition was MgH\(_2\)–67 mol%YH\(_3\), while the samples with 50 mol%YH\(_3\) and 80 mol%YH\(_3\) contained MgH\(_2\) and YH\(_3\) as secondary phases, respectively. From an EDX analysis, the chemical composition of the FCC-type phase was found to be almost same as the nominal composition. Based on these observations, the FCC-type phase was concluded to be a high-pressure hydride. The structure of this high-pressure hydride had been described in Ref. [14]. This sample showed yellowish color and was stable under atmospheric pressure and air.

To investigate the influence of pressure on phases present, MgY\(_2\)H\(_y\) was tried to be synthesized under a pressure ranging from 2 to 5 GPa. Fig. 8 shows X-ray diffraction patterns of MgH\(_2\)–67 mol%YH\(_3\) synthesized at 1073 K for 2 h under a pressure of 2–5 GPa. The sample prepared under 2 GPa consisted of MgH\(_2\) and Mn, while ones prepared under 3 GPa or higher contained the FCC-type high-pressure phase (MgY\(_2\)H\(_y\)). The samples prepared under higher pressures tend to contain more the FCC-type high-pressure phase. Since the cell parameter of MgY\(_2\)H\(_y\) was almost identical regardless of applied pressure, a kinetic effect seems to be involved in the difference in the resultant volume fraction of the high-pressure phase. Since, at a given temperature, a driving
force for the formation of the high-pressure phase is applied. Pressure it seems to be reasonable to find a relationship between pressure and volume fraction. Judging from these observations, the high-pressure range of less than 2 GPa and over 3 GPa can be considered as different criteria to explore novel hydrides in Mg-based systems, even though this might be only adopted in the case of Mg–Mn and Mg–Y systems.

To investigate the thermal stability of MgY$_2$H$_y$, DSC measurement was performed. Fig. 9 shows the DSC curves of MgH$_2$–x mol.%YH$_3$ prepared at 1073 K for 2 h under 5 GPa. As indicated in Fig. 6, MgH$_2$–67 mol.%YH$_3$ was a single phase of MgY$_2$H$_y$, while other samples contained secondary phases. For the sample with 33 mol.%YH$_3$, which contained MgH$_2$, endothermic peak corresponding to dehydrogenation of MgH$_2$ was observed at about 660 K. In addition, for all the samples from $x = 33$ to 100, an endothermic peak with an onset of about 600 K was observed. This peak can be assigned as a dehydrogenation process of the new FCC-type phase. Since YH$_3$ exhibits partial dehydrogenation (2YH$_3$ → 2YH$_2$ + H$_2$) at the same temperature, the FCC-type phase was considered to be thermally stable as well as YH$_3$. The samples with FCC-type high-pressure phase changed into black color from yellowish color after the DSC measurement. From the XRD analysis of MgY$_2$H$_y$ after DSC measurements, it was found that the FCC-structure was maintained even after dehydrogenation [12]. This seems to be the first observation of high-pressure hydride that can hold its crystal structure after dehydrogenation.

Fig. 10 shows the TG and TDS curves of the novel hydride (MgY$_2$H$_y$). The weight of the novel hydride decreased from around 600 K with hydrogen desorption. The amount of hydrogen was estimated to be 1.4 mass% from its weight loss. But from LECO analysis, the total amount of hydrogen was determined to be 3.7 mass%. Therefore the new hydride can be described as MgY$_2$H$_{7.8}$ and the partial dehydrogenation can be said to occur at about 600 K. As for crystal structure, a unit cell formed by four metal atoms had more than 10 H atoms and less than 4 H atoms of which were emitted at about 600 K without the corruption of the crystal structure.

4. Conclusion

Synthesis of the hydrides in Mg–M (M = Mn, Y) systems under high pressures, and the influence of pressure during synthesis on the present phases and their crystal structures have been studied. In Mg–Mn system, the monoclinic hydride of Mg$_3$MnH$_y$ with cell parameters of $a = 0.8819(8)$ nm, $b = 0.4658(4)$ nm, $c = 0.4678(5)$ nm and $\beta = 105.6(1)^\circ$ was synthesized under a high pressure of 3.5 GPa or higher, and the hexagonal hydride was synthesized under less than 3 GPa. The crystal structure of Mg$_3$MnH$_y$ changed reversibly from hexagonal to monoclinic in a pressure range of 3–3.5 GPa. The Mg$_3$MnH$_y$ synthesized under 5 GPa was stable up to around 620 K. From LECO analysis, the hydride content was determined as Mg$_3$MnH$_{5.0...5.6}$.

In Mg–Y system, the high-pressure hydride with yellowish color was synthesized at 1073 K for 2 h under
3 GPa or higher. This phase exhibited an FCC-type structure with a cell parameter of \(a = 0.516\) nm. Its hydrogen content was estimated to be 3.7 mass\%, corresponding to a chemical formula of MgY\(_2\)H\(_{7.8}\). The hydride was partially dehydrogenated around 600 K, and the amount of hydrogen was 1.4 mass\%. The FCC-type structure was stable even after the partial dehydrogenation.

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