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High-pressure synthesis of novel hydrides in Mg–RE–H systems (RE = Y, La, Ce, Pr, Sm, Gd, Tb, Dy)

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Abstract

The high-pressure synthesis of new hydrides of Mg–RE–H systems, where RE = Y, La, Ce, Pr, Sm, Gd, Tb and Dy, were conducted by using a cubic-anvil-type apparatus, and their crystal structure, thermal stabilities and hydrogen contents were investigated. In Mg–Y–H system, newly found MgY_2H_y with a FCC-type structure has been prepared. In MgH_2–x mol% REH (REH = LaH_3, $CeH_{2.5}$ and PrH_3), new hydrides with primitive tetragonal structure were synthesized around $x = 25$–33 under GPa-order high pressures. The lattice constants were $a = 0.8193$ nm, $c = 0.5028$ nm, $a = 0.8118$ nm, $c = 0.4979$ nm and $a = 0.8058$ nm, $c = 0.4970$ nm at $x = 25$ in Mg–La, Ce and Pr systems, respectively. The hydrogen contents of the novel compounds were 4.1, 3.7 and 3.9 mass% in Mg–La, Ce and Pr systems, respectively, and the chemical formulae were found to correspond to Mg_3LaH_9, $Mg_3CeH_{8.1}$ and Mg_3PrH_9. The new hydrides decomposed into Mg and rare-earth hydride at about 600 K (Mg_3LaH_9: 614 K, $Mg_3CeH_{8.1}$: 609 K, Mg_3PrH_9: 630 K) with an endothermic reaction. In MgH_2–x mol% hREH (hREH = GdH_3, TbH_3 and DyH_3), new hydrides with FCC-type structure were synthesized around $x = 67$.

Keywords: High pressure; Hydride; Magnesium; Thermal stability; Rare earth

1. Introduction

Mg-based alloys are well known to exhibit a high hydrogen capacity. They are expected to play an important role as hydrogen storage media, although Mg-based conventional alloys require high working temperature. But there are some problems of their high reaction temperature and low kinetics. To reduce the problems, a number of studies exploring new Mg–RE-based alloys and hydrides have been conducted with conventional metallurgy technique such as melting, sintering and ball milling [1,2]. It seems to reach their limits to develop new compounds by conventional studies.

As another approach, a high-pressure synthesis is an effective technique to explore new compounds in a variety of research fields. In the field of a hydrogen storage media development, this method is used to obtain new hydrides as a different approach from traditional ones. The high-pressure synthesis can be mainly classified into two groups according to pressure transmitting medium, those are, autoclave-type with gas media and the anvil-type apparatuses with solid one. For example, new hydrides of $CsMgH_3$ [3] and $REMg_2H_7$ [4] (RE = La, Ce) have been prepared by using the autoclave-type apparatus, while Mg_3MnH_7 [5] and $Sr_6Mg_7H_{26}$ [6] were reported to be synthesized under a high pressure up to GPa range by using the anvil-type apparatus. Moreover, $Mg_2Ni_3H_{3.4}$ [7,8], $(Ca_{1-x}Mg_x)_2NiH_y$ ($x \leqq 0.4$) [9–12], $MgCaH_y$ [11,12], MgY_2H_8 [13–16], Mg_3MnH_y [16], Mg_4Ni [17], MgCu [17] and $Mg_{51}Cu_{20}$ [17] have been synthesized by using the anvil-type apparatus in our previous works.

In this study, high-pressure synthesis has been used to explore novel Mg–RE-based hydrides by using a cubic-anvil-type apparatus. Since rare-earth elements (RE) have large compressibility of the atomic radii (e.g. the radius of La is reduced more than 12% under 5 GPa), there seems to be possibility to obtain novel hydrides in the Mg–RE–H systems. RE hydrides have also high moles of hydrogen. Therefore, the

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purpose of this study is to explore new hydrides of the Mg–RE systems (RE = Y, La, Ce, Pr, Sm, Gd, Tb, Dy) using the cubic anvil-type apparatus and clarify the crystal structures, thermal stabilities and hydrogen contents of newly found hydrides.

2. Experimental procedures

Raw materials were MgH_2 powder and rare-earth metals. Rare-earth hydride powders were prepared by hydrogenation of the rare-earth metals in an autoclave filled with hydrogen gas. The powders were mixed at nominal composition and pressed into pellets and put into BN containers in argon filled glove box. The mixtures were heated at 1073 K for 2 h under a quasi-hydrostatic GPa order pressure and then quenched.

A phase identification was performed by powder X-ray diffraction (XRD) using Cu Kα radiation. The crystal structures of new hydrides were estimated by ITO12 integrated in the CRYSFIRE program. Then, lattice parameters were refined by CELL program. Thermal stability was investigated using a differential scanning calorimeter (DSC) under Ar-gas flow. The hydrogen content was calculated from a weight loss observed in a thermo-gravimetric analysis (TGA), and was measured by means of fusion extraction analysis (LECO).

3. Results and discussion

In Mg–Y–H system, MgY_2H_y with a FCC-type structure has been prepared at 800 °C under more than 3 GPa as shown in Fig. 1. Fusion extraction analysis showed 3.7 mass% of the hydrogen amount in MgY_2H_y, corresponding to $y = \sim 7.8$. The lattice constant of $MgY_2H_{\sim 7.8}$ was found to be 0.51657(2) nm. This value is smaller than that of YH_3 (0.5602 nm) showing same FCC structure.

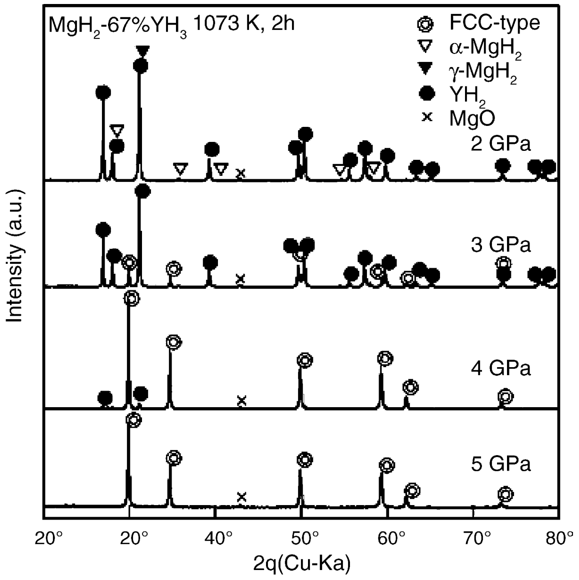

Fig. 1. X-ray diffraction patterns of MgH_2–67 mol% YH_3 prepared at 800 °C for 2 h under 2–5 GPa.

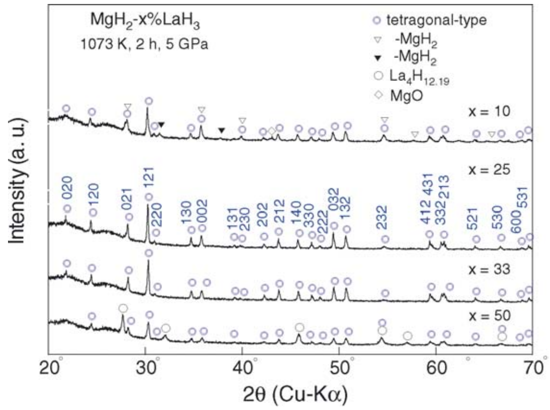

Fig. 2. X-ray diffraction patterns of MgH_2–x mol% LaH_3 prepared at 1073 K for 2 h under 5 GPa (x = 10, 25, 33, 50).

Fig. 2 shows XRD patterns of MgH_2–x mol% LaH_3 (x = 10, 25, 33 and 50) samples prepared at 1073 K for 2 h under 5 GPa. For the samples of x = 25–33, unknown phase appeared as a single phase. The crystal structure was estimated to be primitive tetragonal-type structure and was indexed as this figure. On the other hand, it had been reported that Mg_2LaH_7 synthesized by using the autoclave-type apparatus under 10 MPa also had the another tetragonal-type structure [3], their cell parameters were obviously different from this new tetragonal phase. This new phase was only synthesized under 3 GPa or higher. The cell parameters were a = 0.8193 nm, c = 0.5028 nm at x = 25 and a = 0.8172 nm, c = 0.5015 nm at x = 33.

By fusion extraction analysis, for the sample of x = 25, the amount of hydrogen was estimated to be 4.1 mass% and the chemical formula of the tetragonal phase can be expressed as Mg_3LaH_9. These samples showed yellowish color and were unstable under the atmospheric pressure in air.

Fig. 3 shows the DSC curves of MgH_2–x mol% LaH_3 (x = 10, 25, 30, 33 and 50) samples prepared at 1073 K for 2 h under 5 GPa. For the composition of x = 25–33,

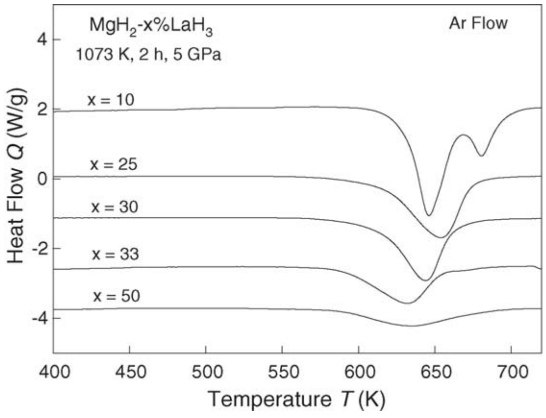

Fig. 3. DSC curves of MgH_2–x mol% LaH_3 prepared at 1073 K for 2 h under 5 GPa (x = 10, 25, 30, 33, 50).

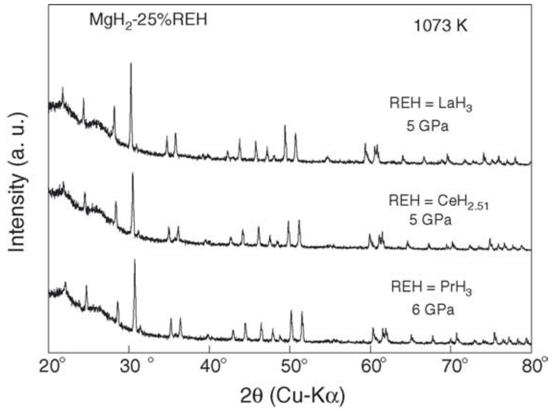

Fig. 4. X-ray diffraction patterns of MgH_2–25 mol% REH (RE = LaH_3, $CeH_{2.5}$, PrH_3) prepared at 1073 K for 2 h under 5 or 6 GPa.

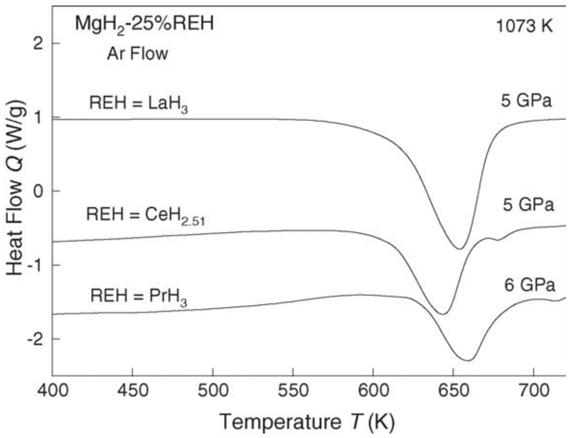

Fig. 5. DSC curves of MgH_2–25 mol% REH (REH = LaH_3, $CeH_{2.5}$, PrH_3) prepared at 1073 K for 2 h under 5 or 6 GPa.

an endothermic peak was observed at about 600 K. From TG analysis, the amount of emitted hydrogen was estimated to be 2.61 mass% for the sample of $x = 25$. The reason of this small amount of emitted hydrogen was found to be caused by partial dehydrogenation reaction ($Mg_3LaH_9 \rightarrow 3Mg + LaH_3 + 3H_2$), which was confirmed by X-ray diffraction analysis before and after DSC measurement. The value of the amount of emitted hydrogen also agreed to this equation. The endothermic temperature of the new hydrides decreased with increasing La content in this range.

Fig. 4 shows XRD patterns of MgH_2–25 mol% REH (REH = LaH_3, $CeH_{2.5}$, PrH_3) samples prepared at 1073 K under 5 or 6 GPa. As the result, the new tetragonal hydride was synthesized in all of these systems. The new hydrides with tetragonal structure were synthesized as single phase at 1073 K, over 3, 4 and 6 GPa in Mg–La, Mg–Ce and Mg–Pr systems, respectively. For Mg–Ce–H system, the novel phase had the solid-solution range similar to Mg–La–H system. For the sample prepared under 3 GPa, raw material phases also appeared with new tetragonal phase differently from Mg–La–H system. On the other hand, for MgH_2–25 mol% PrH_3 samples, tetragonal phase appeared as a single phase at only composition of $x = 25$, and the hydride does not seem to have the solid-solution range, which is different from the other systems. For the sample prepared under 5 GPa, raw material phases also appeared with new tetragonal phase differently from the other systems. The cell parameters of new phase are $a = 0.8118$ nm, $c = 0.4979$ nm at $x = 25$ and $a = 0.8109$ nm, $c = 0.4969$ nm at $x = 33$, and $a = 0.8058$ nm, $c = 0.4970$ nm at $x = 25$ in Mg–Ce and Pr systems, respectively. The hydrogen content of new hydrides were estimated to be 3.7 and 3.9 mass% in Mg–Ce and Pr systems by fusion extraction analysis, respectively. Therefore, the chemical formulae can be expressed as $Mg_3CeH_{8.1}$and Mg_3PrH_9. Each samples in Mg–Ce and Pr system showed reddish and yellowish color, and both samples were unstable under the atmospheric pressure in air. However, in Mg–Sm–H system, Mg and Sm hydrides were not reacted and no newly phases were found in this study. To investigate the thermal stability of the samples, DSC measurements were performed. Fig. 5 shows the DSC curves of MgH_2–25 mol% REH (REH = LaH_3, $CeH_{2.5}$, PrH_3) samples prepared at 1073 K under 5 or 6 GPa. An endothermic peak corresponding to decomposition of new hydrides into Mg and REH with partial dehydrogenation was observed at about 600 K (Mg_3LaH_9: 614 K, $Mg_3CeH_{8.1}$: 609 K, Mg_3PrH_9: 630 K).

In these three systems, the difference of the synthesis condition for new hydrides suggested that the ionic radius of rare-earth element was related to the synthesis pressure. The synthesis condition for new hydrides might be depended on ionic radius ratio between hydrogen ion and each rare-earth ion. If so, the system contained rare-earth element with the smaller ionic radius would be required the higher synthesis pressure to obtain new tetragonal-type hydride, since hydrogen ion has higher compressibility than that of rare-earth ion.

Besides, in MgH_2–x mol% REH systems excepting for Pr system, these novel hydrides were observed in the range of $x = 25$–33. The lattice constants of the hydride were decreased with increasing of rare-earth content, although rare-earth elements have larger ionic radius than that of Mg element. This might be due to the defect structure described as $Mg_{3-\delta}REH_{9-2\delta}$. Judging from the lattice constant, Mg ions would occupy no rare-earth ion sites and on the other hand, rare-earth ions would occupy no Mg ion sites. Moreover, from the reason, the hydride would become to be unstable thermally with increase of rare-earth element.

Fig. 6 shows XRD patterns of MgH_2–67 mol% hREH (hREH = GdH_3, TbH_3, DyH_3) samples prepared at 1073 K under GPa pressure. As the result, the new FCC-type hydride was synthesized in all of these systems. For Mg–Gd–H and Mg–Dy–H systems, the novel phase was synthesized under 3 GPa or higher. For Mg–Tb–H system, the novel phase was synthesized under 6 GPa or higher. GdH_3, TbH_3 and DyH_3 have a hexagonal structure (cf. LaH_3, $CeH_{2.5}$, PrH_2 have a cubic one), and the newly found hydrides with hRE have

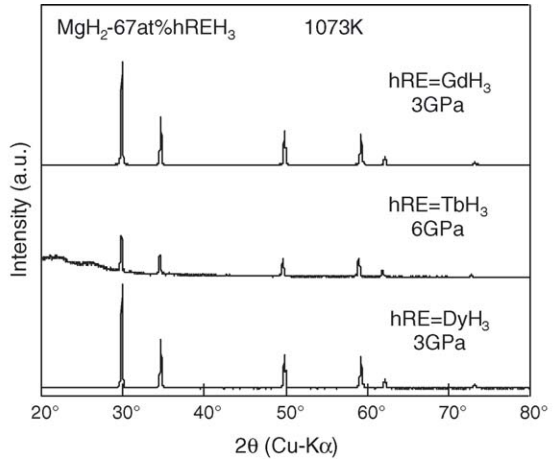

Fig. 6. XRD patterns of MgH_2–67 mol% hREH (hREH = GdH_3, TbH_3 and DyH_3) samples prepared at 1073 K under 3, 6 and 3 GPa pressure, respectively.

also close packed structure, FCC-type. Further studies are required to clarify the detailed reason.

4. Summary

The synthesis of novel hydride in Mg–RE systems (RE = Y, La, Ce, Pr, Sm, Gd, Tb, Dy) by using a high-pressure apparatus has been conducted. In Mg–Y–H system, the new hydride of MgY_2H_y with a FCC-type structure has been prepared at 800 °C under more than 3 GPa. The new hydrides with tetragonal structure were synthesized as single phase at 1073 K, over 3, 4 and 6 GPa in Mg–La, Mg–Ce and Mg–Pr systems, respectively. The chemical composition of the new hydride was around MgH_2–25 at.% REH (REH = LaH_3, $CeH_{2.5}$ and PrH_3). The chemical formulae and lattice constants of the hydrides were found to be corresponding to Mg_3LaH_9: $a = 0.8193$ nm, $c = 0.5028$ nm, $Mg_3CeH_{8.1}$: $a = 0.8118$ nm, $c = 0.4979$ nm and Mg_3PrH_9: $a = 0.8058$ nm, $c = 0.4970$ nm, respectively. The hydrogen contents of the novel compounds were 4.1, 3.7 and 3.9 mass% in Mg–La, Ce and Pr systems, respectively. They were thermally stable up to about 600 K under Ar flow, and decomposed into Mg and rare-earth hydride. For MgH_2–67 mol% $hREH_3$ (hRE = Gd, Tb, Dy), the new hydrides were also obtained and had FCC-type structure.

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