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High-pressure synthesis of novel hydride in Mg–M systems (M = Li, Pd)

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Abstract

Phases present and thermal stability of synthesized new compounds in the Mg–Li–H and Mg–Pd systems by preparing under a high pressure were studied. In the Mg–Li–H system, a new hydride with a tentative composition Mg_2LiH_5 is synthesized by exposing a mixture of MgH_2 and LiH to pressures of 2–5 GPa at 973 K for 4 h. The hydride has a cubic structure with the lattice parameter of 0.4219 nm. In the Mg–Pd system, a new intermetallic compound Mg–20 at.% Pd was synthesized at 1073 K and a pressure exceeding 2 GPa. This phase had a bcc structure with $a = 1.4053(1)$ nm and it transformed into a low-symmetry phase on heating above 663 K. Moreover, hydrogenation of the compound at 650 K for 3 days under hydrogen pressure of 9 MPa, changed into MgH_2 and new hydride Mg_2PdH_x with fcc structure similar to that of Mg_2PdC_x [D. Noréus, B. Bogdanović, U. Wilczok, J. Less-Common Met. 169 (1991) 369–373]. The new hydride dehydrogenated at 586 K that is about 100 K lower than MgH_2.

Keywords: High pressure; Hydrogen-storage materials; X-ray diffraction

1. Introduction

Hydrogen-storage materials have attracted much attention in view of the development of hydrogen energy systems. To increase the storage capacity, a considerable number of works aimed at improving the microstructure and searching for new hydrides or alloys have been conducted [1].

High-pressure synthesis is one of the effective means to obtain new compounds. In the metal–hydrogen systems, an additional degree of freedom for exploring new hydrogen-storage alloys appears if pressure is used as a processing parameter along with the composition and temperature. Many new hydrides such as $CsMgH_3$ [2] and $REMg_2H_7$ [3] (RE = La, Ce) were synthesized in an autoclave under hydrogen pressures in the MPa range, while hydrides like Mg_3MnH_7 [4] and $Sr_6Mg_7H_{26}$ [5] were synthesized in anvil-type apparatuses under pressures in the GPa range. $Mg_2Ni_3H_{3.4}$ [6,7] $(Ca_{1-x}Mg_x)_2NiH_y$ ($x \leq 0.4$) [8–11], $MgCaH_y$ [10,11], MgY_2H_8 [12–15], Mg_3MnH_y [14] and Mg_3LaH_9 [15] were synthesized by using a cubic-anvil-type apparatus in our previous works. A few new intermetallic compounds were also synthesized under high pressure and then explored for hydrogen storage [16].

In this paper, the magnesium–lithium–hydrogen and magnesium–palladium systems were explored. Since both Mg and Li are light elements and Pd has negative hydrogenation enthalpy value, new hydrides of their alloys might have interest as hydrogen-storage materials.

In the Mg–Pd system, intermetallic compounds Mg_6Pd, Mg_4Pd, Mg_5Pd_2, MgPd and $Mg_{0.9}Pd_{1.1}$ are known as equilibrium phases. Furthermore, non-equilibrium intermetallic compounds $MgPd_2$, $MgPd_3$ and Mg_3Pd_5 were prepared by the iodine-catalyzed synthesis [17].

The purpose of this study is to synthesize and explore new hydrides and intermetallic compounds in the Mg–Li–H and Mg–Pd systems under high pressure in the GPa range by using an anvil-type apparatus. The crystal structure, thermal

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stability and the reactivity with hydrogen of the newly found compound are also investigated.

2. Experimental procedures

The starting materials were powders of MgH_2 (90 mass%, the major impurity was metallic Mg), LiH (95 mass%), Mg (99.9 mass%) and Pd (99.9 mass%). The powders were mixed in appropriate amounts and pressed into pellets in a glove box filled with Ar gas. The pellets were put into BN containers. Then, the container was set into a graphite tube heater, and placed into a high-pressure cell made from pyrophyllite. The high-pressure synthesis was carried out in a cubic-anvil-type apparatus.

Phase identification was performed by X-ray diffraction (XRD) using monochromatic Cu Kα radiation. The crystal structures of novel compounds were estimated by ITO13. Then lattice parameters were refined by CELL program. Compositional analysis was performed by scanning electron microscopy and energy dispersive X-ray spectrometer (SEM–EDX). Thermal stability was investigated using a differential scanning calorimeter (DSC) in Ar gas. Hydrogenation of a new compound obtained in the Mg–Pd system was performed at 650 K for 3 days under a hydrogen pressure of 9 MPa. The hydrogen content of the samples was measured by fusion extraction analysis (LECO).

3. Results and discussion

3.1. Mg–Li–H system

Fig. 1 shows X-ray diffraction patterns of MgH_2–x mol% LiH samples prepared by a 4 h exposure to 973 K and 5 GPa. The relatively high background is due to the kapton tape used to avoid oxidation of the samples. As can be seen, MgH_2–33 mol% LiH sample consists almost completely of a new hydride, while the samples with 20 and 50 mol% LiH contain admixtures of the MgH_2 and LiH phase, respectively. Therefore, the composition of the new hydride was assumed to be close to Mg_2LiH_5. The XRD pattern of this hydride can be indexed in a cubic cell with a lattice parameter of $a = 0.4219$ nm.

An exposure of the MgH_2–33 mol% LiH mixture to a lower pressure of 2 GPa gave the same hydride phase. No hydride formation, however, was observed after a 20 h exposure of this mixture to a hydrogen pressure of 8 MPa at 673 K.

The LECO analysis of the new hydride yielded the hydrogen content 5.65 mass% instead of 8.3 mass% corresponding to the Mg_2LiH_5 composition. Presumably, this was due to the partial oxidation of the sample.

3.2. Mg–Pd and Mg–Pd-H system

Fig. 2 shows X-ray diffraction patterns of Mg–x at.% Pd samples prepared by a 4 h exposure to 1073 K and 2 GPa.

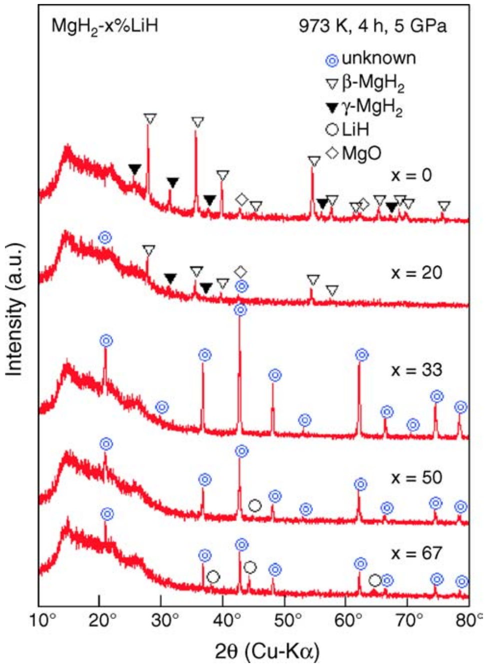

Fig. 1. X-ray diffraction patterns of MgH_2–x mol% LiH samples prepared by a 4 h exposure to 973 K and 5 GPa.

Under this condition, only starting elements or reported compounds were observed excluding the unknown phase which appeared between $x = 18$ and 22. The X-ray diffraction pattern of this unknown phase was undoubtedly different from one of the orthorhombic phase of Mg_4Pd under atmospheric pressure, which was reported to have lattice parameters of $a = 2.8054$, $b = 2.8062$ and $c = 3.8387$ nm [18]. Therefore, there is a possibility that the unknown phase may belong to a newly synthesized compound. In the following, the crystal structure, thermal stability and the reactivity with hydrogen for this phase were investigated.

The unknown phase which appeared at Mg–x at.% Pd was further studied. At first, the sample of Mg–20 at.% Pd was prepared by a 4 h exposure to 1073 K and 2 GPa, and the composition of the main phase was investigated from EDX analysis. As a result, the sample consisted of almost a single phase of the new intermetallic compound and it was found to be Mg–20 at.% Pd corresponding to nominal composition. Therefore, XRD measurement of this sample was performed to clarify the crystal structure. Fig. 3 shows X-ray diffraction pattern of Mg–20 at.% Pd sample prepared by a 4 h exposure to 1073 K and 2 GPa. This phase was found to exhibit a bcc structure with $a = 1.4053(1)$ nm which is indexed as shown in Fig. 3. The observed d-spacings, relative intensities, calculated d-spacings, and corresponding Miller indices are summarized in Table 1. The calculated d-values show a good agreement with the observed ones. To clarify the crystal structure in detail, profile fitting analyses such as Rietveld method will be required.

To investigate the influence of applied pressures during synthesis on the present phase, Mg–20 at.% Pd sample was

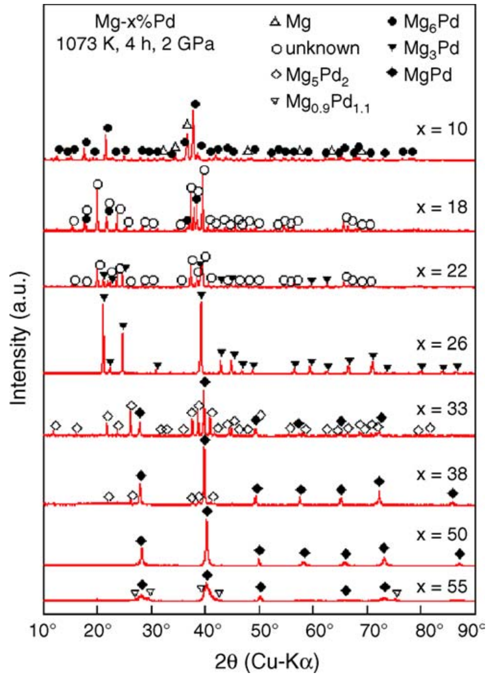

Fig. 2. X-ray diffraction patterns of Mg–*x* at.% Pd samples prepared by a 4 h exposure to 1073 K and 2 GPa.

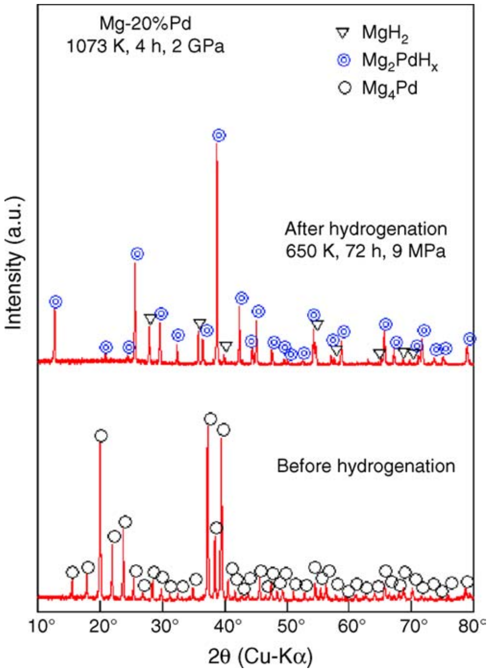

Fig. 4. X-ray diffraction patterns before and after hydrogenation of Mg–20 at.% Pd sample prepared by a 4 h exposure to 1073 K and 2 GPa.

also prepared under 6 GPa. The diffraction pattern of this sample was similar to one of the samples prepared under 2 GPa, although the diffraction intensities were a little different. In short, new compound Mg_4Pd was found to be synthesized at 1073 K and 2–6 GPa.

The thermal stability of Mg_4Pd prepared at 1073 K and 2 GPa was measured under an Ar gas flow by DSC measurement. As a result, the exothermic peaks were observed between 663 and 820 K. From the XRD analysis of the sample after heat-treatment in Ar gas at 823 K for 12 h, it was found that this cubic compound Mg_4Pd before this treatment changed into a low-symmetry structure phase.

To examine the reactivity with hydrogen, it seems likely that optimum condition for hydrogenation will be in temperature below the exothermic temperatures measured by DSC. Therefore, the temperature just below the exothermic temperature was adopted for hydrogenation. As a result, hydrogenation of Mg_4Pd compound was observed under the condition of holding at 650 K for 3 days under hydrogen pressure of 9 MPa and changed into MgH_2 and new hydride Mg_2PdH_x with fcc structure similar to that of Mg_2PdC_x with the space group of $Fd3m$ as shown in Fig. 4. The lattice parameter of the new hydride was $a = 1.2047(1)$ nm.

To investigate the dehydrogenation temperature of new hydride Mg_2PdH_x, the DSC measurement of the sample prepared by exposing Mg_4Pd to hydrogen pressure of 9 MPa at 650 K for 3 days was performed. As a result, the endothermic peak due to hydrogen desorption of the new hydride observed

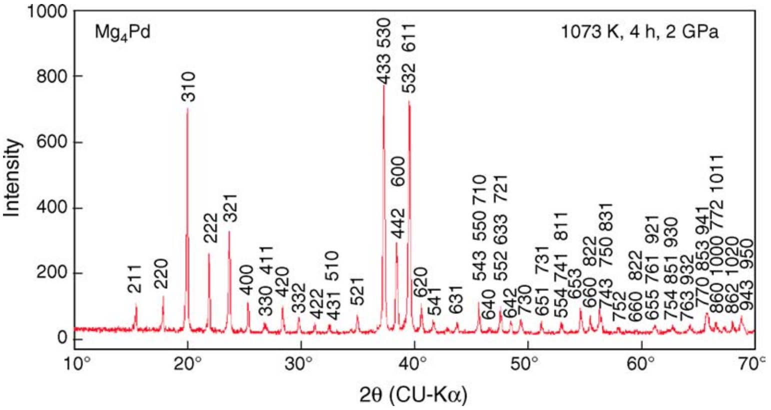

Fig. 3. X-ray diffraction pattern of Mg–20 at.% Pd sample prepared by a 4 h exposure to 1073 K and 2 GPa, and the Miller indices.

Table 1
Observed and calculated *d*-spacing of Mg_4Pd prepared by a 4 h exposure to 973 K and 5 GPa

d-Spacing observed	I/I_{max}	*d*-Spacing calculated	*h k l*
5.7439	11.0	5.7328	2 1 1
4.9727	14.1	4.9646	2 2 0
4.4471	90.9	4.4406	3 1 0
4.0572	31.9	4.0530	2 2 2
3.7580	41.1	3.7530	3 2 1
3.5139	12.1	3.5139	4 0 0
3.3208	3.5	3.3098	3 3 0 4 1 1
3.1426	11.1	3.1399	4 2 0
2.9950	6.5	2.9938	3 3 2
2.8663	3.9	2.8664	4 2 2
2.7543	3.7	2.7539	4 3 1 5 1 0
2.5648	7.1	2.5638	5 2 1
2.4092	100.0	2.4082	4 3 3 5 3 0
2.3419	35.5	2.3403	4 4 2 6 0 0
2.7585	93.5	2.2779	5 3 2 6 1 1
2.2214	11.4	2.2203	6 2 0
2.1674	5.2	2.1668	5 4 1
1.0698	4.2	2.0704	6 3 1
1.9859	12.2	1.9859	5 4 3 5 5 0 7 1 0
1.9475	2.0	1.9473	6 4 0
1.9106	10.9	1.9109	5 5 2 6 3 2 7 2 1
1.8764	4.3	1.8765	6 4 2
1.8452	5.8	1.8438	7 3 0
1.7839	3.3	1.7834	6 5 1 7 3 2
1.7284	4.5	1.7285	5 5 4 7 4 1 8 1 1
1.6785	7.3	1.6784	6 5 3
1.6553	6.4	1.6549	6 6 0 8 2 2
1.6323	7.5	1.6324	7 4 3 7 5 0 8 3 1
1.5878	2.4	1.5900	7 5 2

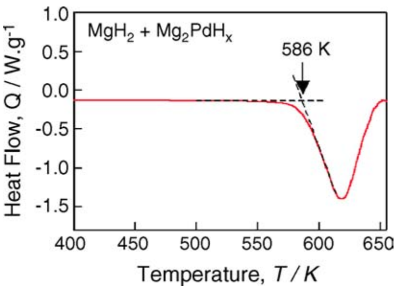

Fig. 5. DSC curve of the sample after hydrogenation of Mg–20 at.% Pd sample prepared by a 4 h exposure to 1073 K and 2 GPa.

at 586 K is shown in Fig. 5. The onset temperature was about 100 K lower than that of MgH_2.

4. Conclusion

The novel compounds were synthesized in Mg–Li–H, Mg–Pd–H and Mg–Pd systems by high-pressure technique using a cubic-anvil-type apparatus. In Mg–Li–H system, the new hydride with a composition of Mg_2LiH_y was synthesized at 973 K for 4 h over 2 GPa. The new hydride was found to exhibit the primitive cubic-type structure with the lattice parameter of $a = 0.4219$ nm. Its hydrogen content was estimated to be 5.65 mass% from LECO analysis. In Mg–Pd system, the new intermetallic compound with a chemical composition of Mg–20 at.% Pd was synthesized at 1073 K for 4 h over 2 GPa. XRD pattern of the new compound was systematically indexed as a bcc-type structure with $a = 1.4053(1)$ nm. The new compound was thermally stable up to 663 K, and transformed into low-symmetry structure phase above the temperature. Moreover, hydrogenation of the compound at 650 K for 3 days under hydrogen pressure of 9 MPa changed into MgH_2 and new hydride Mg_2PdH_x. The new hydride exhibited fcc structure with $a = 1.2047(1)$ nm and dehydrogenated at 586 K that is about 100 K lower than MgH_2.

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