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Crystal structure of novel hydrides in a Mg–Ni–H system prepared under an ultra high pressure

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Abstract

The crystal structure of novel hydrides in the Mg–Ni–H system has been studied using a powder X-ray diffraction and transmission electron microscopy. A cubic-anvil-type apparatus was utilized to prepare samples. The new hydride with a chemical composition of around MgH_2–60 at% Ni was synthesized at 1073 K for 2 h under a pressure as high as 5 GPa. From TGA analysis, the new hydride was found to be $Mg_2Ni_3H_{3.4}$. Orthorhombic and monoclinic crystal systems with a primitive cell were proposed as possible symmetries of the new hydride. X-ray and electron diffraction patterns of the new hydride were indexed in an orthorhombic structure with $a=0.8859(4)$, $b=1.3740(5)$, $c=0.4694(2)$ nm. Moreover, decomposition of the hydride into Mg_2Ni was observed by the transmission electron microscopy.

Keywords: Hydride; Magnesium–nickel–hydrogen system; XRD; TEM; Crystal structure

1. Introduction

High-pressure syntheses are widely used to explore new compounds in a variety of research fields, including high-T_C superconductors and metal hydrides. The high-pressure synthesis can be mainly categorized into two groups in terms of the manner of generating pressures, i.e. autoclave-type and anvil-type apparatuses. As far as the synthesis of hydrides is concerned, autoclaves and anvil-type apparatuses can be used in a pressure range of ≈10 MPa and GPa orders of magnitude, respectively. For example, $LaMg_2H_7$ [1], $Ba_6Mg_7H_{26}$ [2], and Na_2PdH_2 [3] have been prepared by using an autoclave, while using an anvil-type apparatus, Mg_3MnH_7 [4], Sr_2MgH_6 [5], and $Ca_{19}Mg_8H_{54}$ [6] have been synthesized. As can be seen from above, alkaline earth metal systems including Mg are widely explored to obtain new hydrides. One of the reasons would be that alkaline earth metals show high compressibility and a remarkable enhancement of melting points under high pressures. As an example, the melting point of Mg (923 K under an atmospheric pressure) can be increased up to about 1300 K under 4 GPa. This allows solid-state reactions at temperatures above 1000 K between Mg and transition metals such as Mn and Ni, which are not possible under atmospheric pressures.

Recently, the present authors prepared a new hydride in the Mg–Ni–H system by using a cubic-anvil-type apparatus [7]. The new hydride was found to have a chemical composition of around MgH_2–60 at% Ni, and to decompose into Mg_2Ni at around 500 K under an Ar atmosphere. However, the crystal structure of the new hydride remained unknown. The purpose of this study is to clarify the crystal structure, especially the crystal system and lattice parameters, of the new hydride by using powder X-ray diffractometry and transmission electron microscopy.

2. Experimental procedures

Raw materials were MgH_2 (90 mass%) and Ni (99.8 mass%) powders. The compositions of MgH_2–x at% Ni, where x ranges from 30 to 70, were examined. The powder mixture was pressed into a pellet and put into a NaC1 container that is expected to work as electrical insulator and as a gas seal, simultaneously. The container was then put into a graphite tube heater and placed into pyrophyllite used as pressure-transmitting medium. To supply additional hydrogen during the high-pressure synthesis, samples were encapsulated with a mixture of $Ca(OH)_2$ and $NaBH_4$, which worked as a hydrogen source. Boron nitride plates were used as a separator of the hydrogen source and samples to avoid unfavorable reactions.

The high-pressure synthesis was carried out with a

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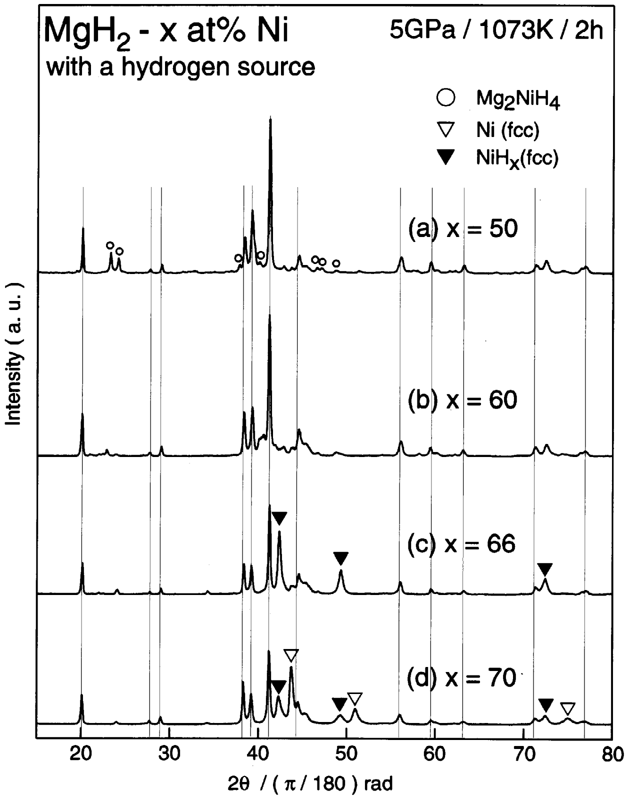

Fig. 1. X-ray diffraction patterns of MgH_2–x at% Ni prepared at 1073 K for 2 h under 5 GPa, where x ranges from 50 to 70. The additional hydrogen source was encapsulated with the samples.

cubic-anvil-type apparatus. Samples were prepared at 1073 K for 2 h under a pressure as high as 5 GPa, which can be generated by a 700-ton oil hydraulic pump. The pressure was increased up to 5 GPa at around 80 MPa min^{-1}, and then the temperature was elevated to 1073 K at 160 K min^{-1} by passing current through the graphite tube heater. After dwelling for 2 h at the process temperature, the electric current was turned off. Since it took only about 30 s to return to ambient temperatures from 1073 K, samples can be regarded as ‘quenched.’ After that, the process pressure was reduced down to atmospheric pressures at around 80 MPa min^{-1}. Phase identification was performed by X-ray diffractometry (XRD). Possible crystal systems to be used to index the XRD data were estimated by the CELL program [8], and ITO12 integrated in the CRYSFIRE program suite [9,10]. The possible space groups were also examined by electron diffraction. The hydrogen content of hydrides were calculated from a weight loss observed in a thermogravimetric analysis (TGA)

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of MgH_2–x at% Ni prepared with additional hydrogen sources at 1073 K for 2 h under 5 GPa. As can be seen in Fig. 1a, in addition to the well-known Mg_2NiH_4 phase, unknown reflections

Table 1
Possible crystal systems and refined cell parameters of $Mg_2Ni_3H_{3.4}$ prepared at 1073 K for 2 h under 5 GPa

Crystal system	Structure type	Lattice constants			
		a (nm)	*b* (nm)	*c* (nm)	*β*
Orthorhombic	–	0.4699(3)	0.8831(5)	0.4581(2)	N/A
Orthorhombic	C	0.8844(5)	1.3751(9)	0.4698(1)	N/A
Orthorhombic	P	0.8859(4)	1.3740(5)	0.4694(2)	N/A
Monoclinic	P	0.8851(3)	1.3729(4)	0.4707(1)	90.3 (1)

Table 2
X-ray diffraction data for the new hydride of $Mg_2Ni_3H_{3\ 4}$ prepared at 1073 K for 2 h under 5 GPa

d-spacing observed	I/I_{max}	*d*-spacing calculated	*h*	*k*	*l*	*d*-spacing observed	I/I_{max}	*d*-spacing calculated	*h*	*k*	*l*
4.4271	28	4.442	0	1	1	2.0010	7	2.003	4	0	1
3.8937[a]	4	3.876	0	2	1	1.9828	4	1.985	2	2	2
3.2224	2	3.222	2	0	1			1.982	4	1	1
3.0785	6	3.074	1	3	1	1.9458[a]	2	1.938	0	4	2
2.4390[a]	1	2.459	3	1	1	1.8675	3	1.861	4	4	0
2.3481	30	2.349	3	2	1	1.6407	10	1.646	5	1	1
		2.347	0	0	2	1.5863	2	1.575	5	4	0
2.2940	33	2.291	1	5	1	1.5561	6	1.555	0	1	3
2.2522	11	2.269	1	0	2	1.5378	2	1.541	1	0	3
		2.239	3	4	0	1.4738	4	1.475	0	3	0
2.2234	14	2.221	0	2	2	1.3232	7	1.324	3	3	3
2.1923[a]	100	2.194	3	3	1	1.3033	8	1.308	4	2	0
2.1582[a]	7	2.154	1	2	2			1.300	2	5	3
2.1111	6	2.108	4	2	0	1.2761[a]	2	1.272	4	1	3
2.0742	5	2.074	2	0	2	1.2472	3	1.256	4	2	3
2.0352	18	2.033	1	3	2	1.2393	4	1.235	3	5	3

[a] These reflections were observed in electron diffraction patterns (see Fig. 2).

were observed. Some of the notable unknown reflections were indicated by thin solid lines. This indicates the formation of a new hydride in the Mg–Ni–H system. As the Ni content was increased, Ni and NiH_x with FCC structures were found instead of getting Mg_2NiH_4 (see Fig. 1c and d). The formation of the NiH_x phase, which can be obtained under ultra-high hydrogen pressures, suggests that hydrogen was being well sealed during the synthesis. Since the Ni-related and Mg_2NiH_4 phases disappeared in Fig. 1b, the new hydride seems to have a chemical composition of around $x=60$. As described elsewhere [7], the samples that were prepared without the additional hydrogen source gave somewhat different XRD patterns even for the same Ni content. This difference implies that the crystal structure of the new hydride might be sensitive to hydrogen contents. In this article, we focus on the crystal structural analysis of the new hydride of $x=60$ prepared with the hydrogen source. As far as the hydrogen content of the hydride is concerned, a weight loss of 1.50 mass% was observed at around 500 K by using TGA. Based on this weight loss, the hydride can be described as $Mg_2Ni_3H_{34}$.

Table 1 summarizes the possible crystal systems suggested by CELL and ITO12 programs. Using the suggested cell parameters as initial values, each cell parameter was refined by a least-squares technique. The refined cell parameters followed by standard deviations in parentheses

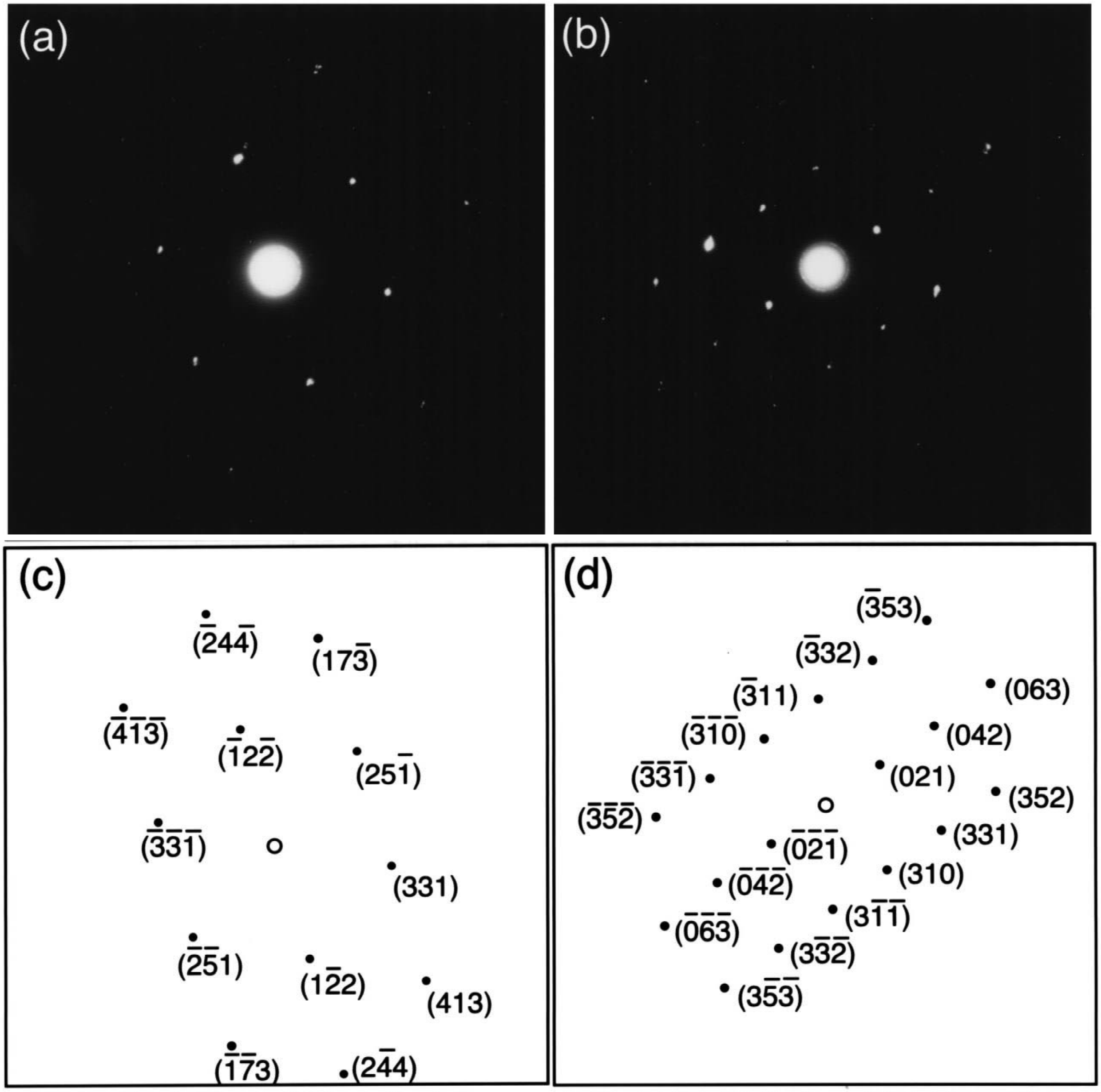

Fig. 2. Electron diffraction patterns of $Mg_2Ni_3H_{3.4}$ prepared at 1073 K for 2 h under 5 GPa, where (a) and (b) were taken with the incident beam parallel to the zone axis of [8 5 9] and [1 3 6], respectively. Calculated patterns of (c) and (d) correspond to (a) and (b), respectively.

are also included in Table 1. Each suggested crystal system can describe the XRD pattern. However, based on electron diffraction patterns, which will be mentioned later, either orthorhombic or monoclinic systems with a relatively large primitive unit cell, which is listed in the third and fourth lines in Table 1, seem to be reasonable. To clarify which crystal system is more appropriate, profile fitting analyses such as Rietveld method will be needed. Therefore, at this point, orthorhombic symmetry with a primitive cell of $a=0.8859(4)$, $b=1.3740(5)$, $c=0.4694(2)$ nm was employed as one of the possible crystal systems because of the higher symmetry group.

Assuming that this new hydride ($Mg_2Ni_3H_{3.4}$) is classified as having orthorhombic phase, the observed d-spacings, relative intensities, calculated d-spacings, and corresponding Miller indices are summarized in Table 2. As can be seen, the calculated d-values show a good agreement with the observed ones. But, it should be noted that, even though the sample can be almost considered as quenched, there is a possibility that a phase transformation might have occurred during pressure release.

To further clarify the crystal structure of the new hydride, electron diffraction (ED) patterns were examined. Fig. 2a and b show the ED patterns taken from two different sample orientations. Along with the observed patterns, calculated ED patterns were plotted as Fig. 2c and d, for which the above orthorhombic crystal structure was used. Fig. 2a and b showed a good agreement with (c) and (d), respectively. Judging from the assigned Miller indices, the direction of the incident electron beam seems to be parallel to the zone axis of [8 5 9] in Fig. 2a and [1 3 6] in Fig. 2b, respectively. In addition, diffraction spots indexed as (hkl), where neither $h+k=2n$ nor $h=2n$ condition was satisfied (e.g. (1 2 2)), as were observed in Fig. 2a. Because of the appearance of these diffraction spots, the C-type orthorhombic structure in Table 1 was excluded as a possible symmetry group. Based on this ED analysis and XRD analysis mentioned above, the orthorhombic structure with a primitive cell of $a=0.8859(4)$, $b=1.3740(5)$, $c=0.4694(2)$ nm was confirmed to be the symmetry for the new hydride.

Moreover, an in-situ observation of decomposition of the new hydride was performed using TEM. As described elsewhere [7], the new hydride is decomposed into the conventional Mg_2Ni phase at around 500 K under Ar atmosphere. Fig. 3 shows the ED pattern taken from the sample mentioned above, but just after trying to converge the electron beam onto a selected region. As the electron beam converged, a bright image of the new hydride suddenly changed, and the selected area gave the completely different ED pattern from the original one. From the d-spacing of diffraction spots, the Mg_2Ni phase was found to be present instead of the new hydride. Judging from the Mg/Ni ratio of the hydride, Ni-rich phase (e.g. $MgNi_2$ or Ni) should also appear after decomposition. However, such an ED spot was not detected in this study. In any case, this decomposition into a thermodynamically stable phase suggests that the new hydride is unstable under the atmosphere or less pressure.

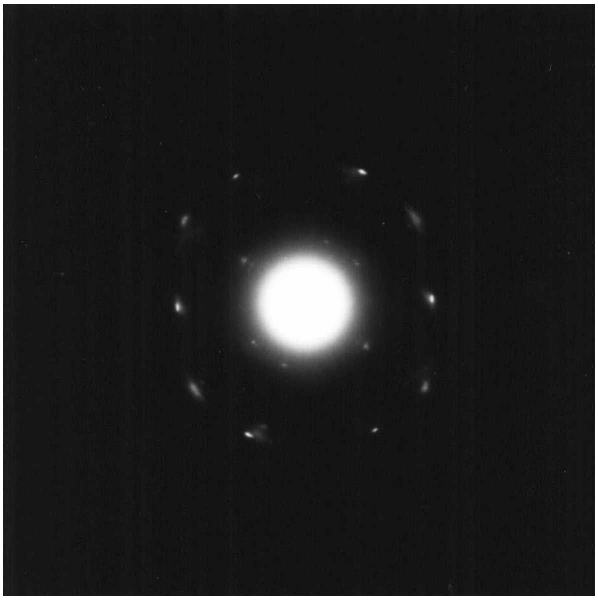

Fig. 3. Electron diffraction pattern of $Mg_2Ni_3H_{3.4}$ decomposed by converging electron beams.

4. Conclusion

The crystal structure of novel hydrides in the Mg–Ni–H system has been studied. The new hydride with a chemical composition of around MgH_2–60 at% Ni was synthesized at 1073 K for 2 h under a pressure as high as 5 GPa. From TGA analysis, the new hydride was found to be $Mg_2Ni_3H_{34}$. Orthorhombic and monoclinic crystal systems with a primitive cell were proposed as possible symmetries of the new hydride. As an orthorhombic structure with $a=0.8859(4)$, $b=1.3740(5)$, $c=0.4694(2)$ nm was employed, XRD and ED patterns of the new hydride were systematically indexed. Moreover, decomposition of the new hydride into Mg_2Ni was observed by TEM.

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