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Crystal structures of novel La–Mg–Ni hydrogen absorbing alloys

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Abstract

Crystal structures of $La_{0.70}Mg_{0.30}Ni_{2.5}Co_{0.5}$ (alloy T1) and $La_{0.75}Mg_{0.25}Ni_{3.0}Co_{0.5}$ (alloy T2) were investigated. From the structural analysis for small particles picked up from crushed ingot, we found that the alloy T1 consisted of Ce_2Ni_7-type and $PuNi_3$-type phases and that the alloy T2 consisted of Ce_2Ni_7-type and Pr_5Co_{19}-type phases. These phases were made up two or three blocks that consisted of one [La_2Ni_4] layer and one to three [$LaNi_5$] layers along *c*-axis. It was found that Mg occupied the La site in the [La_2Ni_4] layer. Selective occupation of Mg at the La site in the [La_2Ni_4] layer makes the alloy stable in repeated hydrogenation and dehydrogenation.

Keywords: Hydrogen absorbing alloys; Crystal structure; Layered structure

1. Introduction

Ni–hydrogen batteries are one of the most popular rechargeable batteries. They have numbers of advantages to other small size rechargeable batteries such as capacity, non-toxicity, same output voltage to dry battery, reasonable price, charge/recharge rate, etc. However, there still is requirement to achieve much higher capacity than the present Ni–hydrogen batteries. Electrode materials that are the media to store energy in the battery are the key to improve the performance of whale the battery. AB_5-type hydrogen absorbing alloys have been used for the negative electrode of Ni–hydrogen battery. However, it seems to be difficult to increase the capacity of AB_5-type alloys dramatically to meet the requirements. Therefore, development of novel hydrogen absorbing alloys that are suitable for the electrode is indispensable to improve the capacity of Ni–hydrogen batteries.

One of the authors has reported new hydrogen absorbing alloy system of La–Mg–Ni (Ni/(La + Mg) = 3–4) [1]. The alloys absorb and desorb hydrogen at room temperature, and their hydrogen capacity measured by the volumetric method is higher than that of conventional AB_5-type alloys. As for electrochemical properties, this system is superior in capacity, cycle life and high rate capability. The authors have found that this alloys have layered structure and showed polytypism that is originated from difference in stacking the crystal structural units along *c*-axis [2].

In the present study, crystal structures of this novel hydrogen absorbing alloys have been investigated using both single crystal structure determination and the Rietveld method using powder diffraction data. We have determined four crystal structures in two alloys, $La_{0.70}Mg_{0.30}Ni_{2.5}Co_{0.5}$ and $La_{0.75}Mg_{0.25}Ni_{3.0}Co_{0.5}$.

2. Experimental

The alloys were prepared by an induction melting method. Chemical compositions of the alloys were measured by the ICP method and they were $La_{0.70}Mg_{0.30}Ni_{2.5}Co_{0.5}$ and $La_{0.75}Mg_{0.25}Ni_{3.0}Co_{0.5}$. Hereafter, $La_{0.70}Mg_{0.30}Ni_{2.5}Co_{0.5}$ and $La_{0.75}Mg_{0.25}Ni_{3.0}Co_{0.5}$ are called the alloy T1 and the alloy T2, respectively.

X-ray powder diffraction data were taken using Rigaku RAX-01 diffractometer with graphite monochromatized Cu Kα radiation. RIETAN2000 was used for Rietveld analysis. Precession photographs for pieces of the alloys picked up

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from lightly crushed ingots were taken using Rigaku precession camera with Mo Kα radiation. Three single crystals were found among pieces of alloys and named T1-A (plate-like shape, 150 μm × 150 μm × 25 μm), T1-B (column-like shape, 50 μm × 60 μm × 200 μm) and T2-B (boxy shape, 135 μm × 160 μm × 200 μm). Single crystal data of the three single crystals confirmed by precession photographs were taken using Rigaku RASA-7R diffractometer with Mo Kα radiation. Software teXsan was used for single crystal structure analysis.

Secondary electron microscope (SEM) and energy dispersive X-ray analysis (EDX) were measured by Hitachi S-2350 with EMAX-2770.

3. Results and discussion

3.1. Chemical composition of the alloy and identification of phases by X-ray diffraction

Table 1 lists the chemical compositions of the alloys measured and that of the metal mixtures before melting. It was confirmed that loss of any metallic elements during preparation was negligible.

Figs. 1 and 2 show the powder X-ray diffraction pattern for the alloy T1. The X-ray pattern shown in Fig. 1 measured between 2θ of 15° and 140° but the data of 15° and 80° were used for crystal structure analysis. There are numbers of small diffraction peaks in the pattern. Fig. 2 is the X-ray diffraction pattern measured lower angle than $2\theta = 20°$ with 100 s of collecting time for each data point. In Fig. 2, three diffraction peaks at $d = 1.217$, 0.8185 and 0.6087 nm were observed, which strongly suggests that this alloy has a large lattice parameter. Indexing of these peaks under an assumption of a layered structure in one direction (c-axis) was not successful. The observed peak position at $d = 0.8185$ nm did not agree with the calculated position at $d = 0.8113$ nm for 0 0 3 reflection from the position of $d = 1.217$ nm (0 0 2) and 0.6087 nm (0 0 4). An assumption of two phases with slightly different lattice parameters led a reasonable agreement to the measured pattern. It can be concluded that the phase A with a lattice parameter of 2.44 nm in one direction and the phase B with a lattice parameter of 2.45 nm existed in the alloy T1.

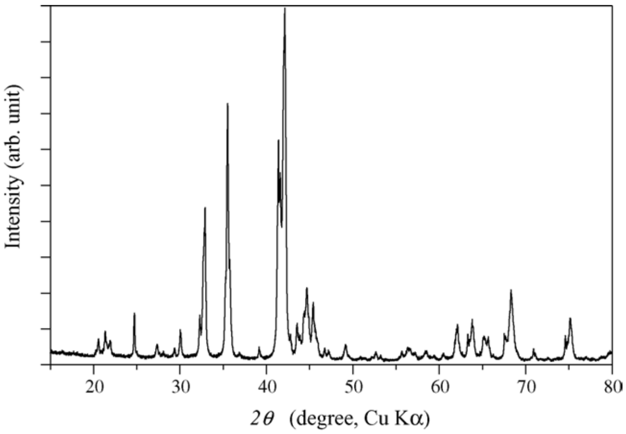

Fig. 1. X-ray diffraction profile of the alloy T1 for 2θ from 15° to 80°.

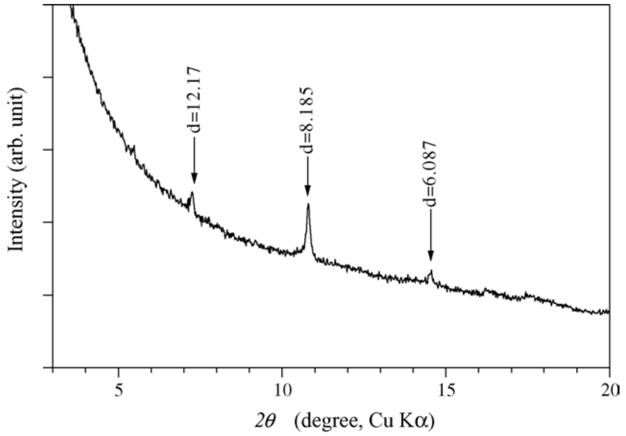

Fig. 2. X-ray diffraction profile of the alloy T1 for 2θ from 3° to 20°.

The same measurement and analysis were carried out for the alloy T2. It was also found that the alloy T2 consisted of two phases with different lattice parameters such as 2.44 and 3.22 nm.

3.2. Crystal structures of La–Mg–Ni–Co alloys

The alloys T1 and T2 were crushed into small pieces and picked up some of them that were looked as single crystals under the optical microscope. Precession photographs were taken for these crystals. After removing some part of the

Table 1

Chemical composition analyses of La–Mg–Ni–Co alloys

	La (wt%)	Mg (wt%)	Ni (wt%)	Co (wt%)	Al (wt%)	Sum (wt%)	Composition
T1							
Starting composition	34.64	2.60	52.26	10.50	0.00	100.00	$La_{0.70}Mg_{0.30}Ni_{2.50}Co_{0.50}$
ICP analysis	34.6 (0.4)	2.6 (0.1)	51.8 (0.6)	10.2 (0.1)	0.1 (0.1)	99.3	$La_{0.70}Mg_{0.30}Ni_{2.48}Co_{0.48}$
EDX analysis	34.0 (0.5)	1.8 (0.2)	53.5 (0.6)	10.6 (0.3)	0.1 (0.2)	100.0	$La_{0.77}Mg_{0.23}Ni_{2.87}Co_{0.57}$
T2							
Starting composition	32.86	2.30	55.54	9.30	0.00	100.00	$La_{0.75}Mg_{0.25}Ni_{3.00}Co_{0.50}$
ICP analysis	32.6 (0.3)	1.8 (0.1)	55.5 (0.7)	9.2 (0.1)	0.2 (0.1)	99.3	$La_{0.76}Mg_{0.24}Ni_{3.07}Co_{0.50}$
EDX analysis	32.6 (0.5)	1.4 (0.2)	56.6 (0.6)	9.2 (0.3)	0.3 (0.2)	100.0	$La_{0.81}Mg_{0.19}Ni_{3.34}Co_{0.54}$

The number in a parenthesis shows standard deviation.

Table 2
Summary of crystallographic data of La–Mg–$(Ni,Co)_x$ system alloys

Crystal no.	T1-A, T2-A	T1-B	T2-B
Chemical formula	$La_3Mg(Ni,Co)_{14}$	$La_2Mg(Ni,Co)_9$	$La_4Mg(Ni,Co)_{19}$
Structure type	Ce_2Ni_7	$PuNi_3$	Pr_5Co_{19}
Molecular weight	1263.29	830.77	1695.85
Crystal system	Hexagonal	Trigonal	Hexagonal
Space group	$P6_3/mmc$	R-3m	$P6_3/mmc$
Cell dimensions			
a (nm)	0.5052(1)	0.5062(1)	0.5042(2)
c (nm)	2.4245(3)	2.4500(2)	3.2232(5)
Volume, V (nm^3)	0.5358(3)	0.5436(2)	0.7097(7)
Z	2	3	2
Density, D_X ($Mg\,m^{-3}$)	7.83	7.61	7.93

crystals and repeated precession photograph measurements, we succeeded in taking single crystal-like photographs for two types of crystal structures in each alloy. It was found that the phase A (T1-A) in the alloy T1 and the phase A (T2-A) in the alloy T2 had an identical structure. Hereafter, we will discuss the phase A (T1-A) and B (T1-B) in the alloy T1 and the phase B (T2-B) in the alloy T2. Table 2 summarizes the crystal structural data of these four phases.

3.3. *Crystal structure of the phase A in the alloy T1 (T1-A)*

Crystallographic data obtained from precession photographs indicates that T1-A had a hexagonal structure with $a = 0.504$ nm and $c = 2.42$ nm. Compared these lattice parameters to that of $LaNi_5$ (hexagonal, space group; $P6/mmm$, $a = 0.5017$ nm and $c = 0.3987$ nm [3]), the lattice parameter of the a-axis is the same but that of c-axis is about six times as much as that of $LaNi_5$. In addition, in precession photographs strong diffraction spots in c^* direction were observed in every six spots. From the extinction rules, possible space group is $P6_3/mmc$ (No. 194), $P6_3mc$ (No. 186) or P-62c (No. 190). The obtained data are found to be similar to those of La_2Ni_7 (Ce_2Ni_7-type structure) that has a hexagonal structure with space group of $P6_3/mmc$ and lattice parameters of $a = 0.5053$ nm and $c = 2.462$ nm [4].

Two polytypes, Ce_2Ni_7-type and Gd_2Co_7-type, were reported for La_2Ni_7 [4]. The lattice parameters obtained by single crystal structure analysis were $a = 0.5052(1)$ nm and $c = 2.4245(3)$ nm, which agreed well with those obtained by precession photographs. Crystal structure of T1-A refined using single crystal data was found to be Ce_2Ni_7-type structure. This structure consisted of two blocks that contained one Laves phase-type $[La_2Ni_4]$ layer and two AB_5-type $[LaNi_5]$ layers. In Ramsdell expression [5], this structure is described as 2H-type structure. The results shows that Mg occupied the La site in the Laves phase-type $[La_2Ni_4]$ layer where La–La distance was 0.32 nm, while the La–La distance in the AB_5-type $[LaNi_5]$ layer was 0.38 nm. Because the atomic radius of Mg is shorter than that of La, Mg tends to occupy the site in the $[La_2Ni_4]$ layer where the La–La distance is shorter. In space group $P6_3/mmc$, the La site and Mg site in the $[La_2Ni_4]$ layer are equivalent in crystallographic point of view. Therefore, crystallographic composition of this phase is expressed as $(La_{2-x}Mg_x)La_2Ni_{14}$. The value of x from the single crystal structural analysis was 0.90(2), which agrees with 0.84 obtained by EDX analysis for this phase.

3.4. *Crystal structure of the phase B in the alloy T1 (T1-B)*

A column-like shape crystal that has the slightly different lattice parameters to the T1-A phase was picked up from the alloy T1. Crystallographic data obtained from precession photographs indicates that this phase has a hexagonal structure with $a = 0.505$ nm and $c = 2.45$ nm. While the lattice parameters of this phase is similar to those of T1-A ($a = 0.504$ nm and $c = 2.42$ nm), difference in the extinction rule was observed in the precession photograph of $(h\,0\,l)$. Typical reflection conditions of rhombohedral structure, $-h+k+l=3n$ in $(h\,k\,i\,l)$ and $l=3n$ in $(0\,0\,0\,l)$, were observed. Three space groups $R32$ (No. 155), $R3m$ (No. 160) and R-3m (No. 166), are possible candidates from this extinction rules. However, the quality of the crystal is not ideal because it was picked up from crushed ingot prepared by conventional melting method. It should be noted that it is possible that the crystal structure is described by the space group that has much lower symmetry. By structure refinement using the single crystal data, it was found that T1-B had a rhombohedral structure with hexagonal axes $a = 0.5062(1)$ nm and $c = 2.4500(2)$ nm. This structure is similar to $LaNi_3$ that has a $PuNi_3$-type structure [3]. The structure of T1-B is clearly different to 2H $CeNi_3$-type structure that is a polytype of the $PuNi_3$-type structure [5].

Kadir et al. refined the crystal structure of RMg_2Ni_9 (R = La, Ce, Pr, Nd, Sm, Gd) using Rietveld method [6]. T1-B phase had the similar structure but chemical composition was remarkably different to the alloys reported by Kadir et al. [6]. The $PuNi_3$-type structure is described as $(La_{2-x}Mg_x)LaNi_9$. The values of x obtained by single crystal structure analysis and EDX measurement were 0.45 and 0.44, respectively, in present work.

This structure consisted of a block that contained one Laves phase-type $[La_2Ni_4]$ layer and one AB_5-type $[LaNi_5]$

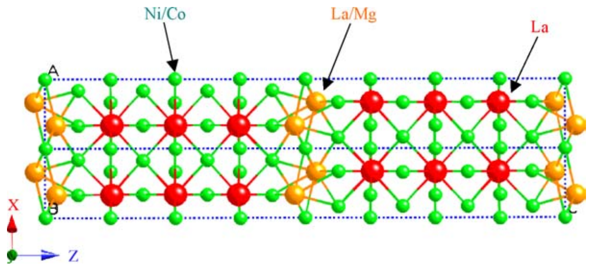

Fig. 3. Crystal structure of T2-B; Pr_5Co_{19}-type structure (space group; $P6_3/mmc$) viewing [0–10] direction.

layer. The block which slides to [1–20] direction by 1/3 of lattice stacks in c-direction and the position of the every third block is equivalent. Mg occupies the 6c site in the [La_2Ni_4] layer. However, the distance of 6c sites was 0.32 nm, which is large for Mg to occupy fully the 6c sites. Occupation by both La and Mg, defects formation and lowering of the symmetry are possible explanation for the occupation of Mg to the 6c sites.

3.5. *Crystal structure of the phase B in the alloy T2 (T2-B)*

Two phases were found in the alloy T2 but one of them (T2-A) had the same structure to T1-A. From precession photograph, the lattice parameters of T2-B were calculated as $a = 0.502$ nm and $c = 3.21$ nm. The lattice parameter of the c-axis was eight time as much as that of $LaNi_5$ (0.3987 nm [3]), which suggests that it has stacking of eight [La_2Ni_4] and [$LaNi_5$] layers. From extinction rules observed, $P6_3/mmc$ (No. 194), $P6_3mc$ (No. 186) or P-$62c$ (No. 190) is a possible candidate for the space group of T2-B. By the structure refinement using single crystal data it was found that T2-B had the Pr_5Co_{19}-type structure ($P6_3/mmc$) [7]. This structure consisted of two blocks that contained one Laves phase-type [La_2Ni_4] layer and three AB_5-type [$LaNi_5$] layers. Mg occupied 50% of the La site in the Laves phase-type [La_2Ni_4] layer. It is reasonable that smaller Mg tends to occupy the La site in the [La_2Ni_4] layer because the La–La distance of the [La_2Ni_4] layer was 0.32 nm while that of the [$LaNi_5$] layer was 0.39 nm. Fig. 3 shows the crystal structure of T2-B. It should be pointed out that Mg occupies only the [La_2Ni_4] layer and it makes the lattice stable even for hydrogenation and dehydrogenation.

3.6. *Rietveld analysis of the alloys T1 and T2*

Rietveld analysis for the alloys T1 and T2 were carried out using the structure model obtained by single crystal analysis. It was found that the alloy T1 contained small amount of the 2H-Pr_5Co_{19}-type La_4MgNi_{19} and C15b-type $LaMgNi_4$ phases in addition to Ce_2Ni_7-type La_3MgNi_{14} and $PuNi_3$-type La_2MgNi_9 phases that were confirmed by the single crystal structure analysis. The phase abundance was 15, 9, 25 and 51%, for 2H-Pr_5Co_{19}-type La_4MgNi_{19}, C15b-type $LaMgNi_4$, Ce_2Ni_7-type La_3MgNi_{14} and $PuNi_3$-type La_2MgNi_9 phases, respectively.

In the alloy T2, three phases were found such as 2H-Pr_5Co_{19}-type La_4MgNi_{19}, Ce_2Ni_7-type La_3MgNi_{14} and $CaCu_5$-type $LaNi_5$. The phase abundance was 75, 22 and 3%, respectively.

4. Conclusions

Two La–Mg–Ni alloys were prepared and investigated their crystal structures using single crystal and powder techniques. Both of alloys contained more than two phases. Crystal structures of three of major phases were analyzed using single crystal data for the small crystals picked up from the crushed ingots. Two phases consisted of the alloy T1 ($La_{0.70}Mg_{0.30}Ni_{2.5}Co_{0.5}$) were Ce_2Ni_7-type La_3MgNi_{14} (space group: $P6_3/mmc$) and $PuNi_3$-type La_2MgNi_9 (space group: R-3m). In addition, 2H-Pr_5Co_{19}-type La_4MgNi_{19} (space group: $P6_3/mmc$) and C15b-type $LaMgNi_4$ (space group: F-43m) were found by the Rietveld analysis in the alloy T1. Two phases consisted of the alloy T2 ($La_{0.75}Mg_{0.25}Ni_{3.0}Co_{0.5}$) were Ce_2Ni_7-type La_3MgNi_{14} (space group: $P6_3/mmc$) and 2H-Pr_5Co_{19}-type La_4MgNi_{19} (space group: $P6_3/mmc$). $LaNi_5$ phase was found by the Rietveld method but its abundance was 3%.

All the phases found in the present work except $LaNi_5$ had the same framework [2]. Two or three blocks that consisted of one [La_2Ni_4] layer and one to three [$LaNi_5$] layers formed the layered structures with lattice parameters from 2.43 to 3.22 nm in c-direction.

Mg occupied only the site in the [La_2Ni_4] layer, which stabilizes the structure for repeated hydrogenation and dehydrogenation.

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