

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

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Available online 24 June 2005

Abstract

Crystal structures of $\text{La}_{0.70}\text{Mg}_{0.30}\text{Ni}_{2.5}\text{Co}_{0.5}$ (alloy T1) and $\text{La}_{0.75}\text{Mg}_{0.25}\text{Ni}_{3.0}\text{Co}_{0.5}$ (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 $\text{Pr}_5\text{Co}_{19}$ -type phases. These phases were made up two or three blocks that consisted of one $[\text{La}_2\text{Ni}_4]$ layer and one to three $[\text{LaNi}_5]$ layers along *c*-axis. It was found that Mg occupied the La site in the $[\text{La}_2\text{Ni}_4]$ layer. Selective occupation of Mg at the La site in the $[\text{La}_2\text{Ni}_4]$ layer makes the alloy stable in repeated hydrogenation and dehydrogenation.

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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 whole 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 ($\text{Ni}/(\text{La} + \text{Mg}) = 3\text{--}4$) [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, $\text{La}_{0.70}\text{Mg}_{0.30}\text{Ni}_{2.5}\text{Co}_{0.5}$ and $\text{La}_{0.75}\text{Mg}_{0.25}\text{Ni}_{3.0}\text{Co}_{0.5}$.

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 $\text{La}_{0.70}\text{Mg}_{0.30}\text{Ni}_{2.5}\text{Co}_{0.5}$ and $\text{La}_{0.75}\text{Mg}_{0.25}\text{Ni}_{3.0}\text{Co}_{0.5}$. Hereafter, $\text{La}_{0.70}\text{Mg}_{0.30}\text{Ni}_{2.5}\text{Co}_{0.5}$ and $\text{La}_{0.75}\text{Mg}_{0.25}\text{Ni}_{3.0}\text{Co}_{0.5}$ 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 $\text{Cu K}\alpha$ 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 K α radiation. Three single crystals were found among pieces of alloys and named T1-A (plate-like shape, 150 μm \times 150 μm \times 25 μm), T1-B (column-like shape, 50 μm \times 60 μm \times 200 μm) and T2-B (boxy shape, 135 μm \times 160 μm \times 200 μm). Single crystal data of the three single crystals confirmed by precession photographs were taken using Rigaku RASA-7R diffractometer with Mo K α 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 $2\theta = 20^\circ$ 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 003 reflection from the position of $d = 1.217$ nm (002) and 0.6087 nm (004). 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.

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.

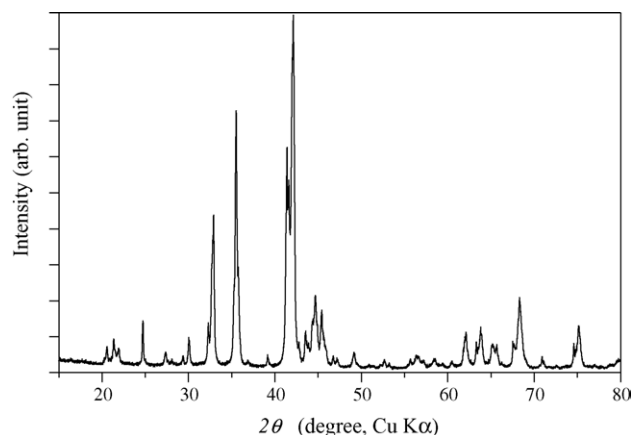


Fig. 1. X-ray diffraction profile of the alloy T1 for 2θ from 15° to 80°.

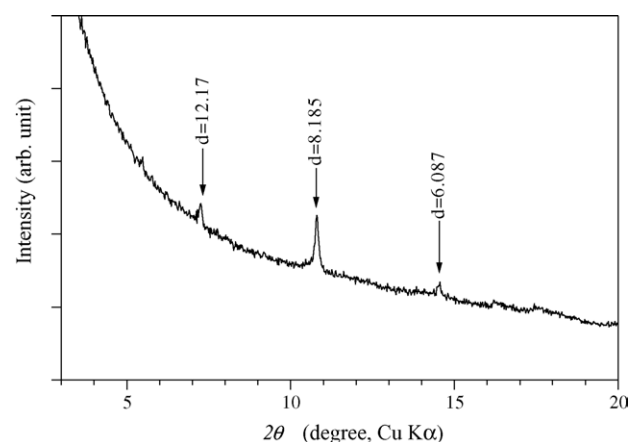


Fig. 2. X-ray diffraction profile of the alloy T1 for 2θ from 3° to 20°.

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

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