Crystal Structure Analysis of La-Mg-Ni-based Hydrogen Storage Alloys

The rare earth-Mg-Ni-based alloy is a promising hydrogen storage material for fuel cells and nickel metal hydride batteries because its hydrogen storage capacity is higher than that of conventional $MmNi_5$-based (Mm: mischmetal) alloys. In 1997, Kadir and Sakai *et al.* reported on $REMg_2Ni_9$ (RE: rare earths) alloys [1]. Subsequently, various alloys with a hydrogen storage capacity of 1-2 wt.% have been reported [2]. The hydrogen storage property of these alloys is dependent on their composition and crystal structure. However, there are few studies on the relationship between them. This is attributable to the complexity of the crystal structure of the alloys. Concerning this alloy system, there have been reports on many kinds of long-period one-dimensional superstructures, in which AB_5 units ($CaCu_5$-type structure) and A_2B_4 unit (Laves structure) are rhombohedrally or hexagonally stacked with a ratio of *n*:1 along the *c*-axis direction [3]. Most of the rare earth-Mg-Ni-based alloys have multi-phase structures consisting of more than one kind of superstructure.

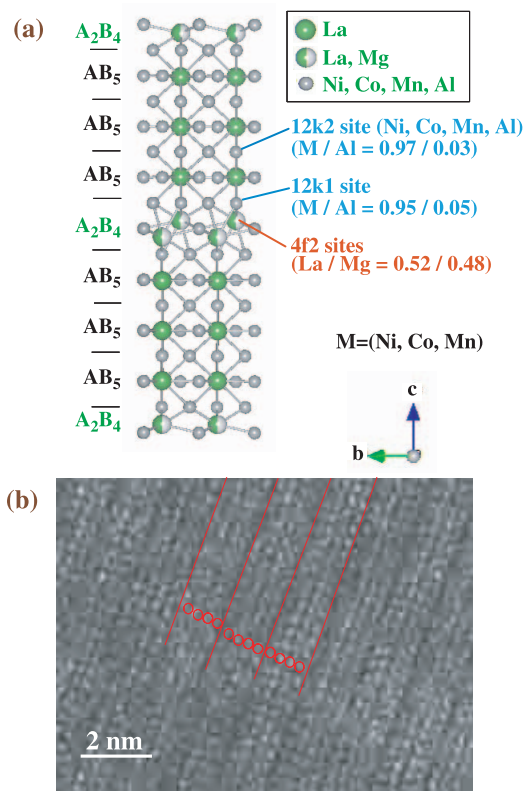

Fig. 1. **(a)** Crystal structure viewing [1 0 0] direction and **(b)** TEM image of 5:19H (Pr_5Co_{19}-type) phase of $La_{0.8}Mg_{0.2}Ni_{3.4-x}Co_{0.3}(MnAl)_x$ alloy.

Therefore, it is difficult to refine the crystal structure using conventional XRD pattern with characteristic X-ray radiations. On the other hand, in synchrotron XRD measurement, the effect of the preferred orientation is suppressed, and the diffraction pattern with high resolution and high intensity is obtained even by a short-time measurement. In this work, the effect of the partial substitution of Ni with Mn and Al on the crystal structure and hydrogen storage property was studied for La-Mg-Ni-based alloys using synchrotron XRD measurements.

$La_{0.8}Mg_{0.2}Ni_{3.4-x}Co_{0.3}(MnAl)_x$ ($0 \leq x \leq 0.4$) alloys were prepared by induction melting. The XRD samples were prepared by sealing the alloy powder with an average particle size of about 20 μm into Lindeman glass capillary with an inner diameter of 0.3 μm. Synchrotron XRD measurements were carried out using a large-diameter Debye-Scherrer camera with an imaging plate at beamline **BL19B2** (wavelength 0.7 Å).

Five kinds of stacking-structured phases, rhombohedral Gd_2Co_7-type (hereinafter 2:7R), hexagonal Ce_2Ni_7-type (2:7H), hexagonal Pr_5Co_{19}-type (5:19H), rhombohedral Ce_5Co_{19}-type (5:19R), and rhombohedral La_5MgNi_{24}-type (1:4R) phases were identified from the XRD patterns. There were also peaks assignable to $CaCu_5$-type phase (AB_5 phase) and C15*b*-$AuBe_5$-type phase (AB_2 phase). Figure 1(a) shows projections onto the (1 -2 0) plane of 5:19H phase. The 5:19 phase was confirmed also by HRTEM observation (Fig. 1(b)).

By means of Rietveld analysis (software: RIETAN-2000 [4]), the abundances of each phase were determined, and the site occupancy and lattice parameters of the phases were refined. Figure 2 shows the Rietveld refinement pattern with synchrotron XRD pattern for $La_{0.8}Mg_{0.2}Ni_{3.25}Co_{0.3}(MnAl)_{0.15}$ alloy, and Fig. 3 shows the relationship between Mn and Al amounts and phase abundance in the $La_{0.8}Mg_{0.2}Ni_{3.4-x}Co_{0.3}(MnAl)_x$ alloys. With the increase in Mn and Al amounts from $x = 0$ to $x = 0.2$, the mass fraction of 2:7H phase decreased, and those of 5:19R, 5:19H, and 1:4R phases increased. For the alloys with $x = 0.15$ and 0.2, 5:19H and 1:4R phases were dominant, respectively. Further substitution to $x > 0.2$ decreased the mass fraction of the stacking-structured phases and increased those of the AB_5 and AB_2 phases. The alloy with $x = 0.4$ contained no stacking-structured phases. In 5:19H and 1:4R phases, Mg occupies the

La sites of A_2B_4 units, and Al occupies the Ni sites between AB_5 units or those between A_2B_4 and AB_5 units (Fig. 1). The stabilization of these phases at a narrow composition range could be related to the preferential occupation of Mg and Al in particular sites.

Hydrogen absorption-desorption characteristics were evaluated by measuring pressure-composition-temperature (P-C-T) curves using a Sievert type apparatus at 80 °C. The hydrogen storage capacity of the alloys with x = 0-0.2 was 1.3 wt.%, which was 1.2 times as high as those of the conventional alloys. The alloy with x = 0.4 showed a lower capacity of 1.1 wt.%. Results of the Rietveld analysis and P-C-T measurements suggest that the capacity decreased with the increasing mass fraction of AB_5 phase, and that stacking-structured phases have a larger capacity than AB_5 phase.

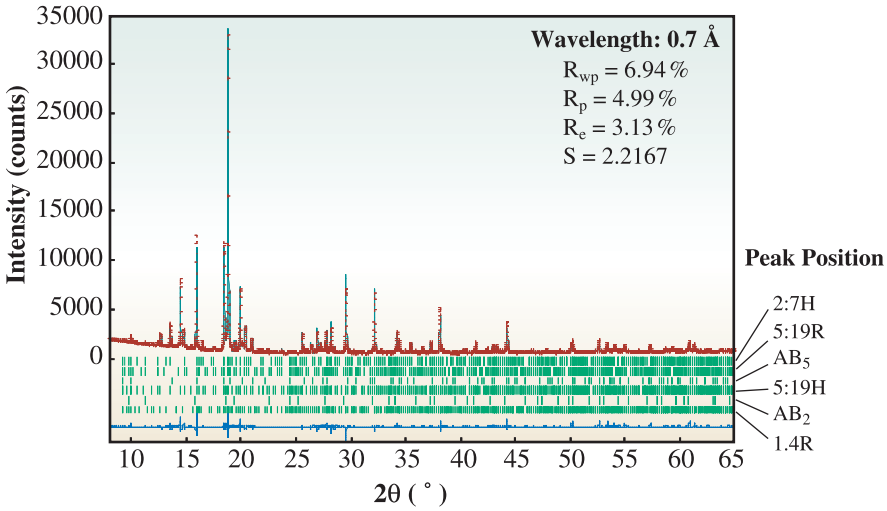

Fig. 2. Rietveld refinement pattern with synchrotron XRD pattern for $La_{0.8}Mg_{0.2}Ni_{3.25}$ $Co_{0.3}(MnAl)_{0.15}$ alloy.

Synchrotron X-ray diffraction measurements and Rietveld analysis elucidated the effect of the partial substitution of Ni with Mn and Al on the crystal structure and hydrogen storage capacity of the La-Mg-Ni-based alloys. This suggests that it is possible to develop a promising electrode alloy with superior discharge capacity and cycle life by further optimizing the alloy composition together with crystal structure analysis.

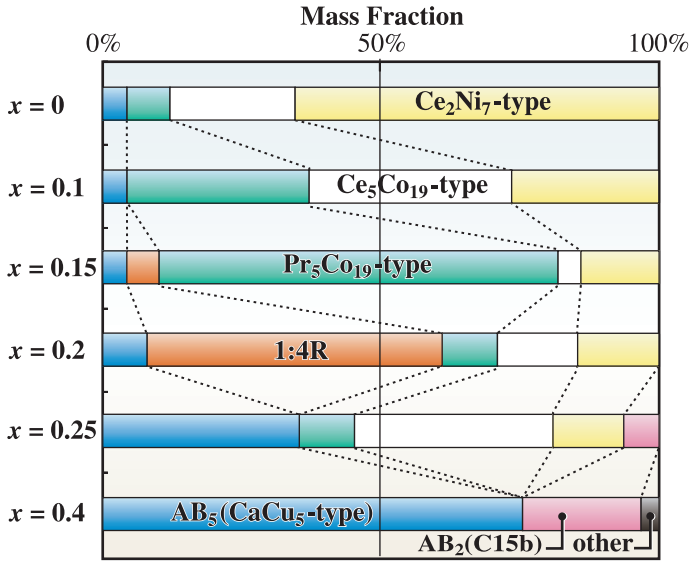

Fig. 3. Phase abundance of $La_{0.8}Mg_{0.2}$ $Ni_{3.4-x}$ $Co_{0.3}(MnAl)_x$ ($0 \le x \le 0.4$) alloys obtained by Rietveld refinement.

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References

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