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 MnNi5-based (Mn: mischmetal) alloys. In 1997, Kadir and Sakai et al. reported on REMg2Ni9 (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 AB5 units (CaCu5-type structure) and A2B4 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. 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.

La0.8Mg0.2Ni3.4-xCo0.3(MnAl)x (0 ≤ x ≤ 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 Gd2Co7-type (hereinafter 2:7R), hexagonal Ce2Ni7-type (2:7H), hexagonal Pr5Co19-type (5:19H), rhombohedral Ce5Co19-type (5:19R), and rhombohedral La5MgNi24-type (1:4R) phases were identified from the XRD patterns. There were also peaks assignable to CaCu5-type phase (AB5 phase) and C15b-AuBe5-type phase (AB2 phase). Figure 1(a) shows projections onto the (1 -2 0) plane of 5:19H phase. The 5:19H 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 La0.8Mg0.2Ni3.4-xCo0.3(MnAl)0.15 alloy, and Fig. 3 shows the relationship between Mn and Al amounts and phase abundance in the La0.8Mg0.2Ni3.4-xCo0.3(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 AB5 and AB2 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.

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.

Masaharu Watada* and Tetsuya Ozaki
GS Yuasa Corporation
*E-mail: masaharu.watada@jp.gs-yuasa.com

References