Substitution Effect of Rare Earth on Hydrogenation for AB₅-Type Alloys

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Substitution effects of rare earth elements for hydrogenation of Mn₅Ni₅Co₀.75Al₀.30Mn₀.40 AB₅-type alloys were investigated, where Mn consisted of La-Pr-Nd-M (M: Ce, Y, Gd, Tm and Lu), and the amount of La and M was adjusted to keep the lattice volume identical which leads to a similar equilibrium hydrogen pressure. The above alloys showed two-phase reaction during hydrogenation, and both the phases had the orthorhombic lattice with a space group of Cmcm after activation. The Ce containing alloy showed a higher equilibrium hydrogen pressure (0.12 MPa) than the others (0.07–0.10 MPa) at 298 K. In addition, this alloy showed the largest lattice volume expansion among the alloys investigated. However, lattice strain of the hydride phases calculated from line broadening in X-ray diffraction peaks showed to be less than 0.9% for all the alloys investigated. [doi:10.2320/matertrans.47.1914]

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1. Introduction

The AB₅-type alloys have been improved for the application to Ni-Hydrogen batteries. The B site in AB₅-type alloys consists of Ni as a major component and Co, Al, Mn and so on. This composition has been optimized to realize significant rechargeable capacity, cycle life and rate capability at room temperature. The A site in AB₅ consists of several light rare earth elements such as Ce, La, Nd, and Pr. The mixture of rare earth elements is called misch metal. One of the reasons why misch metal is used is that the cost of metals are reasonable because expensive separation processes are not needed.

Hydrogen storage alloy shows pulverization characteristics during hydrogenation. These characteristics increase the surface area of the alloy in contact with alkali solution. As a result of contact, rare earth, aluminum and manganese hydroxides formed as corrosion layers on the surface decrease the effective capacity. This pulverization characteristic has been researched from viewpoint of change of crystal structure, lattice volume expansion of hydride and introduce of lattice strain. Especially, LaNi₅ shows 25% volume expansion during hydrogenation, and a large lattice strain was introduced in initial activation process. In order to restrain these lattice volume expansion and lattice strain, the substitution of other elements for Ni in the B site has been carried out. For example, Co substitution restrains expansion of lattice volume, and Al or Sn substituted alloys restrain introduction of lattice defect.

In this paper, we focus attention on the A site rare earth elements that consist of Mm. We investigated the substitution effects of rare earths to expansion of lattice volume and lattice strain obtained from refined profile parameters following a method reported in Refs. 5, 6). A Pseudo-Voigt function containing a Gaussian function and a Lorentzian function was used for expressing peak profiles. Lattice strain was obtained from refined profile parameters following a method reported in Refs. 5, 6). Isotropic strain was calculated as a sum from the corresponding Gaussian parameter and Lorentzian parameter.

2. Experimental

2.1 Preparation of alloys

AB₅-type stoichiometric Mn₅Ni₅Co₀.75Al₀.30Mn₀.40 (Mm: misch metal) alloys were purchased from Santoku Metal Industry Co., Ltd. The composition of B element was the same as that used for the conventional Ni-MH battery. The element consisted of La-Pr-Nd and the 4th rare earth elements. In this work, Ce, Y, Gd, Tm or Lu were selected for the 4th rare earth elements that were partly substituted for La. These elements usually show 3+ valences in their oxides for La, Pr, Nd, whereas the Ce element shows 4+ valences in CeO₂. The amount of substitution was adjusted to make the unit cell volume of the alloys same because there is a linear relationship between the lattice volume and the hydrogen equilibrium pressure in AB₅-type alloys. The chemical composition of the alloys studied is shown in Table 1. These ingots were crushed into powder under 32 μm and was used for the X-ray powder diffraction (XRD) measurements.

2.2 XRD measurements and peak profile analysis

X-ray powder diffraction profiles were measured using a diffractometer (Rigaku RINT2500V) with CuKα radiation. In in-situ XRD measurement, powder sample was filled into a stainless steel holder and covered with a beryllium plate with 0.1 mm thick. The sample was set up in the high-pressure chamber, and activated by 5 hydrogenation-dehydrogenation cycles at 298 K. Diffraction profiles were collected in the 2θ range between 15 and 85 degree at a power of 50 kV and 200 mA.

The diffraction profiles were analyzed by Rietveld refinement program RIETAN-2000. A Pseudo-Voigt function containing a Gaussian function and a Lorentzian function was used for expressing peak profiles. Lattice strain was obtained from refined profile parameters following a method reported in Refs. 5, 6). Isotropic strain was calculated as a sum from the corresponding Gaussian parameter and Lorentzian parameter.

3. Results and Discussion

3.1 XRD and P-C isotherm measurement

Mn₅Ni₅Co₀.75Al₀.30Mn₀.40 alloys (chemical composition is shown in Table 1) studied were activated by 5 hydrogenation-dehydrogenation cycles in stainless steel vessel at 298 K. Then, the activated alloys were taken out in air, and
their XRD profiles were examined to analyze crystal structure and lattice volume respectively. Figure 1 shows XRD profiles of all the alloys studied in the present work. As results of Rietveld analysis, crystal structure of all the alloys studied was orthorhombic with a space group of $\text{Cmmm}$, and lattice volume of these alloys was almost the same value, being in between 0.175 and 0.177 nm$^3$ within the scope of our material design. P-C isotherm results of these alloys are shown in Fig. 2. All the alloys studied showed almost the same reversible hydrogen amount and a little hysteresis, but it should be pointed out that the Ce containing alloy showed higher equilibrium hydrogen pressure than other alloys.

### Table 1  The chemical composition of the MmNi$_{1.55}$Co$_{0.75}$Al$_{0.30}$Mn$_{0.40}$ alloys.

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>M</th>
<th>Pr</th>
<th>Nd</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mm (Ce)</td>
<td>0.34</td>
<td>0.47</td>
<td>0.05</td>
<td>0.14</td>
<td>La$<em>{0.34}$Ce$</em>{0.47}$Pd$<em>{0.09}$Nd$</em>{0.14}$Ni$<em>{1.35}$Co$</em>{0.75}$Al$<em>{0.30}$Mn$</em>{0.40}$</td>
</tr>
<tr>
<td>Mm (Y)</td>
<td>0.41</td>
<td>0.40</td>
<td>0.05</td>
<td>0.14</td>
<td>La$<em>{0.41}$Y$</em>{0.40}$Pd$<em>{0.09}$Nd$</em>{0.14}$Ni$<em>{1.35}$Co$</em>{0.75}$Al$<em>{0.30}$Mn$</em>{0.40}$</td>
</tr>
<tr>
<td>Mm (Gd)</td>
<td>0.56</td>
<td>0.25</td>
<td>0.05</td>
<td>0.14</td>
<td>La$<em>{0.56}$Gd$</em>{0.25}$Pd$<em>{0.09}$Nd$</em>{0.14}$Ni$<em>{1.35}$Co$</em>{0.75}$Al$<em>{0.30}$Mn$</em>{0.40}$</td>
</tr>
<tr>
<td>Mm (Tm)</td>
<td>0.61</td>
<td>0.20</td>
<td>0.05</td>
<td>0.14</td>
<td>La$<em>{0.61}$Tm$</em>{0.20}$Pd$<em>{0.09}$Nd$</em>{0.14}$Ni$<em>{1.35}$Co$</em>{0.75}$Al$<em>{0.30}$Mn$</em>{0.40}$</td>
</tr>
<tr>
<td>Mm (Lu)</td>
<td>0.65</td>
<td>0.16</td>
<td>0.05</td>
<td>0.14</td>
<td>La$<em>{0.65}$Lu$</em>{0.16}$Pd$<em>{0.09}$Nd$</em>{0.14}$Ni$<em>{1.35}$Co$</em>{0.75}$Al$<em>{0.30}$Mn$</em>{0.40}$</td>
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![Fig. 1 XRD patterns of MmNi$_{1.55}$Co$_{0.75}$Al$_{0.30}$Mn$_{0.40}$ alloys after activation at 298 K.](image)

![Fig. 2 PCT curves of (La-Pr-M)Ni$_{1.55}$Co$_{0.75}$Al$_{0.30}$Mn$_{0.40}$ at 298 K. M: Ce(\(\circ\)), Y(\(\bullet\)), Gd(\(\triangle\)), Tm(\(\triangledown\)) and Lu(\(\square\)).](image)

### 3.2 Change of lattice volume by in-situ XRD measurement

In-situ X-ray diffraction measurements were carried out to pursue the change of crystal structure during hydrogenation-dehydrogenation. All the alloys studied showed two-phase reaction between solid solution phase and hydride phase. Both the phases have the orthorhombic lattice with a space group of $\text{Cmmm}$ refined by Rietveld analysis of XRD. Then we deduced lattice volume ratio between two phases, which is related to pulverization and corrosion in alkali solution when we assume adopt for Ni-MH battery. All the alloys studied were hydrided up to $H/M = 0.4$ (alloy composition is MmNi$_{1.55}$Co$_{0.75}$Al$_{0.30}$Mn$_{0.40}$H$_{2.40}$) in in-situ cell, and we measured the XRD profiles through beryllium window. The hydrogen content of $H/M = 0.4$ is the middle point of plateau region. Therefore both the phases contain almost the same mass ratio at this point, and we can analyze both the phases equally. The results of Rietveld analysis of the XRD profile containing Ce or Lu are shown in Figs. 3(a) and (b). Lattice parameters obtained were $a = 0.8685$ nm, $b = 0.5038$ nm, $c = 0.4072$ nm for solid solution phase, and $a = 0.9014$ nm, $b = 0.5270$ nm, $c = 0.4157$ nm for hydride phase of the Ce containing alloy. Structural parameters obtained gave a reliability $R_{wp} = 7.32$, $S = 1.92$ for the structural model ($\text{Cmmm}$). On the other hand, Lu containing alloy showed $a = 0.8863$ nm, $b = 0.5076$ nm, $c = 0.4063$ nm for solid solution phase, and $a = 0.8919$ nm, $b = 0.5181$ nm, $c = 0.4092$ nm for hydride phase. Structural parameters obtained gave a reliability $R_{wp} = 7.53$, $S = 2.01$ for the structural model ($\text{Cmmm}$). The volumetric ratio of the
compositions in AB volumetric ratio of two-phases is affected to the B-side for the Lu containing alloy. In general, we can assume that parameters was 10.8% for the Ce containing alloy, and 3.4% hydride phase to solid solution phase calculated by these parameters was 10.8% for the Ce containing alloy, and 3.4% for the Lu containing alloy. In general, we can assume that volumetric ratio of two-phases is affected to the B-side compositions in AB-type alloy. Our results indicate that the rare earth composition of A site also effects volumetric expansion. The values of volumetric expansion for the alloys containing other rare earths are shown in Fig. 4 (the value for

LaNi$_5$ is reported in Ref. 1). Some significant difference between 3–11% volumetric expansion ratios was observed at H/M = 0.4. Especially, the Ce containing alloy showed the largest volumetric expansion value of 11%. It seems to have a tendency that the alloys containing heavy rare earth showed smaller volumetric ratio than the alloys containing light rare earth.

3.3 Change of lattice strain by in-situ XRD measurement

An anisotropic strain was not observed in all the alloys studied during hydrogenation. We calculated isotropic strain by Rietveld analysis of diffraction profiles. For the solid solution phase, line broadening was observed clearly as hydrogenation going on up to H/M = 0.55. On the other hand for the hydride phase, large line broadening was observed in plateau area. Then after plateau (H/M = ~0.9), diffraction line became sharper. Therefore, isotropic strain of both phases showed maximum value at the middle point of plateau.

Isotropic strain of both the phases is shown in Fig. 5. Though Ce or Y containing alloy showed the largest value compared to the other alloys, these value was only 0.9%. MmNi$_{3.55}$Al$_{0.30}$Mn$_{0.40}$ that was partly substituted by Al and Mn for Ni showed 0.4–0.5% of isotropic strain, while the LaNi$_5$ hydride phase showed 2.5% of isotropic strain at the plateau area reported in Ref. 1. Therefore we can assume that lattice strain is mainly related to the B-side composition in AB$_3$-type alloy. In our study, major difference was not observed in the rare earth composition of A site.

4. Conclusion

We investigated substitution effects of the constituting rare earth elements of AB$_3$-type MmNi$_{3.55}$Co$_{0.75}$Al$_{0.30}$Mn$_{0.40}$ alloys on hydrogenation.

The Ce containing alloy showed a higher equilibrium hydrogen pressure than the other alloys studied in spite of showing almost the same lattice volume. This alloy showed largest lattice expansion of 11% (Others showed 3–8%). The lattice strain was observed to be less than 0.9% for all the alloys studied.
REFERENCES