Hydrogen-Storage Properties and Structure Characterization of Melt-Spun and Annealed Mg–Ni–Nd Alloy*1

Jingtian Yin*2,1, Kazuhide Tanaka*3,1 and Nobuo Tanaka2

1Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan
2Department of Applied Physics, Nagoya University, Nagoya 464-0814, Japan

The hydriding/dehydriding characteristics of a Mg-rich Mg–Ni–Nd alloy produced by melt-spinning and subsequent annealing have been investigated. This alloy absorbs \( \sim 4.7\) mass\% hydrogen \((H/M \sim 1.5)\) quickly between 423 and 573 K and wholly desorbs it at moderate speeds above 453 K. Transmission electron microscope observations and selected-area electron diffraction analyses of this alloy before and after hydriding demonstrate that it consists of multiple phases of Mg-Ni and Nd-hydride precipitated uniformly in a nano-structured Mg matrix. The fast reaction kinetics is caused by an interplay between a catalytic action of the Nd-hydrides and the surrounding nano-sized Mg grains which quickly store or evolve hydrogen across the interfaces.

(Received October 18, 2001; Accepted November 22, 2001)

Keywords: hydrogen storage, magnesium-nickel-neodymium alloy, melt-spinning, nanocomposite structure, hydriding/dehydriding kinetics, catalyst, high-resolution transmission electron microscopy

1. Introduction

The poor hydriding-dehydriding \((H/D)\) kinetics of Mg-based alloys is generally attributed to the poor dissociation ability of metallic Mg for hydrogen molecules and also to the formation of surface hydrides which hinder the further transport of hydrogen into the matrix.1–3) The addition of a catalyst appears to be a simple and effective method to overcome these problems. In our previous works, we have shown that certain Mg-rich Mg–Ni–RE and Mg–Pd–RE alloys \((\text{RE: rare earth})\) exhibit high H-capacities and excellent kinetics,4–7) where a rare-earth element such as La and Nd is considered to act as an efficient catalyst for dissociating \(H_2\) molecules and transferring the H atoms to the surrounding Mg matrix. In addition, reducing the grains of the matrix is thought to be another efficient way to improve the reaction kinetics because it may enhance the inward transport of H atoms along the grain boundaries and thereby reduce the depth of the hydride layer. The effectiveness of refining the microstructures for improving the reaction kinetics has really been proved for Mg-based alloys fabricated by mechanical alloying5–8,9) and melt-spinning.5,10)

The objective of the present study is firstly to examine the hydrogen-storage characteristics of a Mg-rich Mg–Ni alloy added with a small amount of Nd and subjected to melt-spinning and annealing, and secondly to characterize its microstructure by high-resolution transmission electron microscopy \((\text{HRTEM})\) and electron diffraction \((\text{ED})\) for discussing a possible \(H/D\) mechanism in the alloy.

An alloy with composition \(\text{Mg}_{86}\text{Ni}_{10}\text{Nd}_4\) was prepared in the same way as described previously.5,6) Amorphous ribbons \((\sim 20\,\mu\text{m} \text{ thick and } \sim 1\,\text{mm wide})\) were fabricated from this alloy by melt-spinning using a single copper roll, and they were crystallized by annealing at 553 K in vacuum. After being pulverized into powder of 70 mesh \((<210\,\mu\text{m})\), they were subjected to ten hydriding \((\text{for } 15\,\text{ks under } 3\,\text{MPa } H_2)\) and dehydriding \((\text{for } 10\,\text{ks in vacuum})\) cycles at 573 K to achieve full activation and stabilization. The kinetics of the \(H/D\) process was measured with a volumetric method using a Sieverts-type apparatus. Structure observation and phase analysis were employed with HRTEM and ED techniques using a 200 keV microscope \((\text{JEOL:JEM-2010})\) for as-prepared \((\text{before activation})\), \(H\)-charged \((\text{after first hydriding to saturation at } 573\,\text{K})\) and \(H\)-discharged \((\text{after dehydriding at } 573\,\text{K for } 11\,\text{ks})\) powder specimens.

Figure 1(a) shows the hydriding behavior of the as-prepared sample \((\text{melt-spun and crystallized state})\) in the initial activation process at 573 K, where we find that after only one \(H/D\) cycle the alloy manifests an excellent reactivity with hydrogen, providing much faster kinetics compared with that of a binary Mg–Ni alloy without Nd.5) After the second \(H/D\) cycle, the sample reaches a maximum hydriding rate and it is stably kept in the later cycles. The temperature dependence of the hydriding behavior of the completely activated and stabilized sample \((\text{after subjecting to ten } H/D\text{ cycles at } 573\,\text{K})\) is shown in Fig. 1(b). As is evident from the figure, this alloy exhibits remarkably enhanced hydriding kinetics above 423 K absorbing 3.5–4.5 mass\%\(H\) within 1 ks. The absorption rate increases with increasing temperature reaching the maximum rate at 523–573 K. In addition, this alloy exhibits substantially rapid desorption kinetics above 453 K, as shown in Fig. 1(c), although the desorption rate is much suppressed below 423 K. Approximately 80% of the maximum capacity of hydrogen can be desorbed within 15 ks at 453 K, 2 ks at 473 K and 1 ks at 523 K in vacuum.

HRTEM images and the corresponding ED pattern of as-prepared specimen are shown in Figs. 2(a)–(d). In Fig. 2(a), we can observe three different phases coexisting in the visual area: a bright matrix, spherical small particles which are homogeneously embedded in the bright matrix, and a much larger dark phase at the left bottom. Figure 2(c) shows the morphology of the spherical particles with a size of 20–30 nm and very fine grains with a size of 2–5 nm constitut-
Fig. 1 Activation behavior of the Mg–Ni–Nd alloy for the first 7 cycles at 573 K; (b) hydriding of the fully activated and stabilized sample at 523–573 K; (c) dehydriding of the fully activated and stabilized sample at 423–523 K.

Fig. 2 HRTEM images (a), (c), (d) and ED pattern (b) of the as-prepared specimen.

The morphology of the dark phase with ∼ 1 µm in size is shown in Fig. 2(d). Figure 2(b) displays the ED pattern from the whole visual area. Analysis of this diffraction pattern reveals that the as-prepared sample comprises of Mg, Mg₁₂Nd and Mg₂Ni mixed phases, in accordance with our earlier result based on X-ray diffraction.⁵, ⁶) Selected-area electron diffraction (SAED) analyses for the three kinds of phases indicate that the bright matrix consists of nano-sized Mg grains which give rise to continuous diffraction rings, while the spherical particles represent Mg₁₂Nd compound which causes diffraction spots, and the large dark region corresponds to Mg₂Ni giving a smaller number of diffraction spots.

The HRTEM images of the H-charged specimen are illustrated in Figs. 3(a) and (c), where fine spherical particles with a size of about 20–50 nm dispersed uniformly in a bright matrix containing finer grains (approximately 2–8 nm in size) are revealed, together with a coarse dark phase (> 100 nm) visible in certain regions. From the ED pattern shown in Fig. 3(b), coupled with SAED analyses, the matrix and the spherical particles were identified as MgH₂ and Nd₂H₅, respectively. The coarse dark phase was confirmed as Mg₂NiH₄. Thus the present HRTEM investigation reveals that the Mg₁₂Nd phase in the as-prepared sample disproportionated into MgH₂ and Nd₂H₅ after the hydriding, whereas the Mg and Mg₂Ni phases transformed into MgH₂ and Mg₂NiH₄, respectively.

Figures 4(a)–(c) show HRTEM images and the corresponding ED pattern of the H-discharged specimen. Although the discharged specimen exhibits a similar morphology to the as-prepared and H-charged ones, the phase conversion has practically occurred upon dehydriding. The ED pattern reveals that Mg and Mg₂Ni have been recovered from their own hydride phases but the Nd₂H₅ phase remains unchanged after dehydriding. It has been confirmed that Mg, Nd₂H₅ and Mg₂Ni phases are present as the matrix (2–5 nm in grain size), spherical particles (20–50 nm) and larger particles (> 100 nm), respectively, in the discharged specimen.

A summary of the characteristics of the ED patterns is given in Table 1, where the interplanar spacing d and the feature of the diffraction pattern are specified for all the existing phases in the specimens.

We have shown that the Mg₈₆Ni₁₀Nd₄ alloy produced by melt-spinning and subsequent annealing is readily activated in hydrogen atmosphere and can stably absorb and desorb more than 4.5 mass%H in moderate speeds above 453 K. These excellent hydrogen-storage properties of the alloy are strongly related with a nano-sized multiphase structure of the alloy. In the following, we interpret the H/D processes of this alloy on the basis of the HRTEM and ED results shown above.

The amorphous phase formed by melt-spinning simultaneously decomposes into Mg, Mg₁₂Nd and Mg₂Ni phases upon crystallization. The two compound phases are embedded in a Mg matrix composed of very fine grains of 2–5 nm. In the first activation process, most of the Mg₁₂Nd phase decomposes via a irreversible disproportionation reaction:

\[
4\text{Mg}_{12}\text{Nd} + 53\text{H}_2 \Rightarrow 48\text{MgH}_2 + 2\text{Nd}_2\text{H}_5 \quad (1)
\]

Pressure-composition isotherms (PCTs) for Mg–Ni–Nd al-
Table 1 Characteristics of the ED patterns for the as-prepared, H-charged and H-discharged specimens.

<table>
<thead>
<tr>
<th>d-spacing/0.1 nm</th>
<th>Phase (hkl)</th>
<th>Character</th>
<th>d-spacing/0.1 nm</th>
<th>Phase (hkl)</th>
<th>Character</th>
<th>d-spacing/0.1 nm</th>
<th>Phase (hkl)</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.62</td>
<td>Mg₁₂Nd (211)</td>
<td>S</td>
<td>3.13</td>
<td>Nd₂H₅ (112)</td>
<td>S</td>
<td>3.13</td>
<td>Nd₂H₅ (112)</td>
<td>S</td>
</tr>
<tr>
<td>2.97</td>
<td>Mg₁₂Nd (301)</td>
<td>S</td>
<td>2.72</td>
<td>Nd₂H₅ (004)</td>
<td>S</td>
<td>2.72</td>
<td>Nd₂H₅ (004)</td>
<td>S</td>
</tr>
<tr>
<td>2.60</td>
<td>Mg (002)</td>
<td>R</td>
<td>2.51</td>
<td>MgH₂ (101)</td>
<td>R</td>
<td>2.45</td>
<td>Mg (101)</td>
<td>R</td>
</tr>
<tr>
<td>2.56</td>
<td>Mg₁₂Nd (202)</td>
<td>S</td>
<td>2.51</td>
<td>MgH₂ (101)</td>
<td>R</td>
<td>2.45</td>
<td>Mg (101)</td>
<td>R</td>
</tr>
<tr>
<td>2.45</td>
<td>Mg (101)</td>
<td>R</td>
<td>2.26</td>
<td>MgH₂ (020)</td>
<td>XR</td>
<td>2.25</td>
<td>Mg₂Ni (200)</td>
<td>S</td>
</tr>
<tr>
<td>2.25</td>
<td>Mg₂Ni (200)</td>
<td>S</td>
<td>2.25</td>
<td>Mg₂NiH₄ (220)</td>
<td>S</td>
<td>2.25</td>
<td>Mg₂Ni (200)</td>
<td>S</td>
</tr>
<tr>
<td>2.01</td>
<td>Mg₂Ni (203)</td>
<td>S</td>
<td>1.95</td>
<td>Mg₂NiH₄ (116)</td>
<td>S</td>
<td>2.01</td>
<td>Mg₂Ni (203)</td>
<td>S</td>
</tr>
<tr>
<td>1.90</td>
<td>Mg (102)</td>
<td>XR</td>
<td>1.68</td>
<td>MgH₂ (211)</td>
<td>R</td>
<td>1.68</td>
<td>MgH₂ (211)</td>
<td>R</td>
</tr>
<tr>
<td>1.49</td>
<td>Mg₁₂Nd (631)</td>
<td>S</td>
<td>1.51</td>
<td>MgH₂ (220)</td>
<td>R</td>
<td>1.51</td>
<td>MgH₂ (220)</td>
<td>R</td>
</tr>
<tr>
<td>1.36</td>
<td>Mg (112)</td>
<td>R</td>
<td>1.43</td>
<td>MgH₂ (310)</td>
<td>R</td>
<td>1.43</td>
<td>MgH₂ (310)</td>
<td>R</td>
</tr>
<tr>
<td>1.29</td>
<td>Mg₁₂Nd (613)</td>
<td>S</td>
<td>1.16</td>
<td>MgH₂ (321)</td>
<td>R</td>
<td>1.16</td>
<td>MgH₂ (321)</td>
<td>R</td>
</tr>
<tr>
<td>1.17</td>
<td>Mg (104)</td>
<td>R</td>
<td>1.16</td>
<td>MgH₂ (321)</td>
<td>R</td>
<td>1.17</td>
<td>Mg (104)</td>
<td>R</td>
</tr>
</tbody>
</table>

Key: S-spot; R-ring; XR-strong ring

Fig. 3 HRTEM images (a), (c) and ED pattern (b) of the H-charged specimen.

Fig. 4 HRTEM images (a), (c) and ED pattern (b) of the H-discharged specimen.

loy5–6) indicate that in the hydriding process the reaction (2) precedes (3) owing to a lower equilibrium pressure for the former than the latter, and vice versa in the dehydriding process.

In parallel with the above H/D reactions, the Nd hydride with a particle size of 20–50 nm may also undergo a reversible re-
Fig. 5 Catalytic processes of a Nd$_2$H$_5$ particle for dissociating or recombining H$_2$ molecules at the surface, and for evolving or absorbing H atoms at the interface with Mg nanograins.

action:

$$2\text{Nd}_2\text{H}_5 + \text{H}_2 \leftrightarrow 4\text{NdH}_3$$  \hspace{1cm} (4)

This reaction appears to be important to bestow a catalytic activity to the Nd hydride.\(^7\) Since NdH$_3$ is less stable than Nd$_2$H$_5$, the former can readily decompose to the latter by evolving hydrogen and transmitting it, as a gateway, either to the surrounding Mg nanograins in the hydriding process, or to the surrounding hydrogen atmosphere in the dehydriding process, as schematically illustrated in Fig. 5. Here, the Nd hydride formed near the surface of a grain of the powder also behaves as an efficient catalyst for dissociating or recombining the H$_2$ molecules. In addition, the role of nano-sized grain structure of the Mg matrix is quite important to enhance the H/D kinetics, where hydrogen atoms can readily be transported inward or outward by diffusion along the grain boundaries existing in high density.

Acknowledgements

This work is partly supported by the Grant-in-Aid for Scientific Research on Priority Area A of ‘New Protium Function’ from The Ministry of Education, Science, Sports and Culture of Japan. The financial support from NEDO is also acknowledged.

REFERENCES