Hydrogen Storage Properties and Phase Structures of Mg-Rich Mg–Pd, Mg–Nd and Mg–Pd–Nd Alloys

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The hydriding/dehydriding (H/D) rates and pressure-composition isotherms (PCTs) of Mg–Pd, Mg–Nd and Mg–Pd–Nd alloys with \( \mathrm{Mg} \) have been measured, and the characteristics of these hydrogen-storage properties have been discussed in relation with the phase structures and microstructures of the alloys studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). All these alloys exhibit a hydrogen absorbency of \( \approx 5 \) mass\% at 573 K. The PCTs of the alloys containing Pd exhibit three plateau-like regions. A complementary examination of the phase structures, microstructures and PCT characteristics at 523–623 K shows that the H/D kinetics is strongly influenced by the following three factors: (1) A catalytic effect of \( \text{NdH}_{2.5} \) and \( \text{NdH}_3 \) which assist hydriding and dehydriding of Mg matrix; (2) the disproportionation reaction of MgPd to form MgPd\( \text{H}_2 \) and MgH\( \text{H}_2 \), which retards the overall reaction kinetics; and (3) the refinement of the microstructure which enhances the kinetics of all the H/D reactions. A melt-spun and crystallized Mg–Pd–Nd alloy which shows a fine-grained (\( \approx 1 \) \( \mu \)m) microstructure exhibits the best H/D kinetics, especially the desorption kinetics, among the three alloys investigated, and it can be a promising candidate for an efficient hydrogen storage material in the future. The formation of Mg\( \text{PdH}_2 \) at 573 K hydride is suggested from the PCTs of the alloys containing Pd, although it has not been evidenced by XRD and SEM.

(Received June 11, 2001; Accepted September 12, 2001)

Keywords: magnesium-palladium-neodymium system, multi-phase structure, melt-spinning, hydriding/dehydriding kinetics, pressure-composition isotherm, catalytic effect, disproportionation reaction, X-ray diffraction

1. Introduction

Nowadays, in the progress of utilization technology of hydrogen energy, the advent of new hydrogen storage alloys with much higher efficiency than conventional ones, e.g., \( \text{LaNi}_5 \), \( \text{FeTi} \), \( \text{Mg}_2\text{Ni} \), \( \text{TiCrMn} \) etc., is highly desired. The high efficiency generally means that hydrogen gas can readily be stored in an alloy and desorbed out of it to an amount exceeding \( \approx 5 \) mass\% at ambient temperatures. A long cycle life (or stability) of the alloy against the hydriding/dehydriding process is another important factor that determines its efficiency. Much effort has been made to date to develop materials that conform to the above requirements, but to our knowledge none have yet overcome the barriers.

Now, we have recently studied the hydrogen storage characteristics of Mg–Ni alloys in the Mg-rich region added with a small amount of RE (rare earth; La or Nd),1–3) and found that certain ternary alloys with optimized compositions can readily absorb and desorb \( \approx 5 \) mass\% \( \text{H}_2 \) at temperatures around 573 K down to 473 K or lower. These alloys consist of multiphase structures involving Mg, \( \text{Mg}_2\text{Ni} \) and minor La- or Nd-hydrde phases. The latter phase, which has been formed via a disproportionation reaction during the initial activation treatment, acts as a catalysis in the following hydriding/dehydriding (H/D) processes and greatly enhances their kinetics. We have also found that the kinetics is improved much further by refining the microstructure of the alloys through amorphization by melt-spinning and subsequent crystallization procedures. On the basis of these studies, we expect that Mg-rich Mg–Ni–RE alloys can be promising candidates for hydrogen storage alloys with high efficiencies.

In contrast to the studies on the Mg–Ni and Mg–Ni–RE systems, those on Mg–Pd and Mg–Pd–RE alloys are very limited although Pd is expected to have an excellent catalytic effect as well as Ni. Only the hydriding feature of Mg\( \text{PdH}_4 \) has been partly studied to date. The hydriding characteristics of a few Mg–RE alloys have also been studied, but no pressure-composition isotherms (PCTs) have been revealed.4,5) The objective of the present study is to investigate the hydrogen storage properties of Mg-rich Mg–Pd, Mg–Nd and Mg–Pd–Nd alloys in the same way as employed for Mg–Ni and Mg–Ni–Nd alloys,1–3) and to clarify the difference in the catalytic effects among Pd, Ni and Nd as well as their intermetallic compounds with Mg. Effects of the difference in the microstructure of the alloys on the H/D kinetics are also studied.

2. Experimental Procedures

Magnesium-based binary and ternary alloys of compositions Mg\( \text{Pd}_{10} \), Mg\( \text{Nd}_{10} \) and Mg\( \text{Pd}_{4}\text{Nd}_{4} \) were prepared for this study. Appropriate amounts of raw materials of 99.9% purity, a net weight of about 10 g for each alloy, were melted together in a sealed steel crucible in pure Ar of 0.4 MPa at 1273 K, shaken for homogenization and dropped into cold water for rapid cooling. This method of sample preparation was found to be suitable especially for Mg-based alloys with high vapor pressures.2,3) Examination of the alloy ingots by electron-probe microanalysis (EPMA) showed that the composition was almost uniform over the ingots without any indication of macrosegregations. Their chemical compositions measured by EPMA were Mg\( \text{Pd}_{11} \), Mg\( \text{Nd}_{10} \) and Mg\( \text{Pd}_{7}\text{Nd}_{4} \), which were quite close to the initially designed ones, proving that this preparation technique is suitable. These samples are denoted as as-cast (AC) alloys. A part of the Mg\( \text{Pd}_{7}\text{Nd}_{4} \) ingot was subjected to melt spinning to produce amorphous-like ribbons, which were then crystallized by annealing at 573 K

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for 47 ks in vacuum. The sample prepared in this way is expected to have much finer microstructure than the corresponding AC sample, and is denoted as melt-spun (MS) alloy.

Both the AC and MS alloys were crushed and ground into 70 mesh (< 210 µm) powders, and hydrided under 3 MPa H₂ at 573 K for 30 ks and dehydrided afterwards in vacuum at the same temperature. This H/D process was repeated ten times for the purpose of initial activation and stabilization. All these alloys were activated after several H/D cycles; Mg₈₀Pd₁₁ and Mg₈₀Nd₁₀ were readily activated after the second cycle, while Mg₈₀Pd₁₁ and Mg₈₀Nd₁₀ were activated only after the fifth cycle. The H/D kinetics and PCTs of the completely activated samples were measured with a volumetric method using a Sieverts-type apparatus. For PCT measurements in the desorption run, an equilibration time of 10–20 ks was necessary at each point, depending on the alloy species and temperature, to attain the equilibrium state of the sample. The alloy phases and microstructures were examined by X-ray diffraction (XRD) measurement with Cu-Kα radiation and Auger scanning-electron microscope (SEM) observation, respectively.

3. Results

3.1 Hydriding/dehydriding kinetics

The H/D kinetics of all these samples has been measured at temperatures between 373–623 K. Hydriding was performed under ~3 MPa and dehydriding in vacuum. Figure 1 displays (a) hydriding and (b) dehydriding behavior of Mg₈₀Pd₁₁, AC-Mg₈₀Pd₁₁, and MS-Mg₈₀Pd₁₁ at 573 K. It can be seen from this figure that the H/D kinetics of Mg₈₀Pd₁₁ is very poor in comparison with AC- and MS-Mg₈₀Pd₁₁, which can absorb and desorb more than 4 mass% H₂ in moderate speeds. The H/D behavior of Mg₈₀Nd₁₀ (not shown) was similar to the latter. It should be noted here that, in the present volumetric method, the hydriding pressure decreases with increasing hydrogen absorption down to 1.5–2 MPa depending on the amount of the sample. Therefore, the true hydrogen absorbency of an alloy should be evaluated from its PCT curve which will be shown in the following subsection.

Figure 2 displays the H/D behaviors of Mg₈₀Pd₁₁ and AC- and MS-Mg₈₀Pd₁₁ at 523 K. At this temperature the H/D rates of Mg₈₀Pd₁₁ are so sluggish that they are not included in the figure. We find that the hydriding rates (a) of these alloys are similar to those at 573 K, but their dehydriding rates (b) are significantly reduced from those at 573 K. Among the four kinds of alloys investigated, the dehydriding rate is fastest for MS-Mg₈₀Pd₁₁ and slowest for Mg₈₀Pd₁₁. At 523 K, MS-Mg₈₀Pd₁₁ reaches 80% of maximum absorption in ~0.3 ks and 80% desorption in ~10 ks. However, these absorption and desorption rates are still much slower than those of Mg₈₀Nd₁₀, which exhibits the corresponding characteristic times of ~0.02 ks for absorption and ~0.2 ks for desorption. It can therefore be stated that the H/D kinetics of a Mg–Pd alloy is considerably improved by Nd addition and MS processing; nevertheless, it is still inferior to that of a ternary Mg–Ni–Nd alloy with a comparable composition.

3.2 Pressure-composition isotherms

Figure 3 shows the PCT curves of Mg₈₀Pd₁₁ at 523–623 K in the desorption run, where three plateau-like regions I–III can be seen with a hydrogen absorbency of Cₓ(max) = 4.8 mass% (H/M = 1.68). The range of hydrogen concen-
Table 1 Hydrogen absorbency \(c_H(\text{max})\) at 573 K, plateau region and its width, and thermodynamic parameters \(\Delta H\) and \(\Delta S^0\) obtained from the PCT characteristics for the alloy samples investigated.

<table>
<thead>
<tr>
<th>Alloy sample</th>
<th>Hydrogen absorbency</th>
<th>Plateau region and width</th>
<th>(\Delta H) /kJ/(mol H(_2))</th>
<th>(\Delta S^0) /J/(K mol H(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(<em>{50})Pd(</em>{11})</td>
<td>(c_H(\text{max}) = 4.8) mass%</td>
<td>I 0 &lt; (c_H) &lt; 1.8 (\Delta c_H \sim 1.8)</td>
<td>-76.7</td>
<td>-135</td>
</tr>
<tr>
<td>H/M(max) = 1.68</td>
<td>0 &lt; H/M &lt; 0.61 (\Delta H/M \sim 0.61)</td>
<td>II 1.8 &lt; (c_H) &lt; 4.0 (\Delta c_H \sim 2.2)</td>
<td>-76.8</td>
<td>-139</td>
</tr>
<tr>
<td></td>
<td>0.61 &lt; H/M &lt; 1.38 (\Delta H/M \sim 0.77)</td>
<td>III 4.0 &lt; (c_H) &lt; 4.8 (\Delta c_H \sim 0.8)</td>
<td>-73.2</td>
<td>-149</td>
</tr>
<tr>
<td></td>
<td>1.38 &lt; H/M &lt; 1.68 (\Delta H/M \sim 0.30)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg(<em>{90})Nd(</em>{10})</td>
<td>(c_H(\text{max}) = 4.8) mass%</td>
<td>I 0 &lt; (c_H) &lt; 4.8 (\Delta c_H \sim 4.8)</td>
<td>-75.7</td>
<td>-131</td>
</tr>
<tr>
<td>H/M(max) = 1.83</td>
<td>0 &lt; H/M &lt; 1.83 (\Delta H/M \sim 1.83)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC-Mg(<em>{90})Pd(</em>{11})Nd(_4)</td>
<td>(c_H(\text{max}) = 5.0) mass%</td>
<td>I 0 &lt; (c_H) &lt; 3.2 (\Delta c_H \sim 3.2)</td>
<td>-77.7</td>
<td>-136</td>
</tr>
<tr>
<td>H/M(max) = 1.83</td>
<td>0 &lt; H/M &lt; 1.15 (\Delta H/M \sim 1.15)</td>
<td>II 3.2 &lt; (c_H) &lt; 4.5 (\Delta c_H \sim 1.3)</td>
<td>-74.7</td>
<td>-135</td>
</tr>
<tr>
<td></td>
<td>1.15 &lt; H/M &lt; 1.64 (\Delta H/M \sim 0.49)</td>
<td>III 4.5 &lt; (c_H) &lt; 5.0 (\Delta c_H \sim 0.5)</td>
<td>-78.6</td>
<td>-157</td>
</tr>
<tr>
<td></td>
<td>1.64 &lt; H/M &lt; 1.83 (\Delta H/M \sim 0.19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MS-Mg(<em>{90})Pd(</em>{11})Nd(_4)</td>
<td>(c_H(\text{max}) = 4.5) mass%</td>
<td>I 0 &lt; (c_H) &lt; 2.8 (\Delta c_H \sim 2.8)</td>
<td>-73.5</td>
<td>-129</td>
</tr>
<tr>
<td>H/M(max) = 1.64</td>
<td>0 &lt; H/M &lt; 1.00 (\Delta H/M \sim 1.00)</td>
<td>II 2.8 &lt; (c_H) &lt; 4.0 (\Delta c_H \sim 1.2)</td>
<td>-76.2</td>
<td>-138</td>
</tr>
<tr>
<td></td>
<td>1.00 &lt; H/M &lt; 1.45 (\Delta H/M \sim 0.45)</td>
<td>III 4.0 &lt; (c_H) &lt; 4.5 (\Delta c_H \sim 0.5)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>1.45 &lt; H/M &lt; 1.64 (\Delta H/M \sim 0.19)</td>
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Fig. 3 PCT characteristics of Mg\(_{50}\)Pd\(_{11}\) at 523–623 K in the desorption run.

As shown in the following subsection, X-ray diffractographs show that Mg\(_{50}\)Pd\(_{11}\) consists of a two-phase structure of Mg + Mg\(_{5}\)Pd before hydriding (desorbed state), which is transformed to MgH\(_2\) + Mg\(_{5}\)Pd\(_2\) after hydriding. As is discussed in the next section, the region I is associated with a reaction

\[
\text{Mg} + \text{H}_2 \leftrightarrow \text{MgH}_2,
\]

while the region II is associated with one involving decomposition of Mg\(_{5}\)Pd and formation of Mg\(_{5}\)Pd\(_2\). The region III might be related to a hydride formation of Mg\(_{5}\)Pd\(_2\). Approximate values of the thermodynamic parameters, \(\Delta H\) and \(\Delta S^0\) associated with the hydriding reactions in these regions obtained from the Van’t Hoff equation are also given in Table 1.

Figure 4 shows the PCT curves of Mg\(_{90}\)Nd\(_{10}\) at 573 and 623 K in the desorption run. The curve consists of a single plateau region with a hydrogen absorbency of \(c_H(\text{max}) = \)
4.8 mass% (H/M = 1.83), although its low concentration region is heavily curved in comparison with that of Mg₈₀Pd₁₁. X-ray diffractographs show that a two-phase structure of Mg + NdH₂.₅ appears before hydriding (desorbed state), and changes to MgH₂ + NdH₂.₅ after hydriding. Therefore, this plateau is mainly associated with reaction (1) in the sample. A hydriding reaction of

\[ 4\text{NdH}_2.5 + \text{H}_2 \leftrightarrow 4\text{NdH}_3 \]  

(2)

may also be involved in the low concentration range, although no plateau-like feature associated with it has been detected in the PCT curve.

Figures 5 and 6 show the PCT curves of AC- and MS-Mg₈₀Pd₁₁Nd₄, respectively, measured at 523–623 K in the desorption run. The PCTs of the two samples at 573 K are quite similar to each other except for a certain difference in the hydrogen absorbency; \( \text{c}_{\text{H}} \text{(max)} = 5.0 \text{mass}\% \) (H/M = 1.83) for AC sample and 4.5 mass% (H/M = 1.64) for MS sample, respectively. The PCT curve of AC sample manifesting three plateau-like regions I–III is also qualitatively similar to that of Mg₈₀Pd₁₁ shown in Fig. 1. X-ray diffractographs of AC and MS samples, which will be shown in the next subsection, commonly show a multiphase structure of Mg + Mg₈₀Pd₁₁ + NdH₂.₅ before hydriding (desorbed state), which changes to MgH₂ + Mg₈₀Pd₁₁ + NdH₂.₅ after hydriding. These phase structures are similar to those observed in Mg₈₀Pd₁₁ except for a minor inclusion of NdH₂.₅, suggesting that the three plateau-like regions in AC- and MS-Mg₈₀Pd₁₁Nd₄ just correspond to those of Mg₈₀Pd₁₁, and are accompanied with the hydriding reactions of the constituent phases mentioned above.

3.3 X-ray diffraction analyses

Figure 7 shows XRD patterns of as-cast, hydrided and dehydrided Mg₈₀Pd₁₁. The H/D treatments have been performed at 573 K. In the as-cast alloy, Mg (A₃, hcp) and Mg₆₆Pd (fcc) coexist in accordance with the equilibrium phase diagram of the system. After hydriding to the saturation, MgH₂ (C₄, tetragonal) and Mg₆₆Pd₂ (D₈₁, hexagonal) are formed, while after dehydriding the original phases of Mg and Mg₆₆Pd reappear. This means that, in the H/D process of this alloy, a reversible disproportionation reaction

\[ 2/7\text{Mg₆₆Pd} + \text{H}_2 \leftrightarrow 1/7\text{Mg₆₆Pd}_2 + \text{MgH}_2 \]  

(3)

has happened, together with a hydriding reaction given by (1).
Figure 8 shows similar XRD results of Mg₉₀Nd₁₀, where Mg₁₂Nd (D₂₅, tetragonal) and Mg₄₁Nd₅ (tetragonal) coexist in the as-cast alloy in agreement with the phase diagram for this system.⁹ Upon hydriding at 573 K, both compounds irreversibly decompose into MgH₂ and NdH₃ (trigonal),¹⁰ which realter to Mg and NdH₂.⁵ (C1, nearly cubic)¹⁰,¹¹ after dehydriding. Therefore, in the H/D cycle of this alloy, both of the reactions (1) and (2) are expected to be involved. It should be noted in this context that we cannot discriminate between NdH₃ and NdH₂.⁵ in the present XRD analysis because of their structural similarity and, furthermore, NdH₃ once formed may be quickly decomposed to the lower hydride NdH₂.⁵ when the sample is taken out of the reaction chamber for XRD measurements.

Figures 9 and 10 show XRD results on AC- and MS-Mg₈₉Pd₇Nd₄. Except for the fact that the MS sample has been crystallized via the amorphous state and hence provides less sharp diffraction peaks, both samples show essentially similar diffractographs before hydriding, after hydriding and after dehydriding. In the as-cast or as-annealed state, the sample is composed of quaternary phases, i.e. Mg, Mg₅Pd, Mg₁₂Nd and Mg₄₁Nd₅. After hydriding, they are transformed into ternary phases, i.e. MgH₂, Mg₅Pd₂ and NdH₃, while after dehydriding, they are altered into ternary derivative phases, i.e. Mg, Mg₅Pd and NdH₂.⁵, although NdH₃ and NdH₂.⁵ cannot be precisely distinguished as stated above. Thus the phase changes associated with the H/D process in the AC and MS samples are expressed in terms of the combined reactions of (1)–(3).

Fig. 8 X-ray diffractograms of as-cast, hydrided and desorbed Mg₉₀Nd₁₀.

Fig. 9 X-ray diffractograms of as-cast, hydrided and desorbed AC-Mg₈₉Pd₇Nd₄.

Fig. 10 X-ray diffractograms of as-melt spun, annealed, hydrided and desorbed MS-Mg₈₉Pd₇Nd₄.
4. Discussion

To begin with, we discuss the PCT characteristics of the three alloys investigated, among which the simplest is that of Mgs9Nd10 (Fig. 4) which manifests only single plateau region. This alloy consists of Mg + NdH2.5 phases before hydriding. Assuming that Mg is totally transformed to MgH2 and NdH2.5 is also transformed to NdH3 by hydriding, a hydrogen absorbency of H/M = 1.85 is expected for this alloy, which is quite close to 1.83 of experiment (see Table 1). The thermodynamic parameters of $\Delta H = -75.7$ kJ/mol H2 and $\Delta S = -130.7$ J/K mol H2 for the plateau are also consistent with $-74.8$ kJ/mol H2 and $-135$ J/K mol H2, respectively, for the reaction (1) of the major Mg phase. The rather wide curved plateau in the early stage of PCT may be caused by unrelaxed disordered regions near grain boundaries in the fine-grained sample.3

In contrast, the PCT of Mg95Pd11 (Fig. 3) exhibits three plateau-like regions. This alloy is composed of Mg + MgPd phases before hydriding, of which we assume only Mg phase is hydrided in the region I according to the reaction (1). A calculated hydrogen absorption in this region is $\Delta H/M = 0.46$, which is comparable with the observed one of 0.61 (Table 1). The $\Delta H$ and $\Delta S$ values of the region I are also consistent with those mentioned above. On the other hand, the Mg50Pd50 phase is assumed to undergo the disproportionation reaction (3) in the region II. A calculated hydrogen absorption of $\Delta H/M = 0.77$ just agrees with the experimental one (Table 1). Now, the plateau in the region III has a much higher equilibrium pressure than the others. Hence, the reaction product is expected to be less stable. We assume that this plateau represents the formation of Mg50Pd50H14 hydride. The observed hydrogen absorption of $\Delta H/M \sim 0.30$ in the region III suggests $x \sim 5$, although the formation of such a hydride has not been reported to date. In this context, more accurate PCT and XRD studies on the monophase Mg50Pd50 and its hydride are necessary.

The PCTs of AC- and MS-Mg95Pd11Nd4 (Figs. 5 and 6) can be explained in a similar manner in terms of the equilibrium reactions (1)–(3) and the hydride formation mentioned above. Let’s focus on the PCT of the AC sample. This alloy is composed of Mg + MgPd + NdH2.5 phases before hydriding. The region I of the PCT corresponds to hydriding of Mg and NdH2.5 to form MgH2 and NdH3, respectively. A simple calculation shows that the hydrogen absorption accompanying these reactions is $\Delta H/M = 1.18$, being in good agreement with the observed value of 1.15 (Table 1). The region II corresponds to the disproportionation of MgPd to form Mg3Pd2 and MgH2. The calculated value for the hydrogen absorption in this region is $\Delta H/M = 0.49$, which just agrees with the observed value. The region III might be due to the formation of Mg3Pd2Hx as stated above, for which a hydrogen absorption of $\Delta H/M \sim 0.18$ is expected, again being in good agreement with the experiment.

It is noteworthy here that, since the presence of Nd in the alloy has little effect on the PCT as shown above, the main origin for the difference in the PCT behaviors between Mgs9Pd11 and Mg95Pd11Nd4 is the difference in the Pd concentration of the alloys. The former contains a larger amount of Mg50Pd than the latter. Therefore, the width of region I is more strongly reduced and those of regions II and III are more increased in the former than in the latter, resulting in reducing the total hydrogen absorbency of the former in comparison with the latter. This difference in the amount of Mg50Pd also brings a pronounced effect on the H/D kinetics as will be argued below.

We next discuss the H/D rates of these alloys. Figures 1 and 2 indicate that the kinetics, especially the dehydriding rate, is improved in the order: MS - Mgs9Pd11Nd4 > Mgs9Nd10 > AC - Mgs9Pd11Nd4 > Mgs9Pd11. Three factors appear to be involved to control the kinetics in these Mg-rich alloys:

1. In the alloys added with Nd, the H/D rates are markedly enhanced. Neodymium exists uniformly in the alloys as NdH2.5 after the initial activation and stabilization treatments. In the subsequent H/D cycles, it undergoes the reaction (2) and assists to enhance the major reactions (1) and (3) as an efficient chemical catalysis. This explains why Mgs9Pd11 free from Nd exhibits the worst kinetics.

2. The Mg50Pd phase present in the alloys containing Pd undergoes the disproportionation reaction (2) in the H/D process, which is expected to retard the overall rate because it involves a long-range rearrangement of metallic atoms. This explains why Mgs9Nd10 which does not contain Mg50Pd exhibits better kinetics than AC-Mgs9Pd11Nd4 and Mgs9Pd11 containing Mg50Pd.

3. The refinement of the microstructure of an alloy may enhance the kinetics of the reactions (1)–(3) because it may increase the interface regions where the reactions can take place. The MS-Mg95Pd11Nd4 sample produced by melt-spinning and crystallization process at 573 K exhibits a finer microstructure than that of the AC-Mg95Pd11Nd4 sample in the as-cast state, as revealed by the SEM photographs shown in Fig. 11. The former displays a layer structure of ~1 μm in width, while the latter shows a granular structure of ~5 μm in diameter. This difference in the microstructure is expected to explain why the former provides a faster H/D kinetics than the latter. However, the fine grains of the MS sample may grow under H/D cycles particularly at temperatures exceeding 573 K, leading to the degradation of the H/D kinetics. In this context, a more elaborate structural study is necessary, and it is now under way using transmission electron microscopy (TEM).

Through the combined effects of the above three factors, the H/D kinetics of Mg–Pd–Nd alloys is improved or deteriorated. In this respect, the situation is similar to Mg–Ni–Nd alloys which exhibit much better kinetics at temperatures down to 473 K or lower,1–3 except for one important difference. In the Mg–Ni–Nd system, Mg2Ni is precipitated, in place of MgPd, in a Mg matrix. It quickly reacts with hydrogen to form Mg2NiHx without disproportionation and contributes to enhance the H/D reactions of the Mg matrix. This catalytic effect of Mg2Ni coupled with that of NdH2.5 improves the kinetics of the Mg–Ni–Nd alloys in comparison with the Mg–Pd–Nd alloys.
5. Summary and Conclusions

The H/D kinetics and PCT characteristics of Mg–Pd, Mg–Nd and Mg–Pd–Nd alloys with approximately equal Mg contents of \( \sim 90 \text{ at\%} \) have been measured, and discussed in relation with their phase structures and microstructures studied by XRD and SEM observations. All these alloys have hydrogen absorbencies as high as \( \sim 5 \text{ mass\%} \) at 523–623 K. The main results are summarized as follows:

(1) The Mg–Pd alloy, which consists of Mg + Mg₆Pd phases, exhibits three plateau-like regions in the PCT, and they are attributed to the formation of MgH₂, decomposition of Mg₆Pd into Mg₅Pd₂ + MgH₂, and possible formation of Mg₃Pd₂H₁₋₅ hydride with increasing hydrogen content, although the existence of the hydride has not been evidenced by XRD. The H/D kinetics of this alloy is worst of the three, because it does not contain Nd which acts as an efficient catalyst in the H/D processes, and, furthermore, the decomposition of Mg₆Pd proceeds slowly.

(2) The Mg–Nd alloy is composed of Mg + Mg₆NdH₂₋₅ phases after initial activation and stabilization treatments, and it exhibits the PCT with a single plateau region which is mainly attributable to the formation of MgH₂. The H/D rates of this alloy are faster than the Mg–Pd alloy and as-cast Mg–Pd–Nd alloy. This enhancement of kinetics is caused by the catalytic action of NdH₂₋₅ which readily absorbs extra hydrogen to form less stable NdH₃ and thereby assists the hydrogenation of the Mg matrix.

(3) The Mg–Pd–Nd alloy is composed of Mg + Mg₆Pd + NdH₂₋₅ after initial activation and stabilization treatments. It exhibits three plateau-like regions in the PCT, which are attributed to the same hydriding reactions as operating in the Mg–Pd alloy. The NdH₂₋₅ phase acts as an efficient catalysis for hydriding the Mg matrix and Mg₆Pd precipitates, which strongly enhances the H/D rates of the alloy. In addition, by melt-spinning and crystallization treatments, a fine microstructure is readily developed in this alloy, which is quite sufficient to improve the H/D kinetics further. Thus, the melt-spun and crystallized Mg–Pd–Nd alloy exhibits the most excellent H/D kinetics among the alloys investigated. This alloy may be a promising candidate for an efficient hydrogen storage material in the future.

Acknowledgments

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

REFERENCES