Alloying Effect on the Hydrogen Sensing Property of Melt-Spun $\text{Mg}_{90}\text{Pd}_{10}$ Amorphous Alloy

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We have investigated the effect of additional elements, mainly Ni, on the properties of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy, which has the significant sensitivity to hydrogen dissolved in water. The results have shown that the Ni addition to the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy brings about complicated changes in the thermal stability, the electric property and the sensitivity to hydrogen dissolved in water. The sensitivity of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ amorphous alloy has a tendency to decrease with increasing the Ni content. Nevertheless, the Ni addition is more preferable as for the thermal stability of the amorphous phase and the sensitivity to hydrogen than the Cu, Al, Ti or Co addition.

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1. Introduction

Recently, we have investigated the effect of hydrogen on the electrical resistance of melt-spun amorphous alloys, particularly, the Mg-, Ni-, Zr- and Ti-based amorphous alloys.¹⁻³⁾ These amorphous alloys show increases in the electrical resistance after electrochemical hydrogen charging. When the alloys are immersed in hydrogen-dissolved water, the Mg-based amorphous alloys show increases in the electrical resistance while the others do not show any change. Especially, the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy shows a significant increase in the electrical resistance in hydrogen-dissolved water and the increment of the electrical resistance for a certain time increases with the hydrogen concentration in water. In our earlier study,⁴⁾ we also reported that the electrical resistance of the $\text{Mg}_{87}\text{Al}_3\text{Pd}_{10}$ amorphous alloy increases by hydrogen charging and decreases to the initial level by hydrogen discharging. From these results, we have concluded that the Mg-based amorphous alloys, especially, the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy, are applicable to base materials of a hydrogen sensor in water, which detects hydrogen by measuring the electrical resistance change.

In general, the Mg-Ni alloy system is known to have a highly promising hydrogen storage property. Therefore, many investigations have been conducted on this alloy system.⁵⁻⁷⁾ It is interesting to study the effect of the Ni addition on the properties of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy from the viewpoint of material science and practical engineering, because this is an alloy of considerable interest for its potential application to the hydrogen sensor in water. In this work, we have investigated the effect of additional elements such as Ni, Cu, Al and Ti on the properties of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy.

2. Experimental Procedure

Ingots of $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20)

and $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{M}_x$ ($x = 5$ and $10/\text{M} = \text{Cu, Al, Ti and Co}$) alloys were synthesized in an argon atmosphere with a high-frequency induction furnace. From the master alloys, melt-spun alloys of about 0.4 mm width and 14 μm thickness were produced by the single-roller melt-spinning technique. The amorphicity of the melt-spun alloys was examined by X-ray diffractometry (Cu-K α , 40 kV, 30 mA, hereafter denoted as XRD). Thermal stability of an amorphous phase was examined by differential scanning calorimetry (hereafter denoted as DSC) at a heating rate of 0.67 K/s. In order to investigate the sensitivity to hydrogen dissolved in water, we measured the electrical resistance of the amorphous alloy while immersing it in hydrogen-dissolved water. Being cut into a piece with a length of 67 mm and fixed to a sample holder, a part of the ribbon sample, *i.e.*, 47 mm, was immersed in pure water of 500 ml where hydrogen gas was bubbling through a glass filter. The flow rate of hydrogen gas was 0.35 ml/s. The hydrogen concentration in water was measured with a hydrogen sensor (TOA DKK, DH METER DH-35A). The continuous measurement of the electrical resistance of each ribbon sample was performed by the two-probe technique for 600 s after starting the hydrogen bubbling.

3. Results and Discussion

3.1 Amorphicity and thermal stability of the Mg-Pd-Ni amorphous alloys

Figure 1 shows XRD patterns of the melt-spun $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) alloys. Only a broad diffraction peak is observed for each alloy, indicating the formation of a single amorphous phase. As shown in Fig. 1, the peak angle shifts to the larger side monotonously with increasing the Ni content. This suggests that the amorphous structure becomes denser with replacing Mg and Pd with Ni. This may be explained in terms of the atomic sizes of the elements: the atomic radius of Ni (0.125 nm) is rather smaller than those of Mg (0.160 nm) and Pd (0.137 nm). Figure 2 shows DSC curves of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10,$

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Fig. 1 XRD patterns of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys.

Fig. 2 DSC curves of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys.

15 and 20) amorphous alloys. Three exothermic peaks are observed in the curve of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy. The first crystallization reaction corresponds to the precipitation of Mg crystalline phase, the second one to the precipitation of Mg_6Pd crystalline phase and the third one to the crystallization of the amorphous remainder phase according to the previous article.⁸⁾ As shown in Fig. 2, the number of the crystallization peaks decreases with increasing the Ni content, showing that the amorphous alloy is crystallized in a simpler mode. This suggests that the local atomic structure of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ amorphous alloy changes drastically in the compositional range of 0 to 20 at% Ni content. In Fig. 2, it is also apparent that the temperature of the first crystallization peak increases linearly with increasing the Ni content up to 10 at%, and the temperature remains nearly unchanged with the Ni content over 10 at%. Since the higher crystallization temperature means the higher stability of an amorphous phase in the alloy, it can be stated that the Ni addition is effective to increase the thermal stability of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy.

Fig. 3 Specific electrical resistance of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys.

Fig. 4 R/R_0 values of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys immersed in water of 500 ml as a function of hydrogen bubbling time.

3.2 Sensitivity of the Mg-Pd-Ni amorphous alloys to hydrogen dissolved in water

Figure 3 shows the specific electrical resistance (ρ) of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys without hydrogen charging. The specific electrical resistance of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy decreases by 18% when 5 at% Ni is added. However, further Ni addition results in an increase in the specific electrical resistance, varying from 0.57 (5 at% Ni) to 1.11 (20 at% Ni). Figure 4 shows the changes in the electrical resistance of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys immersed in hydrogen-dissolved water for 600 s. The electrical resistance (R) is normalized against the initial one (R_0). The hydrogen concentration in water increases with the bubbling time, and then saturates around 1.0 mass ppm after bubbling for 1000 s.³⁾ As shown in the figure, the electrical resistance of each sample increases with the bubbling time. Table 1 summarizes the R/R_0 values of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys

Table 1 R/R_0 values of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys after the immersion in hydrogen-bubbling water for 600 s.

Alloy	Electrical resistance change (R/R_0)
$\text{Mg}_{90}\text{Pd}_{10}$	1.659
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{95}\text{Ni}_5$	1.052
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{90}\text{Ni}_{10}$	1.045
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{85}\text{Ni}_{15}$	1.029
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{80}\text{Ni}_{20}$	1.023

Table 3 Atomic size ratio and the heat of mixing among the constituent elements for the Mg-Pd-M ($M = \text{Ni, Cu, Al, Ti}$ and Co) alloy systems.

Alloy (Mg-Pd-M)	Atomic size ratio		Heat of mixing, $\Delta H^{\text{mix}}/\text{kJ} \cdot (\text{mole of atoms})^{-1}$	
	$r_{\text{mid}}/r_{\text{min}}$	$r_{\text{max}}/r_{\text{mid}}$	Mg-M	Pd-M
Mg-Pd-Ni	1.096	1.168	-4	0
Mg-Pd-Cu	1.070	1.168	-3	-14
Mg-Pd-Al	1.044	1.119	-2	-46
Mg-Pd-Ti	1.073	1.088	16	-65
Mg-Pd-Co	1.096	1.168	3	-1

Table 2 Properties of melt-spun $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{M}_x$ ($x = 5$ and $10/M = \text{Cu, Al, Ti}$ and Co) alloys. 'Amo.' means the amorphous phase and 'Cry.' means the crystalline phase in this table.

Alloy	Phase	First crystallization temperature, T/K	Specific electrical resistance, $\rho/\mu\Omega\text{m}$	Electrical resistance change (R/R_0)
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{95}\text{Cu}_5$	Amo.	424	0.51	1.005
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{90}\text{Cu}_{10}$	Amo.	438	0.79	1.007
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{95}\text{Al}_5$	Amo.	435	0.56	1.007
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{90}\text{Al}_{10}$	Amo.	434	0.79	1.008
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{95}\text{Ti}_5$	Amo.	417	0.53	1.009
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{90}\text{Ti}_{10}$	Amo.	414	0.38	1.006
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{95}\text{Co}_5$	Amo. + Cry.	—	—	—
$(\text{Mg}_{0.9}\text{Pd}_{0.1})_{90}\text{Co}_{10}$	Cry.	—	—	—

after the immersion in hydrogen-dissolved water for 600 s. The $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy shows a significant increase in the electrical resistance. However, the sensitivity of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy decreases largely even by 5 at% Ni addition. The sensitivity of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ amorphous alloy has a tendency to decrease with increasing the Ni content.

3.3 Synthesis and evaluation of the melt-spun Mg-Pd-M ($M = \text{Cu, Al, Ti}$ and Co) alloys

We also synthesized melt-spun $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{M}_x$ ($x = 5$ and $10/M = \text{Cu, Al, Ti}$ and Co) alloys and investigated the properties including the sensitivity to hydrogen dissolved in water. Table 2 summarizes the results. Alloys with a single amorphous phase can be obtained in the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{M}_x$ ($x = 5$ and $10/M = \text{Cu, Al}$ and Ti) alloys. The Co addition prevents the amorphous formation of the alloys. The addition of these third elements is not effective to increase the first crystallization temperature higher than that of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy. The difference in the atomic size and the heat of mixing among the constituent elements are greatly related to the forming ability of a stable amorphous phase.^{9,10} Table 3 summarizes the atomic size ratio ($r_{\text{mid}}/r_{\text{min}}$ and $r_{\text{max}}/r_{\text{mid}}$) and the heat of mixing among the constituent elements for the Mg-Pd-M ($M = \text{Ni, Cu, Al, Ti}$ and Co) alloy systems. Ti and Co have positive values in the heat of mixing with Mg, which is the main element in the alloys prepared in this work. This is one of the reasons why the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ti}_x$ ($x = 5$ and 10) amorphous alloys crystallize at the low temperatures and the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Co}_x$ ($x = 5$ and 10) alloys can not form a single amorphous phase. As for the sensitivity to hydrogen dissolved in water, the R/R_0 values of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{M}_x$ ($x = 5$ and $10/M = \text{Cu, Al}$

and Ti) amorphous alloys after the immersion in hydrogen-dissolved water for 600 s are smaller than 1.01, resulting in the much lower sensitivity than that of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ amorphous alloys.

In the previous work, the local atomic structures of melt-spun $\text{Mg}_x\text{Pd}_{100-x}$ ($x = 70, 80, 85$ and 90) amorphous alloys were investigated by XRD with synchrotron radiation.¹¹ Consequently, we have found that a medium-range order (MRO) exists in each of the amorphous alloys and that the MRO decreases with increasing the Mg content. Compared with the $\text{Mg}_x\text{Pd}_{100-x}$ ($x = 70, 80$ and 85) amorphous alloys, the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy shows a significant sensitivity to hydrogen dissolved in water. Considering these results, it is conjectured that the difference in the local atomic structure is one of the reasons for the difference in the sensitivity to hydrogen dissolved in water. In other words, the electrical resistance change based on the diffusion of hydrogen in an amorphous phase must be greatly related to the local structure of the amorphous alloy. The addition of the third elements is thought to degrade the characteristic of the local atomic structure of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy and, therefore, lead to various changes in the hydrogen sensing property as well as the thermal stability and the electric property as shown in this work.

4. Summary

We have investigated the effect of the additional elements on the properties of the melt-spun $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy including the sensitivity to hydrogen dissolved in water. The main results are summarized as follows;

- (1) The single amorphous phase can be obtained in the melt-spun $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and

20) alloys. The crystallization process changes into a simpler mode for the higher Ni content alloy. The first crystallization temperature of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ amorphous alloy increases linearly up to 10 at% Ni addition, and the temperature remains nearly unchanged with the Ni content over 10 at%.

- (2) The specific electrical resistance of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy decreases by 18% when 5 at% Ni is added. However, further Ni addition results in the increase in the specific electrical resistance, varying from 0.57 (5 at% Ni) to 1.11 (20 at% Ni).
- (3) The electrical resistance of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys increases in hydrogen-dissolved water. There is a tendency that the sensitivity of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ amorphous alloy to hydrogen decreases with increasing the Ni content.
- (4) The single amorphous phase can be obtained in the melt-spun $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{M}_x$ ($x = 5$ and 10/ $\text{M} = \text{Cu}, \text{Al}$ and Ti) alloys, while not in the melt-spun $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Co}_x$ ($x = 5$ and 10) alloys. The addition of these third elements is not effective to increase the thermal stability of the $\text{Mg}_{90}\text{Pd}_{10}$ amorphous alloy, whereas the Ni addition is effective as mentioned above. The sensitivity of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{Ni}_x$ ($x = 0, 5, 10, 15$ and 20) amorphous alloys to hydrogen

dissolved in water is much larger than that of the $(\text{Mg}_{0.9}\text{Pd}_{0.1})_{100-x}\text{M}_x$ ($x = 5$ and 10/ $\text{M} = \text{Cu}, \text{Al}$ and Ti) amorphous alloys.

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