Structural Analysis of Melt-Spun Mg$_x$Pd$_{100-x}$ (x = 70, 80, 85 and 90) Amorphous Alloys

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Up to now, we have found that Mg-based amorphous alloys show increases in the electrical resistance when they are immersed in hydrogen-dissolved water at room temperature and that the Mg$_{90}$Pd$_{10}$ amorphous alloy shows a significant increase among them.$^{1,2}$ This finding indicates that the Mg-based amorphous alloys, especially, the Mg$_{90}$Pd$_{10}$ amorphous alloy, can be applied to base materials for a hydrogen sensor in water which senses hydrogen by measuring the electrical resistance change.$^{2-5}$ There exists a need to compare the local atomic structures among several Mg-Pd amorphous alloys in order to clarify why the Mg$_{90}$Pd$_{10}$ amorphous alloy shows such a large sensitivity to hydrogen dissolved in water. In this work, we prepared melt-spun Mg$_x$Pd$_{100-x}$ (x = 70, 80, 85 and 90) amorphous alloys and compared the properties and the local atomic structures.

2. Experimental Procedure

2.1 Sample preparation and immersion in hydrogen-dissolved water

Ingots of Mg$_x$Pd$_{100-x}$ (x = 70, 80, 85 and 90) alloys were synthesized in an argon atmosphere with a high-frequency induction furnace. From the master alloys, amorphous alloys of about 0.5 mm width and 14 µm thickness were produced by the single-roller melt-spinning technique. The specific electrical resistance ($\rho$) of the amorphous alloys was measured by means of the direct-current four-probe technique. In order to compare the sensitivities to hydrogen dissolved in water, we measured the electrical resistance ($R$) of the amorphous alloys immersed in hydrogen-dissolved water. Being cut into a piece of 87 mm length and fixed to a sample holder, the alloy sample was partially, i.e. 47 mm, 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 electrical resistance was measured by the two-probe technique for 600 s after starting the hydrogen bubbling.

2.2 Structural analysis by X-ray diffractometry with synchrotron radiation

The local atomic structures of the amorphous alloys were investigated by X-ray diffractometry with synchrotron radiation. As a measurement apparatus, the large Debye-Sherrer camera installed at the BL19B2 beam-line of SPring-8 was adopted. The X-ray diffraction (XRD) measurement was performed at the incident energy of 24 keV. An imaging plate was used as a detector and the exposure time was set to be 3600 s for obtaining a diffraction profile.

3. Results and Discussion

3.1 Sample preparation and immersion in hydrogen-dissolved water

The specific electrical resistance of the Mg$_x$Pd$_{100-x}$ (x = 70, 80, 85 and 90) amorphous alloys is about 0.8 µΩm. As shown in the previous article,$^2$ the hydrogen concentration in water increases with the bubbling time, reaching 0.9 mass ppm in 600 s. Table 1 summarizes the electrical resistance of the Mg$_x$Pd$_{100-x}$ (x = 70, 80, 85 and 90) amorphous alloys immersed in the hydrogen bubbling water for 600 s. The electrical resistance ($R$) is normalized to the resistance ($R_0$) of pure water.

Table 1: Electrical resistance of the Mg$_x$Pd$_{100-x}$ (x = 70, 80, 85 and 90) amorphous alloys immersed in the hydrogen bubbling water for 600 s.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Electrical resistance ($R/R_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>{80}$Pd$</em>{20}$</td>
<td>1.017</td>
</tr>
<tr>
<td>Mg$<em>{80}$Pd$</em>{20}$</td>
<td>1.012</td>
</tr>
<tr>
<td>Mg$<em>{85}$Pd$</em>{15}$</td>
<td>1.013</td>
</tr>
<tr>
<td>Mg$<em>{90}$Pd$</em>{10}$</td>
<td>1.659</td>
</tr>
</tbody>
</table>
against the initial one ($R_0$). As is obvious in Table 1, the Mg$_{90}$Pd$_{10}$ amorphous alloy shows a significant increase in the electrical resistance.

### 3.2 Structural analysis by X-ray diffractometry with synchrotron radiation

Figure 1 shows intensity profiles of the Mg$_x$Pd$_{100-x}$ ($x = 70, 80, 85$ and $90$) amorphous alloys obtained by XRD measurements with synchrotron radiation. Each intensity profile consists of a diffuse main peak followed by several weak and broad peaks, which is characteristic of an amorphous phase. In each intensity profile, we can see the existence of a pronounced prepeak followed by the main peak. Since the prepeak appears at about $Q = 15$ nm$^{-1}$, it is suggested that there is an atomic order with a correlation distance $2\pi/Q = 0.42$ nm or so. This estimation means the order of a few atomic distances. That is, the prepeak suggests the existence of a MRO in the amorphous phase. As shown in Fig. 1, the intensity of the prepeak decreases, that is, the MRO decreases with increasing the Mg content. Figure 2 shows radial distribution functions (RDFs) in the Mg$_x$Pd$_{100-x}$ ($x = 70, 80, 85$ and $90$) amorphous alloys derived from the results of the XRD measurements. The method for obtaining the RDFs was as previously described. The RDF measures the probability of finding the atom’s electron at a distance $r$ from the nucleus, integrated over all angular coordinates. From Fig. 2, it can be seen that the fluctuation of the RDF gets more indistinct with increasing the Mg content. This supports our interpretation that the MRO decreases with increasing the Mg content.

From Fig. 2, it can also be seen that each RDF contains a few peaks in the $r$-value range 0.25 to 0.35 nm. Considering the atomic radii of Pd (0.137 nm) and Mg (0.160 nm), it is expected that each RDF in this range contains peaks attributed to first neighbor Pd-Pd, Pd-Mg and Mg-Mg pairs. Multi-peak fitting by the Gaussian function makes it possible to separate and index the peaks as shown in Fig. 3. Figure 4 summarizes the atomic distances of the first neighbor Pd-Pd, Pd-Mg and Mg-Mg pairs estimated by the results of the multi-peak fitting. It can be seen from Fig. 4 that the atomic distances of the first neighbor pairs in the Mg$_x$Pd$_{100-x}$ amorphous alloy hardly vary with the alloy composition. On the other hand, Fig. 5 summarizes peak areas of the RDFs for...
the first neighbor Pd-Pd, Pd-Mg and Mg-Mg pairs in the Mg\textsubscript{x}Pd\textsubscript{100-x} amorphous alloys. It can be seen from Fig. 5 that the rate of the coordination numbers varies monotonously with the alloy composition.

4. Summary

In this work, we prepared the melt-spun Mg\textsubscript{x}Pd\textsubscript{100-x} amorphous alloys and compared the properties and the local atomic structures. The main results are summarized as follows;

(1) The Mg\textsubscript{x}Pd\textsubscript{100-x} amorphous alloys show increases in the electrical resistance when they are immersed in hydrogen-dissolved water, and the Mg\textsubscript{90}Pd\textsubscript{10} amorphous alloy shows a significant increase among them.

(2) The MRO exists in each of the Mg\textsubscript{x}Pd\textsubscript{100-x} amorphous alloys. The MRO decreases monotonously with increasing the Mg content.

(3) The atomic distances of the first neighbor pairs in the Mg\textsubscript{x}Pd\textsubscript{100-x} amorphous alloy hardly vary although the rate of the coordination numbers varies monotonously with the alloy composition.

These results are important for finding an assumption which explains the significant hydrogen-sensitivity of the Mg\textsubscript{90}Pd\textsubscript{10} amorphous alloy.

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REFERENCES