X-ray Diffraction Study for Mg₄Pd Crystalline and Amorphous Alloys Using Synchrotron Radiation

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*Mg₄Pd and amorphous alloys were prepared and X-ray diffraction patterns of these alloys were measured with synchrotron radiation using the large Debye-Scherrer camera installed at BL19B2 in SPring-8. The X-ray diffraction patterns have been successfully collected for the alloys. Using the X-ray diffraction pattern of the Mg₄Pd crystalline alloy, crystallization stages of the Mg₄Pd and Mg₉Pd amorphous alloys have been reviewed. As a result, the phase precipitated at the first crystallization stage of the Mg₄Pd amorphous alloy has been identified to be Mg₄Pd. In addition, it has been conjectured that the phase precipitated at the third crystallization stage of the Mg₉Pd amorphous alloy is Mg₄Pd, as well.

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1. Introduction

Recently, we have found that the electrical resistance of Mg-Pd and Mg-Pd-based amorphous alloys increases when they are immersed in hydrogen-dissolved water at room temperature, and that the electrical resistance increases and decreases accompanied by hydrogen absorption and desorption, respectively. Therefore, we have proposed the possibility of these amorphous alloys being applied to base materials for a hydrogen sensor in water. In these amorphous alloys, a Mg₉Pd amorphous alloy shows the highest sensitivity to hydrogen dissolved in water. In order to clarify the factors related to the good sensitivity to hydrogen, it is necessary to compare the structural properties among several Mg-Pd amorphous alloys. Especially, the thermal property of an amorphous alloy is one of the most informative properties related to the structure of the alloy. In the previous article, the thermal stability of the Mg-Pd amorphous alloys were investigated by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s, and it was reported that there are two crystallization stages (501 and 571 K) in the DSC curve of the Mg₄Pd amorphous alloy. However, the phase precipitated at the first crystallization stage has not been identified. It has been clarified that the second crystallization stage corresponds to the precipitation of Mg₄Pd and amorphous remainder phases. In an X-ray diffraction (XRD) pattern measured with Cu-Kα radiation, some sharp diffraction peaks of this unknown phase are observed around 2θ = 39°. In addition to these peaks, many other distinct peaks attributed to the unknown phase are seen in the XRD pattern. On the other hand, it was also reported that there are three crystallization stages (438, 485 and 510 K) in the DSC curve of the Mg₉Pd amorphous alloy. It has been clarified that the first and the second crystallization stages are due to the precipitation of Mg and Mg₄Pd phases, respectively. However, the phase precipitated at the third crystallization stage has not been identified. One distinct diffraction peak of this unknown phase appears at 2θ = 39° in an XRD pattern measured with Cu-Kα radiation. As shown in the Mg-Pd binary phase diagram in Fig. 1, the existence of a single Mg₄Pd phase has been confirmed by some researchers. According to the phase diagram, each unknown phase mentioned above is predicted as Mg₄Pd. However, it is impossible to conclude that the unknown phase is Mg₄Pd because there has been no information on the crystal structure of Mg₄Pd including the XRD pattern. Table 1 summarizes structural data of Mg and some Mg-Pd phases. It was reported that the single Mg₄Pd

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Fig. 1 Mg-Pd binary phase diagram.
phase can be obtained at 79.4 ± 1.0 at% Mg. In this work, a crystalline alloy with an ideal composition of Mg₄Pd was synthesized carefully. The purpose of this work is to measure and report the XRD pattern of the Mg₄Pd phase and to confirm each unknown phase mentioned above to be the Mg₄Pd phase. For comparison, the XRD pattern of the corresponding amorphous alloy was also measured.

2. Experimental Procedure

Pure Mg and Pd metals were weighed out in the composition of 80.50 at% Mg. These pure metals were mixed well in an argon atmosphere with a high-frequency induction furnace, followed by the solution treatment in an argon atmosphere at 673 K for 8.64 × 10⁴ s. The chemical composition of the alloy ingot was measured by inductively coupled plasma atomic emission spectrometry (ICP). The fine powder sample of the alloy ingot was loaded into a capillary glass tube with 0.2 mm inner diameter, and the XRD pattern was measured with synchrotron radiation. As a measurement apparatus, the large Debye-Sherrer camera installed at the BL19B2 beam-line of SPring-8 was adopted. An imaging plate was used as a detector. The XRD measurement was performed at the incident energy of 24 keV and the exposure time was set to be 1200 s for obtaining a diffraction profile. Additionally, an amorphous alloy ribbon of 0.5 mm width and 14 μm thickness was produced by the single-roller melt-spinning technique from the alloy ingot. The XRD pattern of the amorphous alloy was measured with an exposure time of 3600 s.

3. Results and Discussion

The chemical composition of the alloy ingot determined by ICP is Mg₄.00Pd (80.01 at% Mg), showing some of Mg has been lost in the melting process. Figure 2 shows the XRD patterns of the Mg₄Pd crystalline and amorphous alloys. As shown in Fig. 2, the diffraction pattern of the crystalline alloy contains many distinct peaks, while that of the amorphous alloy contains only broad peaks. In the diffraction pattern of the crystalline alloy, there are no peaks attributed to Mg₄(0). Mg₅Pd, Mg₅Pd₋₁, Mg₅Pd₋₂, MgO, and MgO₂. Considering that this alloy sample has the ideal composition, i.e. Mg₄0.0Pd, it would appear that the diffraction pattern is attributed to only a single phase of Mg₄Pd. Referring to the previous article, the XRD peaks of the unknown phase obtained at the first crystallization stage of the Mg₄Pd amorphous alloy correspond well to the XRD peaks shown in Fig. 2. For example, the sharp diffraction peaks around 2θ = 39° in the XRD pattern measured with Cu-Kα radiation (λ = 0.154 nm) correspond to the sharp diffraction peaks around 2θ = 12.5° in the XRD pattern measured with synchrotron radiation (λ = 0.05 nm). This supports our conjecture that the first crystallization stage of the Mg₄Pd amorphous alloy is attributed to the precipitation of the Mg₄Pd phase. On the other hand, as for the unknown phase precipitated at the third crystallization stage of the Mg₉Pd amorphous alloy, it is impossible to identify the phase to be the Mg₄Pd phase by the only one XRD peak at 2θ = 39°. Nevertheless, there is still the possibility that the XRD peak is attributed to Mg₄Pd. If this assumption is correct, then the crystallization process of the Mg₉Pd amorphous alloy can be expressed as follows; Mg₉Pd → Mg₄Pd → Mg₄Pd + Mg₉Pd + Mg₄Pd, which is reasonable in the light of the phase diagram shown in Fig. 1.

4. Summary

In summary, we have successfully prepared the crystalline alloy with the ideal composition of Mg₄Pd. The XRD pattern has been obtained clearly with synchrotron radiation. As a result, the unknown phase precipitated at the first crystallization stage of the Mg₄Pd amorphous alloy has been identified to be Mg₄Pd. In addition, we have proposed the possibility that the unknown phase precipitated at the third crystallization stage of the Mg₉Pd amorphous alloy may be Mg₄Pd, as well. In order to understand the crystal structure of Mg₄Pd in detail, further investigations are now in progress.

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