Journal of Alloys and Compounds 253–254 (1997) 90–93

Hydrogen absorption in an icosahedral ZnMgY alloy

A.P. Tsai[a,]*, A. Niikura[b], K. Aoki[c], T. Masumoto[b]

[a]National Research Institute for Metals, Tsukkuba, 305 Japan
[b]Institute for Materials Research, Tohoku University, Sendai, 980 Japan
[c]Kitami Institute of Technology, Kitami, Hokkaido, 090 Japan

Abstract

Hydrogen absorption in a stable icosahedral (i-) $Zn_{50}Mg_{42}Y_8$ alloy has been studied by X-ray diffraction, transmission electron microscopy and differential scanning calorimetry. The i-phase decomposed to a hexagonal Zn_2Mg Laves phase, YH_3 and MgH_2 after hydrogenation under 3 MPa hydrogen pressure at 573 K for 259.2 ks. Two stages of hydrogenation for the i-phase were identified; $\text{i-ZnMgY}+xH_2 \rightarrow \text{i-ZnMgYH}_{2x}$ in the initial stage and then $\text{i-ZnMgYH}_{2x}+H_2 \rightarrow Zn_2Mg+YH_2+MgH_2$. DSC curve of the fully hydrogenated (3 MPa, 573 K, 259.2 ks) sample revealed an endothermic peak around 730 K corresponding to the hydrogen desorption. The transformations between the icosahedral and crystalline phases due to hydrogen absorption and desorption are reversible.

Keywords: Quasicrystal; Zinc–magnesium–yttrium; Hydrogenation; Reversible reaction

1. Introduction

Quasicrystals [1], a new category of structure with forbidden rotational symmetries and non-periodic atomic array, reportedly have a highly ordered structure. Little attention has been paid to hydrogen absorption in quasicrystals, mainly due to two reasons. First, most of the stable quasicrystals are based on Al which does not chemically favor for hydrogen absorption. Second, although some quasicrystals contain large amounts of Mg (50 at%) which is favorable for hydrogen absorption, they are metastable and have poor thermal stability and would decompose to crystalline phases at a temperature below that of hydrogen absorption. Recently, a new class of icosahedral quasicrystals have been found in the Zn–Mg–rare earth metal (RE) systems [2,3]. These icosahedral phases are stable and contain Mg and RE in excess of 50 at% and are ideal candidate for studying hydrogen absorption in a quasicrystalline structure. In this study, we report the measurements of hydrogen absorption in a stable icosahedral $Zn_{50}Mg_{42}Y_8$ alloy with a highly ordered structure. Furthermore, we explain the hydrogenation mechanism and the interaction between hydrogen atoms and quasicrystalline lattice.

2. Experimental details

The alloy used in the present study, $Zn_{50}Mg_{42}Y_8$ was prepared from a mixture of pure Zn, Mg and RE in a pyrolytic boron-nitride crucible under an argon atmosphere using a high frequency induction furnace. Pulverized samples (crushed to a grain size less than 100 mesh) were slowly reacted with high purity hydrogen (99.99999%) under pressure between 1 and 4 MPa and at 573 K for various times. The samples were examined by X-ray diffractometry and then by transmission electron microscopy (TEM) before and after hydrogen absorption. The samples for TEM observation were prepared by crushing the alloy in ethanol and transferring onto a carbon microgrid. The amount of hydrogen absorbed was determined by measuring the change in hydrogen pressure in a constant volume reactor. Hydrogen desorption behavior was examined by differential scanning calorimetry (DSC).

3. Results

$Zn_{50}Mg_{42}Y_8$ composed mainly of an icosahedral phase(i-ZnMgY) coexisting with a minute amount of crystalline phases, has been reported previously. A selected area electron diffraction pattern taken with an incident

---

*Corresponding author. Fax: +81 298 531092; e-mail: aptsai@tamamori.nrim.go.jp

0925-8388/97/$17.00
PII S0925-8388(96)03059-9

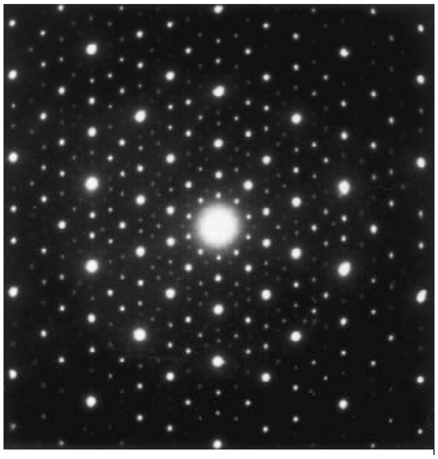

Fig. 1. Selected area electron diffraction pattern taken with an incident beam along a five-fold axis for an icosahedral $Zn_{50}Mg_{42}Y_8$ alloys before hydrogenation.

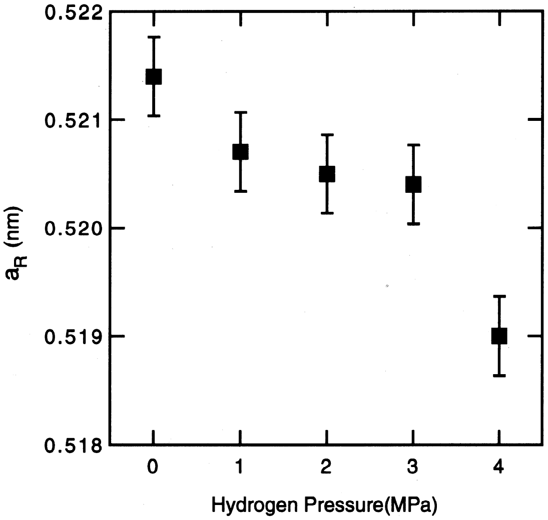

Fig. 3. Changes in a_r and peak width with hydrogen pressure for (211111) and (221001) diffraction peaks estimated from Fig. 2.

beam along a five-fold (*a*) axis of i-ZnMgY showing some characteristics of the icosahedral phase is reproduced in Fig. 1. Hydrogen absorption curves in the initial stage for the i-ZnMgY alloy, obtained at 573 K under 2 and 3 MPa hydrogen pressure, confirmed that hydrogen absorption progressed in the sample (not shown). For example, the amount of hydrogen absorbed was about 0.1 after 1 h when expressed as the hydrogen-to-metal atom ratio. Fig. 2 shows the evolution of two main diffraction peaks, (211111) and (221001), under various hydrogen pressures for i-ZnMgY treated at 573 K for 21.6 ks. The changes in lattice parameter with hydrogen pressure as derived from Fig. 2 are plotted in Fig. 3. The incorporation of hydrogen causes a decrease in the lattice parameter (a_R) from 0.522 nm to 0.519 nm, i.e. a reduction of about 0.6%. The lattice parameters a_R were estimated from the two most intense peaks indexed with (211111) and (221001) using the relation described by Elser [4].

Powder X-ray diffraction patterns for i-ZnMgY hydrogenated at 573 K under 3 MPa hydrogen pressure for various times are shown in Fig. 4. As expected, after hydrogenation for 259.2 ks the i-phase fully transformed to two hydrides, MgH_2 and YH_2, and a Zn_2Mg Laves phase. One can notice that the diffraction peaks of the three crystalline phases have concurrently appeared in the sample after hydrogenation for 86.4 ks.

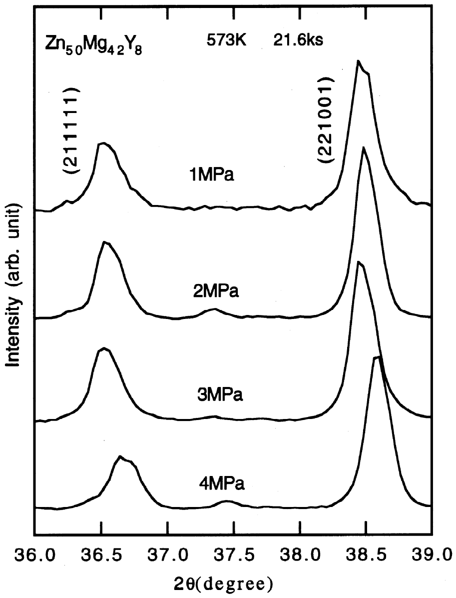

Fig. 2. Powder X-ray diffraction patterns showing the evolution of two main diffraction peaks of i-ZnMgY during hydrogenation at 573 K for 21.61 ks under various pressures.

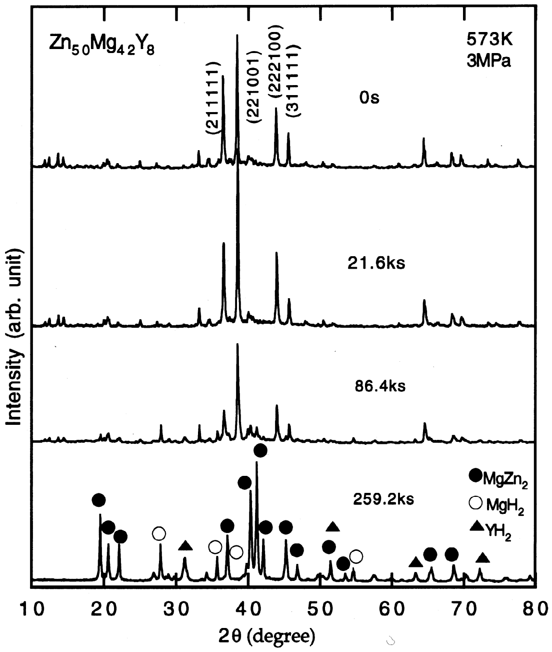

Fig. 4. Powder X-ray diffraction patterns of the i-ZnMgY alloy hydrogenated at 573 K under a hydrogen pressure of 3 MPa for various times.

4. Discussion

There are two plausible explanations for the decrease in a_R with hydrogen pressure. First, hydrogen atoms may substitute for one of the constituent elements of the quasicrystalline structure. Since the atomic size of hydrogen is much smaller than that of Zn, Mg and Y, such a substitution would cause a significant decrease in a_R. Second, the formation of MgH_2 and YH_2 hydrides may reduce the Mg and Y concentration in the i-phase. Taking the atomic radii (1.37, 1.60 and 1.81 for Zn, Mg and Y, respectively) into account, we can speculate that some of the decrease in a_R results from a loss of the two larger species from the i-phase and a transfer towards the hydrides. Based on the X-ray diffraction pattern, the i-phase and the hydrides co-exist after hydrogenating for 86.4 ks. This suggests that the i-phase hydrogenated through the route of hydride formation. On the basis of the these results, some routes of hydrogen absorption in i-ZnMgY can be imagined. Since Zn does not form a hydride, hydrogen dissolved in i-ZnMgY would associate preferentially with Mg and Y.

$$\mathrm{i-ZnMgY} + \mathrm{H_2} \rightarrow \mathrm{i-ZnMgYH}_x \qquad (1)$$

The incorporation would lead to a decrease in a_R due to a reduction of the Mg and Y atom concentrations in an ideal icosahedral cluster. When the Y and Mg concentration falls below an allowable limit, the icosahedral structure would no longer exist. Finally, it decomposes into the Laves Zn_2Mg phase and two hydrides.

$$\mathrm{i-ZnMgYH}_{2x} \rightarrow \mathrm{Zn_2Mg} + \mathrm{H_2Mg} + \mathrm{H_3Y} \qquad (2)$$

Fig. 5 shows the DSC curves for $Zn_{50}Mg_{42}Y_8$ hydrogenated for various times. The melting of Mg_7Zn_3 is responsible for the endothermic peak around 600 K. One can see that an endothermic peak between 700 and 750 K appears after hydrogenation and gradually becomes more intense with hydrogenation time. In order to identify the origin of the endothermic peak, we examined the structural change due to annealing for the alloy hydrogenated for 259.2 ks. As can be seen from Fig. 6, the i-phase transformed to three crystalline phases after complete hydrogenation, and it could be recovered from the phases upon heating to 850 K. Thus, we can assert that the endothermic peak at high temperature in Fig. 5 is associated with hydrogen desorption. The endothermic peak due to the melting of Mg_7Zn_3 completely disappeared after hydrogenation for 259.2 ks implying that not only the i-phase but also Mg_7Zn_3 have been fully hydrogenated.

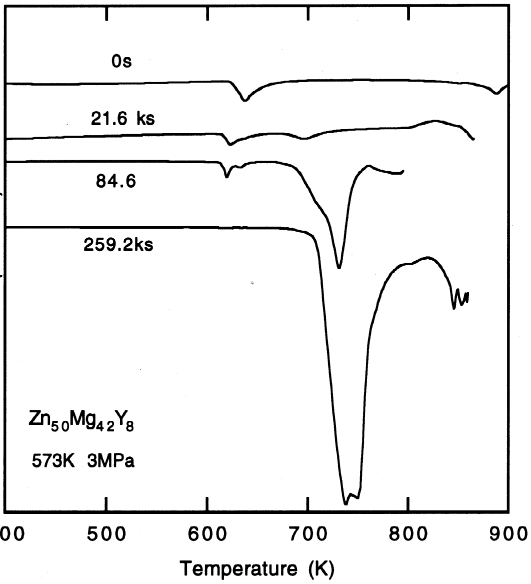

Fig. 5. DSC curves for i-ZnMgY hydrogenated for various times.

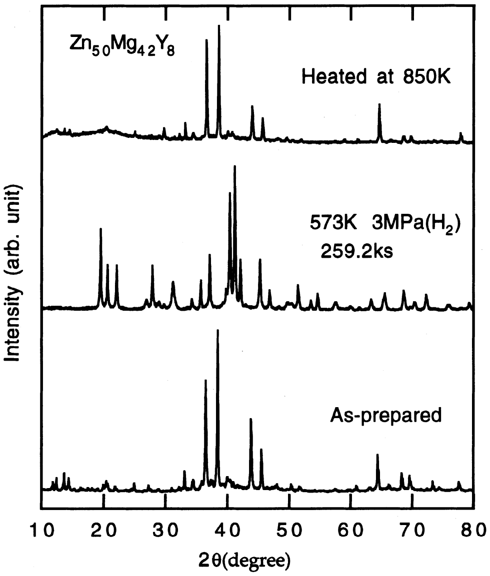

Fig. 6. Powder X-ray diffraction patterns showing the structural change due to hydrogen absorption and desorption.

One example [5] of hydrogen absorption in a quasicrystal has been reported earlier in Ti-based (Ti+Zr>80 at%) quasicrystals. The absorption of hydrogen in that case resulted in a large expansion of a_R up to about 7% in contrast to the decrease observed in the Zn–Mg–Y system. This implies that the hydrogen atoms in the Ti-based quasicrystals are located at interstitial sites (tetrahedral sites) and expand the quasilattice spacing. Since these alloys were prepared by rapid solidification, a large amount of defects is expected to be present and these might promote hydrogen absorption.

5. Summary

In conclusion, we have examined hydrogen absorption in a stable Zn–Mg–Y quasicrystal. The quasilattice parameter, a_R, of the i-phase decreased with increasing hydrogen pressure and hydrogenation time. After hydrogenation at 573 K for 259.2 ks, the i-phase transformed to three crystalline phases: Zn_2Mg Laves phase, Y_3H and MgH_2. On the basis of the change in a_R and the formation of the final products after complete hydrogenation, it was concluded that the probable route for hydrogen absorption is: $\text{i-ZnMgY} + x\text{H}_2 = \text{i-ZnMgYH}_{2x}$, and then $\text{i-ZnMgY} + \text{H}_2 = \text{Zn}_2\text{Mg} + \text{YH}_3 + \text{MgH}_2$. The i-phase structure was recovered after hydrogen desorption, indicating that the transformations induced by hydrogen absorption and desorption are reversible.

References

[1] D. Shechtman, I. Blech, D. Gratias and J.W. Cahn, *Phys. Rev. Lett., 53* (1984) 1951.

[2] A. Niikura A.P. Tsai, A. Inoue and T. Masumoto, *Philos. Mag. Lett., 69* (1994) 351.

[3] A.P. Tsai, A. Niikura, A. Inoue, T. Masumoto, Y. Nishida, K. Tsuda and M. Tanaka, *Philo. Mag. Lett., 70* (1994) 169.

[4] V. Elser, *Phys. Rev. B, 32* (1985) 4892.

[5] A.M. Viano, R.M. Stroud, P.C. Gibbons, A.F. McDowell, M.S. Conradi and K.F. Kelton, *Phys. Rev. B, 51* (1995) 12 026.