Hydrogen Absorption and Desorption by Quasicrystalline and Related Approximant Powders Produced by Mechanical Alloying in the Mg–Al–Zn System

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Icosahedral quasicrystalline (i-phase) $\text{Mg}_{44}\text{Al}_{15}\text{Zn}_{41}$ and related Frank-Kasper (cubic approximant) phase powders, which were produced by mechanical alloying from the elemental powder mixture and subsequent heat treatment, respectively, have been hydrogenated with hydrogen gas at a temperature of 573 K and a hydrogen pressure of 4.2 MPa. The hydrogen solubility limit for both powders is almost the same and was estimated to be about 16 at%, and no crystallographic structural dependence was found for the hydrogen solubility. The approximant phase powder was structurally stable after hydrogenation but the i-phase powder decomposed into the approximant and MgZn_2 intermetallic phases. Hydrogen desorption occurred at temperatures above about 600 K for both powders and was accompanied by the evaporation of zinc. The kinetics of the hydrogen desorption as well as the zinc evaporation were slightly different in each powder because of the formation of the MgZn_2 phase in the i-phase powder after hydrogenation.

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1. Introduction

Since the discovery of the first quasicrystal in an aluminum alloy in 1984 by Shechtman *et al.*,¹⁾ numerous kinds of quasicrystals have been found. The quasicrystal was thermally unstable, so that it could be produced only by rapid solidification of the melt. Thermally stable quasicrystals, which could be produced by an isothermal heat treatment, were discovered after that. Quasicrystals, such as Mg–Al–Zn ^{2–4)} and Al–Cu–Fe ,⁵⁾ have also been reported to be produced by a mechanical alloying (MA) process. MA, in which elemental powders are poured in a vial along with spheres of a hard material and collisions among the powders, and the spheres and the vial walls result in powder fragmentation and rewelding, could yield powders that have high chemical and structural internal energy, leading to the formation of extended solid solutions or metastable phases with crystalline or amorphous structures.⁶⁾

Most research on quasicrystals has focused on physical or metallurgical aspects. Quasicrystals are generally brittle up to temperatures of a few hundred degrees Celsius, limiting their uses. However, several industrial applications have been recently proposed for quasicrystals;^{7,8)} that is, (a) as surface coating materials, such as a lubricant or thermal barriers, because of their low friction coefficients due to the low surface energy and their softening behavior at high temperatures, (b) as reinforcing particles or precipitates in metal matrix composites, (c) as thermoelectric materials, and (d) as hydrogen-storage materials. For application of quasicrystals as hydrogen-storage materials, Kelton *et al.*⁹⁾ and Viano *et al.*^{10,11)} have focused on a Ti–Zr–Ni quasicrystal. They have

demonstrated that a Ti–Zr–Ni icosahedral quasicrystal, prepared by a rapid quenching technique, absorbed hydrogen to a level exceeding that of hydrides of technological interest, such as hydrides in LaNi_5 and TiFe, and that desorption of the hydrogen could also occur at reasonable temperatures, promising a new hydrogen-storage material for fuel-storage and battery applications. Wehner *et al.*¹²⁾ have reported that a Zr–Ni–Cu–Al quasicrystal could be charged with hydrogen electrolytically up to a maximum $[\text{H}]/[\text{M}]$ of 1.9. Studies on the hydrogenation of quasicrystals have just started, and a search for quasicrystals with appropriate properties for hydrogen storage (promising pressure-composition-isotherms and cycling ability) is required. In this report, we focus on the icosahedral quasicrystal in the Mg–Al–Zn system because the crystallographic structures of the quasicrystal and related approximant in this system have been characterized well.¹³⁾ We investigate the hydrogenation of Mg–Al–Zn quasicrystal powder produced by MA as well as that of the related approximant phase powder produced by subsequent heat treatment after MA. The formation process of the icosahedral quasicrystal powder by MA and the phase variation after subsequent heat treatment are also investigated in detail.

2. Experimental Procedures

Commercially pure Mg (99.9%), Al (99.9%) and Zn (99.9%) powders were used as starting materials in this study. A powder mixture with a chemical composition of $\text{Mg}_{44}\text{Al}_{15}\text{Zn}_{41}$ was poured into stainless steel vials (45 mL) with stainless steel balls (14 mm in diameter). The initial mass of the powder mixture before MA was approximately 8.5 g and the ball-to-powder weight ratio was approximately 8 : 1. The vials containing the powder mixture and the balls

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were evacuated by a rotary-pump and then back-filled with an argon gas (99.999%) several times in a glove box, and the final argon gas pressure was 0.1 MPa. MA was carried out by a Frisch Pulversette 7 planetary ball mill. The ball acceleration was 15 g (the corresponding motor speed was 3200 min^{-1} .) and the maximum alloying time was 30 h. To avoid any temperature increases during MA, the alloying period of 0.5 h was alternated with an equal rest time. At an adequate milling time, small amounts of the powders were withdrawn from the vials for X-ray diffraction (XRD) measurements and were set back again, and then an additional MA was continued. The crystal structural change of the powder mixture was investigated by XRD and transmission electron microscopy (TEM). XRD measurement was performed by a JEOL JDX-11PA, using Cu $K\alpha$ radiation at 30 kV and 20 mA. TEM observation was performed by a JEM-200 CXII at an accelerating voltage of 200 kV.

Hydrogenation of the MA powder was performed in a high-pressure vessel, which was made of stainless steel. The vessel containing the powder was evacuated by a rotary pump and then back-filled with pure (99.99999%) hydrogen gas. Then the vessel was heated by an electric heater surrounding the vessel and was kept at a temperature of 573 K. The initial hydrogen pressure at 573 K was either 4.2 MPa or 3.6 MPa, the hydrogen pressure change in the vessel was monitored by a pressure transducer, and then the hydrogen concentration in the powder was calculated. The hydrogen evolution kinetics were analyzed by thermal desorption spectroscopy (TDS). The schematic diagram of the TDS main system is shown in Fig. 1. The sample was mounted in a quartz tube, and the system was pumped down to a vacuum level of 10^{-6} Pa using a turbomolecular pump and a sputter-ion pump; the sample was then heated to 1300 K at a heating rate of 0.33 K/s (20°C/min) by an infrared gold-image furnace. During heating, hydro-

gen partial pressure (ion current of H_2^+) in the TDS system was monitored every 15 seconds (thus, every 5 K in temperature) with an ULVAC QMS-400 quadrupole mass spectrometer (QMS) and the total pressure was also recorded by a pen recorder. The TDS system is also equipped with two kinds of vessels, whose volume are measured (Fig. 2), to quantify hydrogen evolution rate. Prior to filling hydrogen gas into the vessels, both vessels were evacuated to a vacuum by a turbomolecular pump; then an ultra-high purity (99.9999%) hydrogen gas (0.1 MPa) was loaded into V1 vessel (23.4 mL). The hydrogen gas in the V1 vessel was then loaded to V2 vessel (386.0 mL) to reduce the number of hydrogen molecules in the V1 vessel, and the quantitative analyses with the QMS were carried out at room temperature until the hydrogen gas in the V1 vessel was completely released. Thus, once the area of a measured spectrum (H_2^+ ion current vs. measuring time diagram) equals the number of hydrogen molecules filled in the V1 vessel, the hydrogen evolution rate/ H_2^+ ion current can be calculated. The hydrogen evolution rate calibrated by the quantitative analysis was 1.24×10^{21} hydrogen atoms (0.62×10^{21} hydrogen molecules) $\text{s}^{-1} \text{ A}^{-1}$.

3. Results and Discussion

XRD patterns of $\text{Mg}_{44}\text{Al}_{15}\text{Zn}_{41}$ powder mixtures mechanically alloyed for several alloying times are shown in Fig. 3, in which the pattern at an alloying time of 0 h means no MA (before MA). At an early stage of MA (2.5 h), the MgZn_2 intermetallic phase appears, and additional MA produces new XRD peaks, which can be indexed as an icosahedral quasicrystal phase (i-phase). Further MA did not change the Bragg angle positions, but, the X-ray intensities become somewhat lower. Ivanov *et al.*²⁾ and Mizutani *et al.*^{3,4)} have also reported the formation of an Mg–Al–Zn quasicrystal on the basis of their XRD measurements. However, it is necessary to determine the quasicrystalline structure by TEM because a selected area electron diffraction (SAD) pattern showing five-fold symmetry is strong evidence for the formation of quasicrystals. Eckert *et al.*⁵⁾ have reported the formation of an Al–Cu–Mn quasicrystal produced by MA, but in that case they have observed a SAD pattern having only Debye-Scherrer rings (no five-fold symmetry) because of grain sizes ranging from some nanometers up to some tens of nanometers. They measured the radii ratios between certain Debye-Scherrer rings in the SAD pattern showing the golden ratio,

Fig. 1 Schematic diagram of thermal desorption spectroscopy system.

Fig. 2 Separate line for quantitative analysis of hydrogen.

Fig. 3 X-ray powder diffraction patterns of the $\text{Mg}_{44}\text{Al}_{15}\text{Zn}_{41}$ powder mixture mechanically alloyed for several alloying times. Time increases vertically upward from pattern to pattern.

Fig. 4 Selected area electron diffraction pattern for the $\text{Mg}_{44}\text{Al}_{15}\text{Zn}_{41}$ powder mixture after mechanical alloying for 7.5 h.

i.e., $\tau = (1 + \sqrt{5})/2$, which is also evidence of the quasicrystalline structure. Figure 4 shows a SAD pattern for the powder mixture after MA for 7.5 h. This SAD pattern indicates Debye-Scherrer rings like those reported by Eckert *et al.*⁵⁾ in an Al–Cu–Mn powder mixture. The radii ratio of the Debye-Scherrer rings between a and b marked in Fig. 4 is very close to the golden ratio, suggesting that the obtained MA powder mixture in this study is also very fine quasicrystal or nano-quasicrystal which is randomly oriented crystallographically. It might be comparatively difficult for a mechanically alloyed powder mixture to take a SAD pattern showing five-fold symmetry because the MA process makes starting elemental powders finer due to mechanical collision.

Figure 5 shows *in situ* high-temperature XRD patterns, in which a special hot-stage was used under an argon gas flow,

Fig. 5 *In-situ* high-temperature X-ray powder diffraction patterns for the $\text{Mg}_{44}\text{Al}_{15}\text{Zn}_{41}$ powder mixture produced after MA for 30 h.

for the quasicrystal powder produced after MA for 7.5 h. The heating rate was 20 K/min. The X-ray intensities of the peaks at room temperature (303 K) corresponding to the i-phase increase with increasing heating temperatures up to 573 K, which could indicate that the quasi-crystallinity increases. The indices labelled in Fig. 5 for the i-phase (quasicrystal) follow the scheme proposed by Elser.¹⁴⁾ At heating temperatures of 623 K, the cubic Frank-Kasper phase (approximant) also appears, the i-phase fully transforms to the approximant phase at temperatures above 723 K, and then the melting point is reached at about 823 K. After cooling back to room temperature from 823 K, the approximant phase appears again. A SAD pattern for the i-phase powder (MA for 7.5 h) that was heated at 573 K also showed Debye-Scherrer rings as same as those shown in Fig. 4, but some diffraction spots became clearly visible, which agrees fairly well with the *in situ* XRD experiments.

Hydrogen absorption and desorption kinetics were investigated for the quasicrystal (i-phase) powder produced after MA, as well as for the approximant (cubic Frank-Kasper) phase powder produced by subsequent heat treatment. Those kinetics are compared and the effect of the crystallographic structural difference on those kinetics and the phase stability during hydrogen absorption will be discussed later. Figure 6 shows hydrogen concentrations in the i-phase powder as a function of hydrogenation time at a temperature of 573 K and the initial hydrogen pressure of 4.2 MPa. This i-phase powder was obtained after MA for 7.5 h. Because the i-phase powder was heated at 573 K during hydrogenation, the quasicrystallinity of the i-phase is the best (see Fig. 5). Hydrogenation gradually occurs for the i-phase powder and the concentration

Fig. 6 Hydrogen concentrations in the i-phase powder as a function of hydrogenation time at temperature of 573 K and an initial hydrogen pressure of 4.2 MPa.

Fig. 7 Hydrogen concentrations in the approximant phase powder as a function of hydrogenation time at a temperature of 573 K and an initial hydrogen pressure of 4.2 MPa.

level of hydrogen reaches about 16 at% after a hydrogenation time for 14 h, so that the hydrogen solubility limit for the i-phase is about 16 at% for the given hydrogenation conditions. Hydrogen concentrations in the approximant phase powder as a function of hydrogenation time at temperature of 573 K and an initial hydrogen pressure of 4.2 MPa are shown in Fig. 7. This approximant phase powder was obtained after cooling the melt of the MA powder (MA for 7.5 h) to room temperature (see Fig. 5). The hydrogen solubility for the approximant phase is also about 16 at%, which is nearly the same as that for the i-phase, but a longer hydrogenation time was necessary to reach the hydrogen solubility limit for the approximant phase powder (about 32 h). This is probably due to surface contamination, such as an oxide film, of the approximant phase powder, which was produced during a cooling process of the melt of the MA powder. There seems to be no effect of crystallographic structural difference between the quasicrystal and the cubic approximant on the hydrogen solubility.

Figure 8(a) and (b) show the XRD patterns of the i-phase and the approximant phase powders, respectively, after the hydrogenation experiments for 50 h. An unknown peak is observed in both patterns at a Bragg angle 2θ of about 35.5° . It is also observed that the i-phase powder decomposes into the cubic approximant (Frank-Kasper phase) and the MgZn_2 intermetallic phases after hydrogenation. However, the ap-

Fig. 8 X-ray powder diffraction patterns of (a) the i-phase and (b) the approximant phase powders after the hydrogenation experiments for 50 h.

proximant phase powder maintains its original crystal structure even after hydrogenation. Thus, it is concluded that after hydrogenation the approximant phase is structurally more stable than the i-phase.

TDS spectra of hydrogen ($M/e=2$) for the i-phase and the approximant phase powders after hydrogenation at 573 K and at initial hydrogen pressure of 3.6 MPa were shown in Figs. 9(a) and (b) respectively, in which heating rate is 20 K/min. Although the i-phase powder was transformed into the approximant and the MgZn_2 phases after hydrogenation (Fig. 8), we still refer to it as the i-phase powder. In both powders, hydrogen desorption originates at about 600 K, and several peaks are observed in the TDS spectra. For the i-phase powder, the accelerated hydrogen desorption occurs at about 670 K and the desorption continues until reaching the melting point for the i-phase powder. For the approximant phase powder, hydrogen desorption is accelerated at about 650 and at 750 K, and then the desorption decreases when approaching the melting temperature. Some peak temperatures included in each TDS spectrum might be similar but the highest TDS peak temperature is different. Because the microstructural difference in both powders after hydrogenation is the MgZn_2 phase, the slight difference in the hydrogen desorption kinetics was strongly dependent on the MgZn_2 phase. During the TDS experiments, the surfaces of the quartz tube, in which the powder samples were mounted, turned to a metallic color, so at least one elemental metal from the powder mixture, may have been evaporated during the hydrogen

Fig. 9 Thermal desorption spectra of hydrogen ($M/e = 2$) for (a) the i-phase and (b) the approximant powders after the hydrogenation at 573 K and an initial hydrogen pressure of 3.6 MPa.

desorption. Figures 10(a) and (b) show TDS spectra of zinc ($M/e = 65$) from the i-phase and the approximant powders, respectively, after hydrogenation at 573 K and at an initial hydrogen pressure of 3.6 MPa (the heating rate was 20 K/min.). Note that the units of the vertical axes (Zn ion current) are arbitrary and different from those shown in the hydrogen evolution rate (Fig. 9). In both powders, two kinds of TDS peaks corresponding to the evolution of the zinc were found at about 650 and 750 K. These peak temperatures are almost the same in both powders. However, the TDS peak at the lowest temperature side (at 650 K) is much higher for the i-phase powder than that for the approximant powder, probably because of the formation of the MgZn_2 in the i-phase powder after hydrogenation.

4. Conclusions

Mechanical alloying of elemental powder mixtures having chemical compositions of $\text{Mg}_{44}\text{Al}_{15}\text{Zn}_{41}$ produced an icosahedral quasi-crystalline (i-phase) fine powder. The subsequent heat treatment at 723 K or cooling the melt of the MA powder to room temperature transformed it to the cubic Frank-Kasper (cubic approximant) phase. After hydrogenation of these powders at a temperature of 573 K and at a hydrogen pressure of 4.2 MPa, the hydrogen solubility limit for both powders were found to be almost the same, about 16 at%, and no crystallographic structural dependence between the i-

Fig. 10 Thermal desorption spectra of zinc ($M/e = 65$) for (a) the i-phase and (b) the approximant powders after hydrogenation at 573 K and an initial hydrogen pressure of 3.6 MPa.

phase and the approximant phase was found for the hydrogen solubility. The approximant phase powder was structurally stable after hydrogenation but the i-phase powder decomposed into the approximant and the MgZn_2 intermetallic phases. Hydrogen desorption occurred at temperatures above about 600 K for both powders, accompanied by the evaporation of zinc. The desorption kinetics of hydrogen and zinc are slightly different in each powder because of the formation of the MgZn_2 phase in the i-phase powder after hydrogenation.

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REFERENCES

- 1) D. Shechtman, I. Blech, D. Gratias and J. W. Cahn: *Phys. Rev. Lett.*, **53** (1984), 1951–1953.
- 2) E. Ivanov, B. Bokhonov and I. Konstanchuk: *J. Mater. Sci.*, **26** (1991), 1409–1411.
- 3) U. Mizutani, T. Takeuchi, T. Fukunaga, S. Murasaki and K. Kaneko: *J. Mater. Sci. Lett.*, **12** (1991), 629–632.
- 4) U. Mizutani, T. Takeuchi and T. Fukunaga: *Mater. Trans., JIM*, **34** (1993), 102–108.
- 5) J. Eckert, L. Schultz and K. Urban: *Appl. Phys. Lett.*, **52** (1989), 117–

- 119.
- 6) P. L. Martin and D. A. Hardwick: *Intermetallic Compounds*, Vol. 1, Ed. by J. H. Westbrook and R. L. Fleischer, John Wiley, (1994), pp. 637–660.
- 7) D. J. Sordélet and J. M. Dubois: *MRS Bulletin*, **22** (1997), 34–37.
- 8) P. C. Gibbons and K. F. Kelton: *Physical Properties of Quasicrystals*, Ed. by Z. M. Stadnik, Springer, (1999), pp. 403–431.
- 9) K. F. Kelton and P. C. Gibbons: *MRS Bulletin*, **22** (1997), 69–72.
- 10) A. M. Viano, R. M. Stroud, P. C. Gibbons, A. M. McDowell, M. S. Conradi and K. F. Kelton: *Phys. Rev. B*, **51** (1995), 12026–12029.
- 11) A. M. Viano, E. H. Majzoub, R. M. Stroud, M. J. Kramer, S. T. Mixture, P. C. Gibbons and K. F. Kelton: *Phil. Mag. A*, **78** (1998), 131–141.
- 12) B. I. Wehner, J. Meinhardt, U. Koster, H. Alves, N. Eliaz and D. Eliezer: *Mater. Sci. Eng.*, **A226–228** (1997), 1008–1011.
- 13) C. Janot: *Quasicrystals A Primer*, 2nd ed., Clarendon Press, Oxford (1997), pp. 78–85.
- 14) V. Elser: *Phys. Rev.*, **B32** (1985), 4892–4898.