Hydrogen Pressure-Composition Isotherms for Ti₄₅Zr₃₈Ni₁₇ Amorphous and Quasicrystal Powders Produced by Mechanical Alloying

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Pressure-composition isotherms (PCTs) for amorphous and icosahedral (i) quasicrystal powders produced by mechanical alloying of $Ti_{45}Zr_{38}Ni_{17}$ powder mixtures were measured at temperatures of 473 K and 523 K at low-hydrogen pressures, lower than 0.1 MPa. Sloping plateau-like features on PCTs were observed at equilibrium hydrogen pressures lower than 1 kPa, below an H/M (hydrogen to metal atom ratio) ≈ 1.2 and ≈ 1 for the amorphous and i-phase powders respectively. The plateau-like region for the i-phase powder was steeper and narrower than that for the amorphous powder, implying some small differences between the local structures of the i-phase and the amorphous phase. After the PCT measurements, an increase in the nearest-neighbor atom spacing and an expansion of the quasilattice were observed for the amorphous and i-phase powders respectively. Impurities from some unsynthesized elemental material and a Ti_2Ni type phase were also present. These also absorbed hydrogen, shown by an expansion of their crystal lattices. However, no crystal hydride formation was observed in any of the powders.

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1. Introduction

Icosahedral (i) quasicrystals are presumed to contain more tetrahedral interstitial sites than normal crystals,¹⁾ suggesting that the i-phase could be a hydrogen-storage material if some atoms of the i-phase have an adequate affinity for hydrogen. Ti-Zr-Ni icosahedral (i) quasicrystals, in which Ti and Zr have a strong chemical affinity for hydrogen, produced by melt-spinning or annealing, can store large quantities of hydrogen, almost twice the hydrogen storage capacity of LaNi₅ by weight percent, indicating their potential as new hydrogenstorage materials.¹⁻⁵⁾ We have previously reported the formations of amorphous and i-phase powders by mechanical alloying (MA), high-pressure hydrogen loading of the powders, microstructural changes during the early stage of hydrogen cycling, and activation of the powders against hydrogen gas.^{6,7)} This paper presents preliminary results of pressurecomposition isotherm (PCT) measurements obtained at relatively low-hydrogen pressures for the amorphous and i-phase powders produced by MA.

2. Experimental Procedure

Commercially pure Ti (99.9%), Zr (99.9%), and Ni (99.9%) elemental powders were used as starting materials in this study. A powder mixture with a chemical composition of $Ti_{45}Zr_{38}Ni_{17}$ was poured into stainless-steel vials, which also contained stainless-steel balls. MA was carried out in a Fritsch Pulverisette 7 planetary ball mill in argon gas atmosphere. The details of sample handling and milling have been described previously.⁶

Hydrogen absorption PCTs at low-pressure hydrogen were measured at temperatures of 473 K and 523 K by a Sieverts' type apparatus. The powder sample, whose weight was about 0.5 g, was wrapped in an aluminum foil and was inserted into a stainless-steel tube. The tube was then evacuated to a vacuum level of 10^{-4} Pa by a turbo-molecular pump. The change in hydrogen pressure was measured by capacitance manometers, whose measurable upper limit was 0.13 MPa. The hydrogen concentration (H/M) was calculated from both the pressure change and from the weight gain after the PCT measurement using a Cahn micro-balance with a measurement accuracy of $\pm 5 \,\mu g$. The details of the Sieverts' apparatus and the PCT measurement were reported by Kim *et al.*⁸⁾ Powder X-ray diffraction (XRD) measurements were made using a Rigaku geigerflex with Cu-K α radiation at 35 kV and 30 mA to identify the phases before and after PCT measurements. The microstructures were also examined using a JEOL 2000FX transmission electron microscope (TEM) operated at 200 kV.

3. Results and Discussion

Figures 1(a) and (b) show XRD patterns for the powders after MA for 25 h and after subsequent annealing in a vacuum at 773 K for 2 h respectively. We previously reported that an amorphous state could be obtained after MA for 20h (measured by XRD) and that there was no prominent XRD peak corresponding to crystal phases, except a broad peak corresponding to the amorphous phase.⁶⁾ The present MA condition is the same as the previous one. However, the powder mixtures mechanically alloyed even after a longer time, 25 h, still have unsynthesized elemental crystals (Ti, Zr, and Ni), probably due to different batches of the elemental powders. XRD peaks corresponding to the elemental powders are not strong when compared to the background X-ray intensity. Hereafter, this powder is referred to as the amorphous powder, as in previous papers.^{6,7)} The amorphous phase transforms to the i-phase and a Ti₂Ni type crystal phase (fcc structure, lat-

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Fig. 1 X-ray diffraction patterns for the Ti₄₅Zr₃₈Ni₁₇ powder mixtures (a) after mechanical alloying for 25 h, and (b) after subsequent annealing at 773 K for 2 h. "T" marked with indices in (b) represents the Ti₂Ni type phase, and "i" represents the i-phase.

tice parameter, a = 1.21 nm) after subsequent annealing at 773 K (Fig. 1(b)), as reported previously.⁷⁾ The peaks for the i-phase in Fig. 1(b) have been indexed using the scheme reported by Bancel *et al.*⁹⁾ Hereafter, this powder is referred to as the i-phase powder, as in previous paper.^{6,7)} Figures 2(a) and (b) show TEM selected area diffraction (SAD) patterns for the amorphous and i-phase powders respectively. The SAD pattern for the amorphous powder contains a halo and some diffraction spots (indicated by arrows in Fig. 2(a)). Weak Debye-Scherrer rings due to elemental powders were also sometimes observed. These results agree well with the XRD measurement for the amorphous powder (Fig. 1(a)). The SAD pattern for the i-phase powder indicates that the i-phase is very fine and randomly oriented crystallographically.

PCTs for the amorphous and i-phase powders at temperatures of 473 K and 523 K are shown in Figs. 3(a) and (b) respectively. For both powders at both temperatures, a plateaulike region is observed, but they have a small slope. The plateau pressure increases with increasing temperature, but remains lower than 1 kPa for both powders. Amorphous alloys are normally considered to be disordered metals, without long-range topological order.¹⁰⁾ Although it is difficult to determine the local structure around hydrogen in amorphous alloy due to the absense of long-range order hydrogen atoms are considered to primarily occupy tetrahedral sites in amorphous alloys.¹¹⁾ No plateau is generally evident for amorphous phase even though plateau clearly appears for the corresponding crystalline system.¹¹⁾ A Ti-based¹²⁾ and a Zr-based¹³⁾ amorphous alloy reported recently showed clear plateau at hydrogen pressures of about 100 kPa and 2 MPa respectively at some temperatures, suggesting the possibility of amorphous hydride formation. Hydrogen pressures for PCT measurement were normally in the range between 1 kPa



Fig. 2 Selected area electron diffraction patterns for the $Ti_{45}Zr_{38}Ni_{17}$ powder mixtures (a) after mechanical alloying for 25 h, and (b) after subsequent annealing at 773 K for 2 h. The arrows in (a) indicate diffraction spots, and the indices in (b) are for the i-phase.

and several MPa. To our knowledge, there is no report for a plateau-like feature in an amorphous alloy, with an equilibrium hydrogen pressure lower than 1 kPa. The plateaulike pressures detected for the amorphous and i-phase powders in this study are lower than 1 kPa, which is lower than usually studied for PCT measurements. PCT measurements at a higher equilibrium pressure of hydrogen for our alloys are also necessary, but our results suggest that an amorphous phase may also have plateaus at lower-hydrogen pressures. As mentioned earlier, the i-phase powder also contains the Ti₂Ni type crystal phase (hereafter, this phase is referred to as the $(Ti, Zr)_2Ni$ phase to distinguish it from the binary Ti_2Ni phase). The PCT for alloys containing two or more phases can be generally obtained by superimposing the PCT for each phase, although the total hydrogen concentration (H/M) in the alloy should be adjusted by the amount in each phases of the alloy. Since no PCT data for the (Ti, Zr)₂Ni phase have been reported, it is difficult to investigate the influence of that phase on the PCT measurements for the i-phase powder. But, Buchner et al.¹⁴⁾ reported that the binary Ti₂Ni phase absorbed great amount of hydrogen interstitially, forming four kinds of hydride phases, Ti2NiH0.5, Ti2NiH, Ti2NiH2, and Ti₂NiH_{2.5}, showing clear flat plateaus at about 11 kPa (for $Ti_2NiH_{0.5}$ and Ti_2NiH), 66 kPa, and 0.1 MPa at a temperature of 423 K. Taking these results into account and assuming that the influence of Zr to the PCT is the same as that of Ti (although there is an atomic size difference between them), it is concluded that the amount of the (Ti, Zr)₂Ni phase in the i-phase powder must be very small, because the equilibrium hydrogen pressures as well as the plateau-like pressures detected in this study are far less than those for the Ti₂Ni phase. A PCT at 623 K for a Ti₄₅Zr₃₈Ni₁₇ i-phase ribbon obtained by melt-spinning, reported by Kim et al.,⁸⁾ showed that equilibrium hydrogen pressure remained low (less than 0.5 kPa) below H/M \approx 1, after which it increased sharply with increasing H/M. Although the present heating temperatures are lower than these (623 K), our PCT results are very close to those for the rapidly quenched i-phase ribbon, also indicating that the contribution of the (Ti, Zr)₂Ni phase to the present PCT is very small. We previously reported that the maximum amount of hydrogen that could be loaded into the amorphous and i-phase powders at high-pressure hydrogen was almost same, about 60 at%,6) indicating structural similarities, such as the number and type of interstitial sites favored by hydrogen, between the amorphous phase and the i-phase. Comparing the shapes of the PCTs reported here for the amorphous and i-phase powders, the plateaus for the i-phase powder are steeper and narrower than those for the amorphous powder, suggesting that the local structure, which influences the binding energy of hydrogen with the surrounding metal atoms, of the i-phase is slightly different from that of the amorphous phase. The enthalpy and entropy changes of hydriding at 0.5 of H/M for the i-phase powder, which can be estimated roughly from the two PCT results, are about $-48 \text{ kJ}(\text{mol } \text{H}_2)^{-1}$ and $-43 \text{ JK}^{-1}(\text{mol } \text{H}_2)^{-1}$, indicating that a temperature needed for the equilibrium hydrogen pressure of 0.1 MPa is about 1100 K, which is very close to that for a titanium hydride. PCT measurements at different temperatures are now in progress, and high-pressure PCT measurements are also planned. The final results of these studies will be reported elsewhere.

XRD patterns for the amorphous powder after PCT measurements at 473 K and 523 K are shown in Figs. 4(a) and (b) respectively. The broad amorphous peak and small peaks corresponding to elemental Ti and Zr shift to lower angles with hydrogenation (when compared with XRD pattern before PCT measurement shown in Fig. 1(a)), indicating an expansion of the nearest neighbor atom distances and the crystal lattices in the amorphous and crystal elements respectively. Because Ni has no strong chemical affinity for hydrogen, the (111) peak of Ni has not shifted to lower angle after the PCT measurements. No crystal hydride phase was detected in the amorphous powders, even by TEM.

XRD patterns for the i-phase powder after PCT measurements at 473 K and 523 K are shown in Figs. 5(a) and (b) respectively. After the PCT measurement, XRD peaks corresponding to the i-phase and the $(Ti, Zr)_2Ni$ phase shift to the lower angles, indicating exapssions of the quasilattice and the crystal lattice. As reported previously,⁷⁾ the (511) peak of the $(Ti, Zr)_2Ni$ phase appears on the higher angle side of the (110000) of the i-phase due to a difference in the degree



Fig. 3 Pressure-composition isotherms for (a) the amorphous and (b) the i-phase powders at temperatures of 473 K and 523 K.



Fig. 4 X-ray diffraction patterns for the amorphous powder after the pressure-composition isotherm measurements at (a) 473 K and (b) 523 K.

of expansion between the quasilattice and the crystal lattice after the PCT measurement. The quasilattice constants¹⁵⁾ before and after PCT measurement at 523 K (H/M \approx 1.3) are calculated to be 0.519 nm and 0.550 nm respectively, corresponding to a 6.0% expansion of the quasilattice. The lattice parameters of the (Ti, Zr)₂Ni phase before and after the PCT measurements, on the other hand, are 1.21 nm and 1.27 nm respectively, indicating a 5.0% expansion of the lattice. The variations of the lattice parameters of the Ti₂Ni phase after forming four kinds of hydride, Ti₂NiH_{0.5}, Ti₂NiH, Ti₂NiH₂, and Ti₂NiH_{2.5}, were also reported by Buchner *et al.*¹⁴⁾ in connection with the PCT measurements shown earlier; the



Fig. 5 X-ray diffraction patterns for the i-phase powder after pressure-composition isotherm measurements at (a) 473 K and (b) 523 K. "T" marked with indices in (a) represents the Ti₂Ni type phase, and "i" represents the i-phase.

lattice parameter of the Ti₂Ni crystal increased by approximately 5.3% with increasing hydrogen concentration. This suggests that the (Ti, Zr)₂Ni phase absorbed almost the maximum amount of hydrogen in the lattice and may have formed the (Ti, Zr)₂NiH_{2.5} phase. In our previous hydrogenation study for the i-phase powder at high-pressure hydrogen,⁷¹ we reported a 2.5% increase of the lattice parameter of the (Ti, Zr)₂Ni phase with a 6.6% increase of the quasilattice constant of the i-phase. Mintz *et al.*¹⁶⁾ reported that oxygen dissolved in a Ti₂Ni phase up to 14 at% and that the presence of oxygen reduced the maximum hydrogen uptake capacity of the Ti₂NiO_x compound, suggesting that the oxygen concentration in the (Ti, Zr)₂Ni phase in our previous study is more than that in this study.

4. Conclusions

Preliminary results from hydrogen pressure-composition isotherm (PCT) measurements for amorphous and i-phase powders produced by mechanical alloying were reported. Sloping plateau-like pressures were observed at equilibrium hydrogen pressures lower than 1 kPa for both powders. Following the plateau equilibrium pressure increased relatively sharply with increasing H/M (hydrogen to metal atom ratio). The plateau-like region for the i-phase powder was steeper and narrower than that for the amorphous powder, implying that the local structure, which influences the binding energy of hydrogen with the surrounding metal atoms, is slightly different between the i-phase and the amorphous phase. The enthalpy and entropy changes of hydriding at H/M = 0.5 for the i-phase powder, estimated tentatively from the two PCT results, were about $-48 \text{ kJ}(\text{mol H}_2)^{-1}$ and $-43 \text{ JK}^{-1}(\text{mol H}_2)^{-1}$ respectively. No crystal hydride formation was observed in either powder after PCT measurements at 473 K and 523 K.

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