Analysis of local sites of deuterium in $Ti_{53}Zr_{27}Ni_{20}$ alloys

Sang-hwa Lee[a,b], Ashfia Huq[c], Wenge Yang[d], Jaeyong Kim[a,b,*]

HPSTAR
676-2018

[a] Department of Physics, Hanyang University, 04763 Seoul, South Korea
[b] HYU-HPSTAR-CIS High Pressure Research Center, Hanyang University, 04763 Seoul, South Korea
[c] Spallation Neutron Source, Oak Ridge National Laboratory, 37831, TN, USA
[d] Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, PR China

ARTICLE INFO

ABSTRACT

TiZr-based alloys are known to absorb a large amount of hydrogen, and as such have been proposed as candidate materials for hydrogen storage applications. For the easy synthesis of samples, as-cast TiZrNi alloys were prepared and deuterated using a lab-built isotherm measurement system to locate the atomic positions of host metals with deuterium before evaluating their technical usefulness. Results of Rietveld refinements measured from simultaneous fit of X-ray and neutron diffraction patterns revealed that slowly cooled $Ti_{53}Zr_{27}Ni_{20}$ alloys have a C14 Laves phase ($P6_3/mmc$) with lattice constants of a = 5.27 and c = 8.31 Å with atomic compositions of 52.25, 28.27 and 19.48 at. % for Ti, Zr, and Ni, respectively. Deuterium atoms sit in tetrahedral sites formed by Ti_2Zr_2 and Zr_2Ni_2. The exact locations of the deuterium atoms are (0.412, 0.462, 0.594) and (0.430, 0.569, 0.250) of Wyckoff positions in a xyz coordinate system. The formation of a hydride phase was unavoidable even at low concentrations of deuterium, and was identified to TiD_2.

1. Introduction

TiZr-based alloys are known to store a large amount of hydrogen due to the high affinity of host metal atoms with hydrogen [1–3]. In fact, alloys made with TiZrNi store hydrogen at a maximum of a hydrogen to host metal atom ratio (H/M) of near 2 at ambient condition [4–6]. In this alloy, the presence of Ni prevents the sample from increasing the absorption energy of hydrogen, moderating the binding energy and making it a good candidate material for hydrogen storage. TiZrNi alloys exhibit various phases depending on the cooling rates from liquids. When this alloy was slowly cooled, a C14 Laves phase was formed, while a quasi-periodic structure was found if the alloy was rapidly quenched [7].

The C14 or $MgZn_2$-type phase is a hexagonal structure ($P6_3/mmc$) with a general formula of AB_2, where A is the larger of the two elements. The radial ratio of A to B is 1.225 for hard spheres. In a TiZrNi system, the Laves phase coexists with icosahedral quasicrystals in liquids and forms first at ambient condition in a wide range of Ti, Zr and Ni compositions [8]. Understanding the structure and hydrogen atom positions in the C14 phase is important because the alloy absorbs hydrogen in tetrahedral coordinated interstitial sites with a total of 17 interstices per AB_2 structure [9]. Due to the structural similarity of the phase with quasicrystals, recent studies have proved that the capacity of absorbed hydrogen in $Ti_{53}Zr_{27}Ni_{20}$ quasicrystals exceeds 3.94 wt %

at 40 GPa [10].

It is believed that the nucleation process and the structure of the C14 phase can provide clues on the formation of the stable icosahedral phase, and hydrogen atoms in this system can probe the local structure of quasicrystals. Because of its simple preparation, once the structural stability of the C14 phase is known, as-cast samples are expected to replace the meta-stable alloys for hydrogen storage application. However, a few studies have reported on the structure and atomic positions in deuterated alloys of $Ti_{53}Zr_{27}Ni_{20}$ alloys that have a similar hydrogen absorption property with the quasicrystals at the same composition. Therefore, it is very important to identify the locations of the host metal and hydrogen atoms in as-cast C14 Laves phase of $Ti_{53}Zr_{27}Ni_{20}$ alloys, and to evaluate the hydrogen absorption capacity under ambient conditions.

The structure and exact atomic positions with occupancies of the constituent elements of this phase were determined using a Rietveld refinement, which was successfully obtained by simultaneous fit to both X-ray and neutron diffraction data. Deuterium was loaded into the sample to achieve an effective scattering cross-section area of the neutron diffraction data.

2. Experimental details

Raw materials of Ti, Zr and Ni were purchased from Alfa Aesar with

---

purities of 99.99, 99.94 and 99.90 %, respectively. The mass of each element was measured using an electric balance with 10^{-4} g of accuracy. As-cast ingots were prepared by arc-melting with 2.5 g of the mixed elements on a Cu hearth with water-cooling in an Ar atmosphere. The melting and cooling process was repeated three times for homogeneity of the samples by flipping the ingot.

It is known that a thick oxygen layer covers the surface of the sample and prevents the sample from hydrogen penetration. For loading of hydrogen at low hydrogen pressure, an oxygen layer was removed by applying an Ar-plasma etching and a thin Pd coating was applied to prevent further oxidation when the samples were exposed to air [11]. Due to the exothermic reaction of hydrogen and the relatively high binding energy of hydrogen with Ti and Zr atoms, slow loading with partial absorption of hydrogen was required. To introduce the desired amount of hydrogen in the sample, a laboratory-built Pressure-composition-Temperature (P-c-T) system was employed and the change of hydrogen pressure was monitored. As a result, deuterium was loaded with a deuterium to host metal atom ratio (D/M) of 1.05, which is nearly half of the reported maximum value [9].

Powder X-ray and neutron diffraction data for the samples were measured using X-ray diffractometer (D-8 Discover, Bruker, Cu-K$_\alpha$ radiation) and at POWGEN/BL-11A beamline (wave length of 1.066 Å) of spallation neutron source at Oak Ridge national laboratory, respectively. The structure and atomic positions of host metal and deuterium in Ti$_{53}$Zr$_{27}$Ni$_{20}$ samples were analyzed using General Structure Analysis System (GSAS) [12]. Atomic positions were simulated and visualized using a Visualization for Electronic and STructural Analysis (VESTA) software.

3. Results and discussions

The results of X-ray and neutron diffraction patterns measured from as-cast Ti$_{53}$Zr$_{27}$Ni$_{20}$ alloy samples are shown in Fig. 1. The simultaneous fit to X-ray and neutron diffraction data revealed that the sample is a single phase of a hexagonal closed packed structure (space group 194, $P6_3/mmc$) with lattice constants of a = 5.27 and c = 8.31 Å, which is very close to the ones reported by Majzoub et al. [13]. The Rietveld refinement results, including atomic coordinates and occupancies, are shown in Table 1. The best value of χ^2, which indicates the statistical goodness of the fit, for X-ray diffraction, and neutron diffraction

Table 1
Rietveld refinement results of as-cast Ti$_{53}$Zr$_{27}$Ni$_{20}$ sample measured from the combined X-ray and neutron diffraction data (a = 5.27, c = 8.31 Å).

Atom	Wyckoff position	x	y	z	Occupancy	Uiso
Ti/Ni	2a	0	0	0	0.82/0.18	0.005/0.198
Zr/Ti	4f	0.333	0.667	0.066	0.80/0.20	0.010/0.055
Ti/Ni	6h	0.837	0.674	0.250	0.46/0.54	0.057/0.008

patterns were 2.58 and 3.46, respectively. The results showed that in the AB$_2$ structure, A-sites (4f) were occupied either by Ti or Zr, whereas the B-sites (2a, 6h) were positioned by Ti or Ni. The summation of the partial occupancies of the sites yielded the actual concentrations of 52.25, 28.27 and 19.48 at. % for Ti, Zr and Ni, respectively, which is very close to the nominal composition. This result demonstrates the uniformity of the sample with no mass loss of elements during the preparation.

To analyze the structure of deuterated Ti$_{53}$Zr$_{27}$Ni$_{20}$ alloy samples, deuterium was loaded by using a computer-controlled P-c-T system at 300 °C. The amount of absorbed deuterium calculated by gas law was D/M value of 1.05. The X-ray and neutron diffraction patterns with simultaneous fit of Rietveld refinement for deuterated Ti$_{53}$Zr$_{27}$Ni$_{20}$ alloys are shown in Fig. 2. To obtain the best fit within a reasonable physical decoration, we fixed the occupancies of the host metals and refined the deuterium positions and occupancies. In fact, X-ray and neutron diffraction patterns revealed that the sample maintained the C14 structure with a hint of a presence of an impurity phase. The values of lattice constants increased to a = 5.54 and c = 9.04 Å, which suggests the cell volume expansion from 201 to 223 Å^3, after partial deuteration. The formation of an impurity phase was noted at the momentum vector q values of 2.4 in X-ray diffraction and from 2.7 to 3.1 in neutron diffraction patterns (see Fig. 2(a) and (b)). The impurity phase was not indexed by (Ti,Zr)H$_2$ or ZrH$_2$ phase (PDF: 17–0314) that are frequently observed in Ti$_{45}$Zr$_{38}$Ni$_{17}$ alloys. Rather, a q value of 2.4 matched with (111) peak of TiH$_2$ (PDF: 65–1028). Due to the lack of further diffraction peaks at a higher q, however, a complete analysis for the impurity phase was not possible. After excluding of the impurity phase, the χ^2 values for the neutron diffraction data significantly decreased from 15.54 to 7.66.

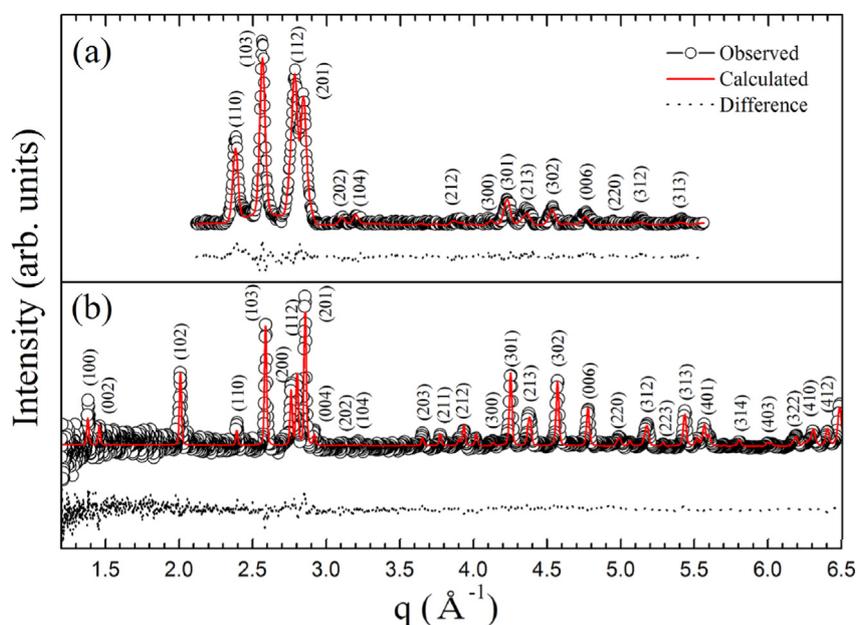The positions and occupancies of metals and deuterium are listed in

Fig. 1. Results of Rietveld refinements for (a) X-ray and (b) neutron diffraction patterns measured from as-cast Ti$_{53}$Zr$_{27}$Ni$_{20}$ alloys. The diffraction data and calculated peaks for C14 phase are shown with circles and solid lines, respectively. The difference between the data and simulation is shown in dots.
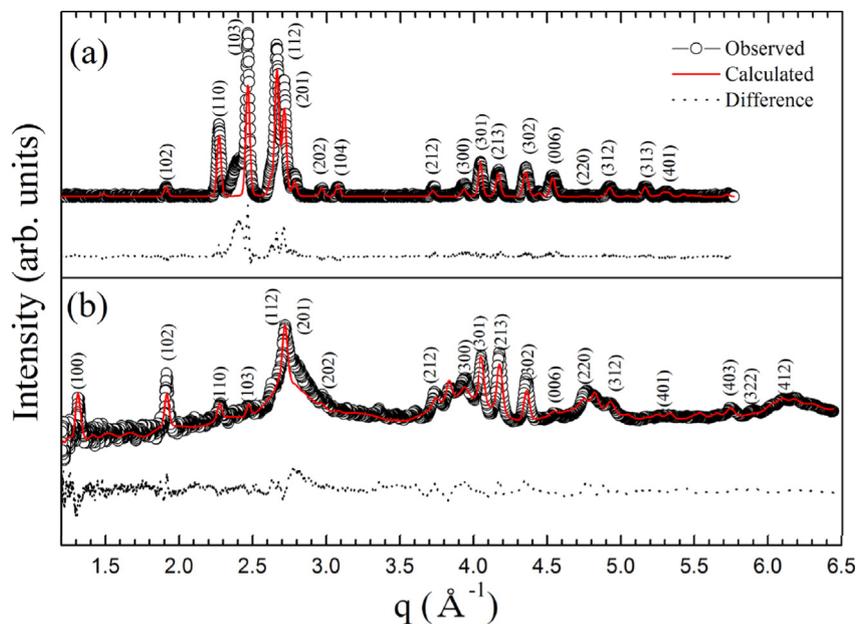
Fig. 2. Results of Rietveld refinements for (a) X-ray and (b) neutron diffraction patterns measured from partially deuterated $Ti_{53}Zr_{27}Ni_{20}$ alloys. The diffraction data and calculated peaks for C14 phase are shown with circles and solid lines, respectively. The difference between the data and simulation is shown in dots.

Table 2
Rietveld refinement results of deuterium loaded $Ti_{53}Zr_{27}Ni_{20}$ sample measured from the combined X-ray and neutron diffraction data (D/M: 1.05, a = 5.54, c = 9.04 Å).

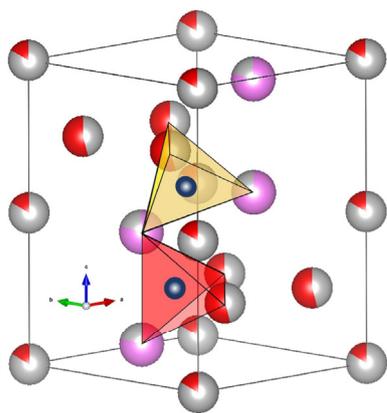| Atom	Wyckoff position	x	y	z	Occupancy	Uiso
Ti/Ni	2a	0	0	0	0.82/0.18	0.005/0.198
Zr/Ti	4f	0.333	0.667	0.075	0.80/0.20	0.010/0.055
Ti/Ni	6h	0.835	0.670	0.250	0.46/0.54	0.057/0.008
D	12k	0.412	0.462	0.594	0.40	0.005
D	6h	0.430	0.569	0.250	0.16	0.032

Fig. 3. Structure modeling of as-cast $Ti_{53}Zr_{27}Ni_{20}$ C-14 Laves phase with deuterium positions is illustrated by using VESTA. Ti, Zr, Ni and D are represented in grey, pink, red, and blue, respectively. The fraction of the color of the atom represents the occupancy of the shared site. The tetrahedrons are indicated with solid lines. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2. According to the results, there is no particular site that is 100% occupied by deuterium. Instead, deuterium atoms are uniformly distributed in the sample, and partially take in the available interstitial sites. If deuterium atoms were not uniformly loaded, peak splitting in the patterns should be noted. In a C14 Laves phase, hydrogen is known to locate in the center of tetrahedral interstitial sites [14–16]. There are

three tetrahedral interstitial sites to host deuterium in the system; 24l, 12k, 6h formed by Zr_2TiNi, Ti_2Zr_2, Zr_2Ni_2. Our best fit to neutron diffraction data revealed that deuterium fills the 12k and 6h Wyckoff sites with occupancies of 0.40 and 0.16, respectively. The distances between Ti-Zr in Ti_2Zr_2 tetrahedron at 12k site increased from 3.04 to 3.29 Å, and the one of between Zr-Zr at 6h site increased from 3.06 to 3.33 Å. One needs to note that 24l site is still unoccupied because of the partial absorption of deuterium. The results of the refinement yielded that the actual amount of deuterium was D/M of 0.74. The difference of the value compared to the one estimated by P-c-T measurement system was due to the formation of a hydride phase after deuterium loading. Modeling of the atomic positions for the host metals and deuterium are illustrated in Fig. 3 using VESTA software.

4. Conclusions

To investigate the local structure of C14 Laves phase in TiZr-based alloys and to evaluate the potential of these materials for hydrogen storage applications, as-cast $Ti_{53}Zr_{27}Ni_{20}$ samples were prepared by using an arc-melting of elements and deuterated using a computer controlled gas-handling system. The positions and partial occupancies of host metal and deuterium atoms were determined by simultaneous fit of X-ray and neutron diffraction data using a Rietveld refinement method. The atomic concentrations of the host metals in as-cast alloys were matched with the nominal ones. The estimation of the atomic positions and concentrations of deuterium in partially deuterated samples revealed that 11% of volume expansion occurred after the deuteration. Deuterium atoms reside in tetrahedron interstitials formed by Ti_2Zr_2 and Zr_2Ni_2. The difference between the nominal and actual amount of deuterium in the sample was attributed to the formation of TiD_2 hydride phase. These findings are valuable in that they identify the locations of host metals and deuterium in TiZrNi alloys of the Laves phase, and can be used for the evaluation of the materials for hydrogen storage applications.

References

[1] R.M. Stroud, A.M. Viano, P.C. Gibbons, K.F. Kelton, S.T. Misture, Appl. Phys. Lett. 69 (1996) 2998.
[2] S.H. Lee, S.B. Choi, E. Ito, J.Y. Kim, J. Nanosci. Nanotechnol. 10 (2010) 7680.
[3] A.Yu Moroov, E.I. Isaev, Yu Kh Vekilov, Crystallogr. Rep. 52 (6) (2007) 975.
[4] K.F. Kelton, J.J. Hartzell, R.G. Hennig, V.T. Huett, A. Takasaki, Phil. Mag. 86 (2006) 957.
[5] R.G. Hennig, K.F. Kelton, A.E. Carlsson, C.L. Henley, Phys. Rev. B 67 (2003) 134202.
[6] R.G. Henning, E.H. Majzoub, A.E. Carlsson, K.F. Kelton, C.L. Henley, W.B. Yelon, S. Misture, Mater. Sci. Eng., A 294–296 (2000) 361.
[7] R.L. Berry, G.V. Raynor, Acta Crystallogr. 6 (1953) 178.
[8] J.P. Davis, E.H. Majzoub, J.M. Simmons, K.F. Kelton, Mater. Sci. Eng., A 294–296 (2000) 104.
[9] I. Levin, V. Krayzman, C. Chiu, K.-W. Moon, L.A. Bendersky, Acta Math. 60 (2012) 645.
[10] To be published.
[11] J.Y. Kim, P.C. Gibbons, K.F. Kelton, J. Alloy. Comp. 266 (1998) 311.
[12] C. Larson, R.B.V. Dreele, Los Alamos National Lab, Report No. LAUR (1994), pp. 86–748.
[13] E.H. Majzoub, R.G. Henning, K.F. Kelton, Phil. Mag. Lett. 83 (2003) 65.
[14] H.A. Peretti, A. Visintin, L.V. Mongni, H.L. Corso, J. Andrade Gamboa, D. Serafini, W.E. Triaca, J. Alloy. Comp. 354 (2003) 181.
[15] A. Visintin, H.A. Peretti, C.A. Tori, W.E. Triaca, Int. J. Hydrogen Energy 26 (2001) 683.
[16] D.M. Kim, S.W. Jeon, J.Y. Lee, J. Alloy. Comp. 279 (1998) 209.