Local atomic structure around Ni, Nb, and Zr atoms in Ni-Nb-Zr-H glassy alloys

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Abstract. In order to elucidate the hydrogen effect on the atomic configuration in the Ni-Nb-Zr glassy alloys, we measured Ni, Nb, and Zr K-edge XAFS spectra of the Ni-Nb-Zr glassy alloy films with two different chemical compositions, i.e., Ni42Nb28Zr30 and Ni36Nb24Zr40, and their hydrogen-charged ones, i.e., (Ni42Nb28Zr30)0.91H0.09 and (Ni36Nb24Zr40)0.89H0.11. The Fourier transforms of the XAFS oscillations of these samples clearly shows that there is a significant difference in the structural response between the Zr30at.% and the Zr40at.% alloys when hydrogen atoms are charged. The curve-fitting analysis indicates that the hydrogenation does not alter the local alignment around the three metal atoms for the Zr30at.% alloy, but for the Zr40at.% alloy; it elongates the inter-atomic distances of Zr-Zr, Zr-Nb and Nb-Ni. On the basis of the curve fitting analysis, we propose the distorted icosahedral Zr5Ni5Nb3 cluster models. The XANES spectra at each (Ni, Zr and Nb) edge of (Ni36Nb24Zr40)0.89H0.11 also present the distinct shape from the other samples. The pre-edge peak (shoulder) vanishes or weakens, suggesting the conversion of the electronic state of the metal ions owing to the hydrogenation. The post-edge energy region shows clear multi-scattering effects from hydrogen atoms by charging these.

1. Introduction

Recently, a dc current-induced voltage oscillation was observed at room temperature in (Ni36Nb24Zr40)0.901H0.099 glassy alloy ribbons of about 1-mm width and 30-μm thickness and an electrode distance of 20 mm [1]. The I-V characteristic provided evidence of the Coulomb staircase at ~300 K. However the mechanism of this phenomenon has not been clarified yet. The structural model can give the basic information on the phenomenon of the Coulomb oscillation. Thus, in order to elucidate the hydrogen effect on the atomic configuration in the Ni-Nb-Zr glassy alloys, we measured Ni, Nb, and Zr K-edges XAFS spectra of the Ni-Nb-Zr glassy alloy films with two different chemical
compositions, i.e., \( \text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{30} \) (Zr30-H0) and \( \text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40} \) (Zr40-H0), and their hydrogen-charged ones, i.e., \( (\text{Ni}_{42}\text{Nb}_{28}\text{Zr}_{30})_{0.91}\text{H}_{0.09} \) (Zr30-H9) and \( (\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40})_{0.89}\text{H}_{0.11} \) (Zr40-H11).

In this proceeding, at first, the results of the EXAFS analysis, of which a part has been reported in [2], are briefly described. The XANES spectra of these glassy alloys are substantially presented, and the alteration in pre-edge- and post-edge-spectral features is discussed in terms of the coordinating position of the hydrogen atoms.

2. Experiments

The amorphous alloy ribbons of Zr30–H0 and Zr40–H0 are made from their argon arc-melted ingots by rotating wheel methods under an argon atmosphere. The width and thickness of the ribbons were \( \sim 2.5 \text{ mm} \) and \( 16–26 \mu\text{m} \), respectively. Hydrogen was charged electrolytically in 0.5 M H\(_2\)SO\(_4\) and 1.4 g/L H\(_2\)NCSNH\(_2\) at room temperature with the current densities of 30 A/m\(^2\) [3]. We used hydrogen-doped samples of Zr30–H9 and Zr40–H11 in comparison with the Zr30–H0 and the Zr40–H0 alloys.

The XAFS spectra were measured at the bending magnet beamline BL14B2 of SPring-8 in Hyogo, Japan [4]. The incident x-rays were monochromatized by a silicon double crystal monochromator. The net planes used are (311) for the Nb and Zr K-edges and (111) for the Ni K-edge. The intensities of the higher harmonics of the incident x-rays were reduced by two Rd-coated mirrors. The spectra were taken in a normal transmittance mode. To obtain the appropriate x-ray absorption intensity, the two sheets of ribbon were stacked in the Nb K- and Zr K-edge measurements, while one sheet of ribbon was in optimum thickness for the Ni K-edge measurements. The samples were cooled down to \( \sim 20 \text{ K} \) in order to reduce thermal disorder. The XAFS spectra were analyzed by codes Athena and Artemis [5]. The curve-fitting analysis was carried out in \( R \)-space, where the amplitude reduction factor, \( S_0^2 \), is assumed to be unity.

3. Results and discussion

3.1. Fourier transforms of EXAFS oscillation and curve-fitting analysis

![Figure 1](image)

Figure 1. The magnitudes of the FTs of \( k^3 \)-weighted XAFS oscillations (\( |F(r)| \)) of Zr30–H0 (dotted lines), Zr30–H11 (dashed lines), Zr40–H0 (dashed-dotted lines), and Zr40–H11 (solid lines) at (a) Ni, (b) Nb, and (c) Zr K-edges.

The magnitudes of the Fourier transforms (FTs) of the \( k^3 \)-weighted EXAFS oscillations (\( |F(r)| \)) of the glassy alloys are depicted in figures 1(a)–1(c) for Ni, Nb, and Zr K-edges, respectively. The analyzed FT ranges are 2.7–13.3, 3.0–12.0, and 2.9–13.5 Å\(^{-1} \) for the Ni, Nb, and Zr K-edges, respectively. Note that the phase shift correction has not been carried out.

As can be seen in figure 1, there is a close resemblance between the FT spectra of Zr30–H0 and Zr30–H9 for each absorption edge. On the other hand, the FT spectra of Zr40–H0 are clearly different from those of Zr40–H11. The height of first nearest neighbor peak of the Zr40 at.% alloy decreases significantly for all the three K-edges after hydrogen charging. There is also a significant difference between Zr40–H0 and Zr40–H9 in the shape of FTs of the Nb and Zr K-edges around \( r = 2.6–3.5 \text{ Å} \).
These results clearly indicate that hydrogen doping essentially does not alter the local structures around the three atoms for the Zr30at.% alloy but fairly modifies those for the Zr40at.% alloy.

In order to analyze the results quantitatively, the curve-fitting analysis has been carried out with the following conditions. For Nb K-edge, only the first neighbor peaks (assumed as Nb-Ni) are treated. For Zr K-edge, the first and second nearest neighbor peaks (assumed as Zr-Ni and (Zr-Zr/Zr-Ni), respectively) are treated in the fitting analysis. It is supposed that the second nearest neighbor peak consists of Zr-Zr and Zr-Nb, but collected them into one shell, assuming the same backscattering amplitude and phase shift for the both the paths. The first nearest neighbor peak in Ni K-edge is probably derived from at least three contributions (Ni–Ni, Ni–Nb, and Ni–Zr). Consequently, the number of the fitting parameters becomes so large that we could not obtain reliable fitting results for Ni K-edge.

The results of the analysis are summarized as follows:
(1) The Nb-Ni distance of Zr30at.% alloy is essentially unchanged (2.55 → 2.54 Å), but that of Zr40 at.% alloy becomes longer (2.54 → 2.59 Å), after the hydrogenation.
(2) The Zr–Ni distances for the Zr30 and Zr40at.% alloys are almost identical (2.63–2.64 Å), independent of hydrogen treatment.
(3) The Zr–Zr/Zr–Nb distances of Zr30at.% alloys are essentially unchanged (3.24→3.25 Å), but the that of the Zr40at.% alloy significantly elongates (3.25→3.33 Å), after the hydrogenation.

The hydrogen-induced expansion of the Zr–Zr distance has been also reported by Sakurai et al. [6] on (Ni0.6Nb0.4)100–xZr x (x=30, 50) glassy alloys by the Zr K-edge XAFS and x-ray diffraction [7]. However, the expansion of Nb–Ni distance of the Zr40at.% alloy has not been reported by the others. The difference in the structural response between Zr30 and Zr40at.% alloys probably comes from the difference in site where hydrogen atoms are located. In Zr30at.% alloy, hydrogen atoms plunge into somewhere outside the clusters, since no significant change in bond length was observed. The elongation of Zr–Zr/Zr–Nb and Nb–Ni distances in Zr40–H11 alloy is associated with an occupation of hydrogen in tetrahedral sites surrounded by Zr and Nb or Zr, Nb, and Ni atoms in the clusters.

Based on the above-mentioned results, we propose two probable distorted icosahedron cluster models with the chemical composition of Zr 5Ni 5Nb 3 for the Zr–Nb–Ni ternary glassy alloys [2]. It is known that icosahedronlike polyhedra play an important role to stabilize the structure of metal-metal-type glassy alloys [8]. In fact, the average coordination numbers calculated for both cluster models fairly agree with the coordination numbers estimated by XAFS.

3.2. XANES
Figure 2 shows the XANES spectra of the glassy alloys at the K-edge of (a) Ni, (b) Nb, and (c) Zr K-edges. The intensities are normalized by the edge-jump for comparison.

![Figure 2](image-url). The XANES spectra of Zr30–H0 (dotted lines), Zr30–H11 (dashed lines), Zr40–H0 (dashed-dotted lines), and Zr40–H11 (solid lines) at (a) Ni, (b) Nb, and (c) Zr K-edges.
The rather weak but explicit pre-edge peaks (Ni K-edge) or shoulders (Nb and Zr K-edges) are recognized at the edge for all elements except in the Zr40-H11, indicated by arrows in the figures. The pre-edge peaks are usually observed in at the K-edge XANES spectra of 3d or 4d transition metals, and assigned to the transition from a 1s state to a nd state. In the case of an isolated atom, the electron transitions with the total angular momentum change of \(\Delta L = 2\) induced by absorbing photons, e.g. \(s \rightarrow d\) or \(p \rightarrow f\), are essentially dipole-forbidden, because the both initial and final states have a same parity. In the solid state, however, when the site position of the component of a material is non-invariant under the inversion operation, these transitions are partially allowed because of the mixing of the different parity through the crystal field or the lattice vibrations of odd types. As can be seen in figure 2, the pre-edge peaks of the XANES spectra of Zr40at.% alloy are substantially weakened by hydrogenation at the Nb and Zr K-edges. In contrast with Nb and Zr K-edges, the pre-edge peak at the Ni K-edge is less affected by the hydrogenation. These facts suggest that the hydrogen atoms occupy the highly symmetric sites surrounding at Nb or Zr atom to prevent the \(d \rightarrow p\) mixing, and the less hydrogen atoms may exist around the Ni atoms in Zr40-H11. The results of XANES are in consistent with the results described in Sect 3.1., which indicates that the absorbed hydrogen atoms surround preferentially Nb and Zr atoms [2].

Furthermore, the post-edge spectra support the analysis described above. From figure 2 (a), the post-edge spectrum for the Ni K-edge is less affected by the hydrogenation. On the other hand, these for the Nb and Zr K-edges are rather strongly modified by the hydrogenation. Here, it should be noticed that the modification shows similar tendency in both the Nb and Zr K post-edges. This finding implies that the hydrogen atoms coordinate around these atoms in a similar manner in both cases because the multi-scattering paths by the hydrogen atom surrounding these metal atoms are analogical. These results are consistent with those of the XAFS analysis. Since the kinetic energy of photo-electron in XANES region is much lower than that in EXAFS region, the spectra will directly affected even by light atoms such as H atoms. Thus, the XANES part of the XAFS spectra is more sensitive to the coordination of light atoms such as hydrogen than the EXAFS part.

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