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Depth Profiles of Absorbed Hydrogen in Ni-Nb-Zr Amorphous Alloy Ribbons by Glow Discharge Optical Emission Spectroscopy

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Abstract

Depth profiles of absorbed hydrogen introduced by electrochemical charging and light elements were analyzed in Ni-Nb-Zr-H amorphous alloy ribbons using a glow discharge optical emission spectrometer. It was clarified that the absorbed hydrogen was comparatively well-distributed on the sample surface and that the content of the hydrogen decreased with increasing depth from the surface. That is, the amount of absorbed hydrogen on the surface was about 17 at %, while that inside the specimens decreased to several atomic percent. The depth profiles of the hydrogen which were close to the surface were slightly different between those on the roller side and those on the free side in the melt-spun ribbon. The difference is thought to originate from the existence of oxygen impurity on the surface and from the difference of the Zr content.

Keywords

Amorphous Ribbon, Hydrogen Absorption, Glow Discharge Optical Emission Spectroscopy, Depth Profile

1. Introduction

It has been known that Ni-based bulk metallic glassy alloys indicate high thermal stability, ultra-high strength, good ductility and excellent corrosion resistance [1] [2]. In addition of comparatively low material cost, Ni-based bulk metallic grassy alloys are thought to be promising candidates for engineering materials. The Ni-Nb-

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Zr ternary alloy system has been known to form an amorphous phase in a wide concentration region by rapid quenching, and furthermore, grassy alloys were also synthesized in the range of 50 to 70 at% Ni, 5 to 35 at% Nb and 5 to 45 at% Zr [3]. Some interesting properties of this system have been intensively investigated. Excellent hydrogen permeability in melt-spun amorphous $(Ni_{0.6}Nb_{0.4})_{50}Zr_{50}$ alloy exceeding that of Pd has been reported by Yamaura *et al*. [4] [5], and mechanical properties of hydrogen absorbed amorphous ribbons have also been investigated by Kawashima *et al*. [6]. Recently, Fukuhara *et al*. have reported very unique electrical transport properties, such as super conductivity, electron avalanche behaviors and the Coulomb-blockade oscillations, in hydrogen absorbed amorphous ribbons of $[(Ni_{0.6}Nb_{0.4})_{1-x/100}Zr_{x/100}]_{100-y}H_y$ ($30 < x < 50$, $0 < y < 20$) [7] [8]. They have pointed out that a local structure exists and that the localization effect of the hydrogen outside and/or inside spaces of distorted icosahedral $Zr_5Ni_5Nb_3$ clusters plays important roles in their various electrical transport properties.

In our previous investigations, we reported that the amount of hydrogen absorbed by electrochemical charging in a $Ni_{36}Nb_{24}Zr_{40}$ amorphous alloy ribbon can be controlled by changing the current density [9]. By systematic investigations, it was clarified that the magnitude of the temperature coefficient of the resistivity increased with an increase of the absorbed hydrogen in amorphous ribbons and that the electrical resistivity depended on time, that is, the absolute value of the electrical resistivity increased gradually with showing two-steps increasing. It has been thought that such behavior is due to the migration of hydrogen from the sample surface. Therefore, it is necessary to analyze the behavior of the hydrogen as well as the direction of the depth in the amorphous alloy ribbon in order to clarify the previously reported behavior of the unique electrical resistivity. In the present study, we analyzed the content of light elements as well as details of the composition of the constituent elements with the depth of the ribbon specimens of $Ni_{36}Nb_{27}Zr_{37}$ alloy containing absorbed hydrogen introduced by electrochemical charging.

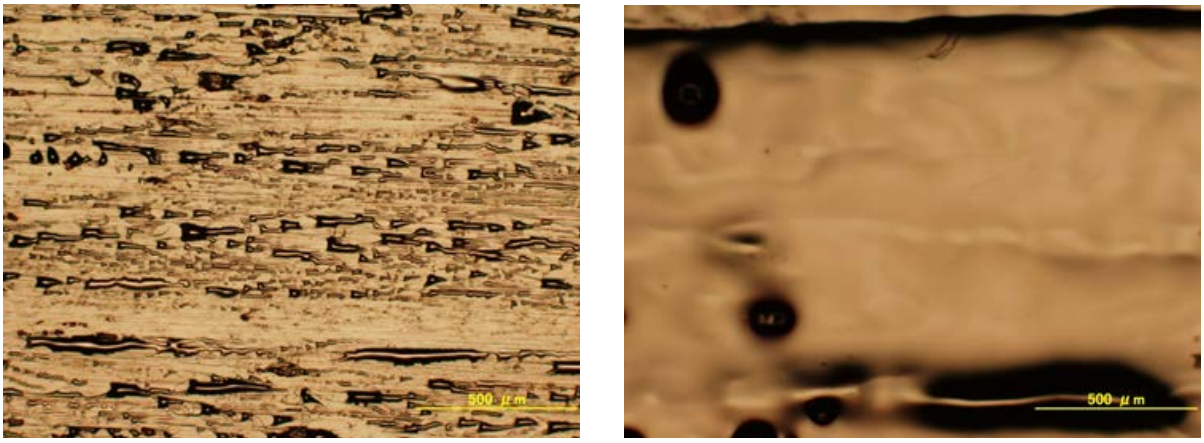
2. Experimental Procedures

Mother alloy of Ni-Nb-Zr was prepared by arc melting in an argon atmosphere and amorphous ribbons were made by a single roller melt-spinning technique. The roll speed was about 25 m/s. The thickness and width of the fabricated ribbon were 64 μm and 10 mm, respectively. Specimens with absorbed hydrogen were made by electrochemical charging in 0.5 M H_2SO_4 + 1.4 g/L thiourea (H_2NCSNH_2), the liquid temperature being kept at 300 K. Electrochemical charging was carried out under conditions of a current density of about 37 A/m^2 for 2 or 8 hours. The microstructure was observed with an optical microscope and the phase state was confirmed by X-ray diffraction with Cu-Kα radiation. The depth profile of the absorbed hydrogen was analyzed using a glow discharge optical emission spectrometer (GDOES, J-5000RF, Horiba).

3. Results and Discussion

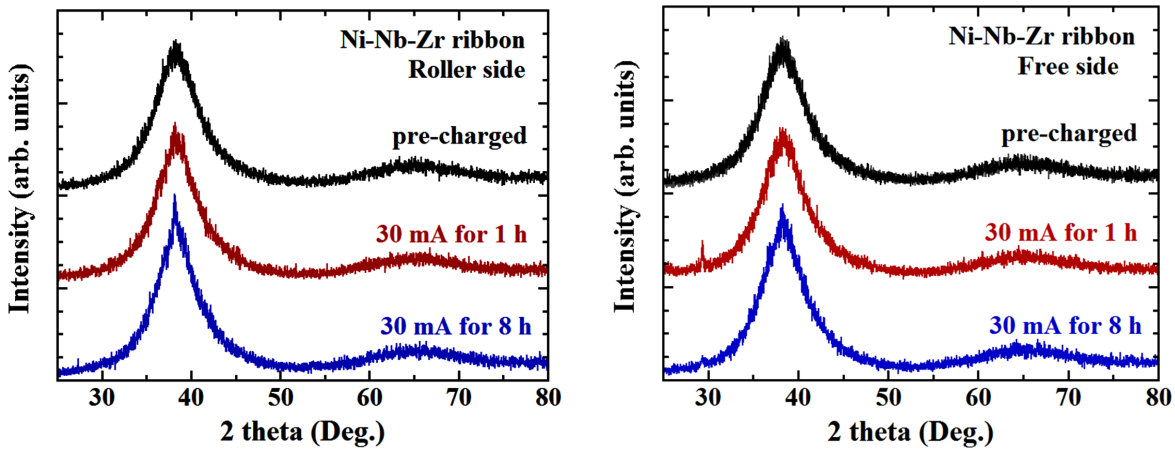
Figure 1 shows microstructures in the surface of pre-charged specimens observed with an optical microscope for melt-spun ribbon of $Ni_{36}Nb_{27}Zr_{37}$ on the roller side (a) and on the free side (b). Here, the roller side means the side in contact with the roller during the melt-spinning and the free side is the outer side of the ribbon. The morphology of the surface on these sides is completely different. The surface on the roller side is flat and has many voids. The free side is shinier than the roller side, and also exhibits concavity and convexity of the surface. It is generally known that the cooling rate is strictly different between the roller side and the free side. The morphology of each side does not change so much between before and after electrochemical charging for hydrogen absorption.

X-ray diffraction (XRD) patterns of the melt-spun ribbon for $Ni_{36}Nb_{27}Zr_{37}$ and those of specimens electrochemically charged for 1 or 8 hours with a current density of about 37 A/m^2 are indicated in figures. **Figure 2(a)** and **Figure 2(b)** are observed XRD patterns on the roller side and on the free side, respectively. Halo-type diffraction patterns are observed, indicating the amorphous state although tiny peaks are confirmed for the specimens with electrochemical charging. In the case of Lanthanoid-based amorphous alloys, such as (La, Ce)-Co-Al, it has been confirmed that the sample surface was crystallized after hydrogen charging [10]. No shift of the main peak around at 40 degree was confirmed. In previous studies of Ni-Nb-Zr melt-spun ribbons with electrochemical changing, a slight peak shift was observed depending on the amount of the absorbed hydrogen [9]. In the present specimens, it is expected that the amount of absorbed hydrogen did not change so much depending on the charging time.



(a) (b)

Figure 1. Microstructures observed with an optical microscope for $Ni_{36}Nb_{27}Zr_{37}$ melt-spun ribbon on the roller side (a) and on the free side (b).



(a) (b)

Figure 2. X-ray diffraction patterns of melt-spun ribbon for $Ni_{36}Nb_{27}Zr_{37}$ and electrochemically charged specimens for 1 and 8 hours with a current density of about 37 A/m^2 on the roller side (a) and on the free side (b).

Figures 3(a)-(f) show depth profiles for the light elements, together with those for Ni, Nb and Zr elements for melt-spun $Ni_{36}Nb_{27}Zr_{37}$ amorphous ribbons obtained by the electrochemical charging for 0, 2 and 8 hours on the roller side (a)-(c) and on the free side (d)-(f), respectively. It is said that some kinds of light element impurities are basically exist in the surface. Especially, amounts of oxygen and carbon are comparatively large, although they decay with depth. It is clarified that there is a considerable amount of oxygen impurity on the free side. The hydrogen is also contained in the surface of the as-charged ribbons of (a) and (d), and remains at a depth compared with other light elements in (b), (c), (e) and (f). The hydrogen is the absorbed one by electrochemically charging, and the actual amounts will be discussed in later. In order to focus on the composition of Ni, Nb and Zr elements, the numerical values of these elements, which are obtained from the results in **Figure 3** as normalized as the total value while becomes 100 at%, are indicated in **Figures 4(a)-(f)**.

Compositions of the three elements on the surface considerable deviate from the nominal compositions, and the amount of Zr is significantly rich. Furthermore, behavior of the composition distribution is different between the roller side and the free side, that is, the content of the Zr element is greater on the free side than that on the roller side. However, the distributions do not change so much after electrochemical charging. These conditions are similar to the reported ones by Kawashima *et al*. by X-ray photoelectron spectroscopy (XPS) analyses [6]. They also investigated the surface composition of $N_{36}Nb_{24}Zr_{40}$ amorphous ribbon by XPS and concluded that the surface composition of the alloy after hydrogenation was almost the same as that of the pre-charged

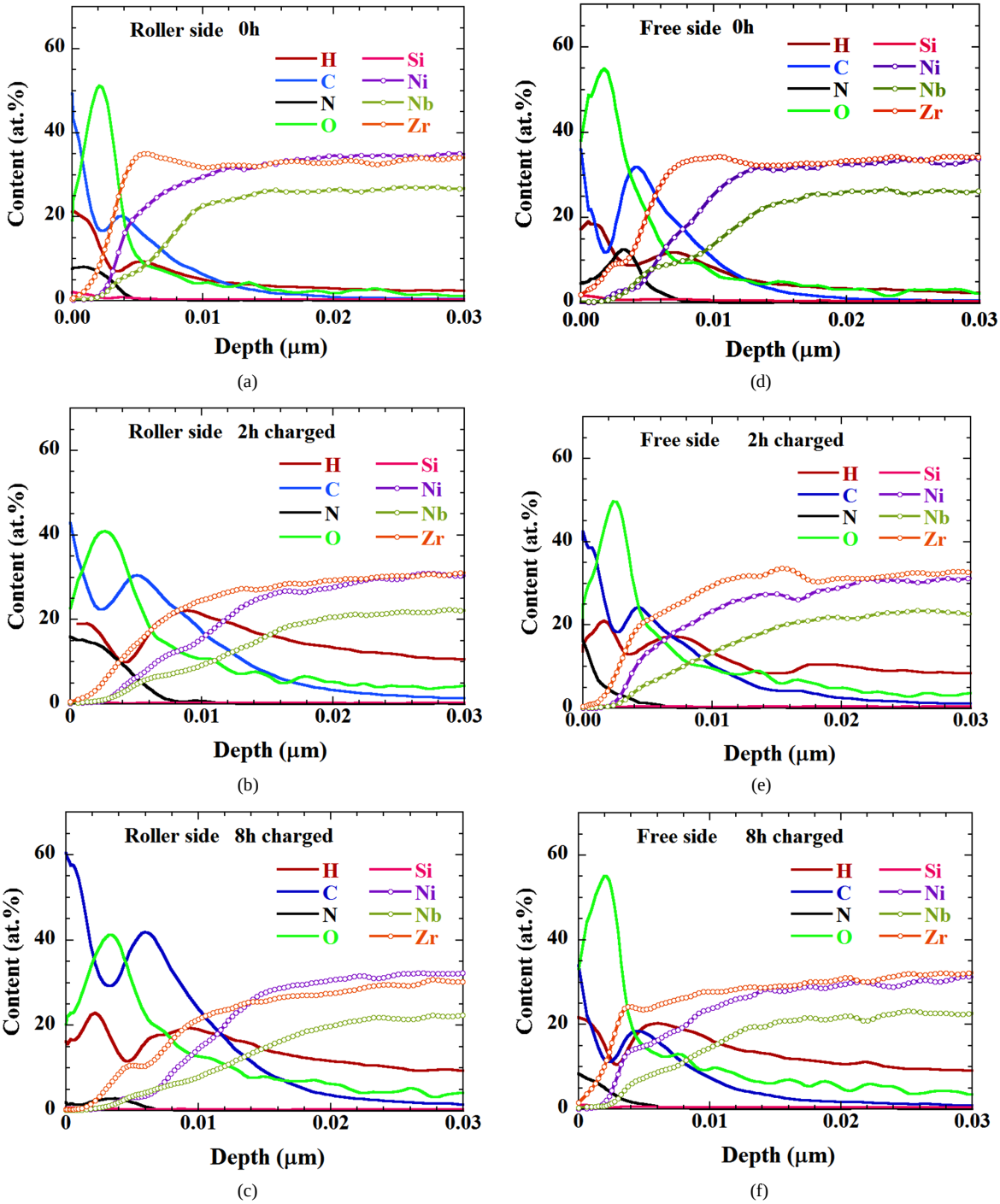


Figure 3. Depth profiles for the light elements, together with those for Ni, Nb and Zr elements for the melt-spun $Ni_{36}Nb_{27}Zr_{37}$ amorphous ribbons obtained by the electrochemically charging for 0, 2 and 8 hours in the roller side (a)-(c) and in the free side (d)-(f), respectively.

specimen and that the Zr content on the free side surface was larger than that on the roller side [6]. The difference of the compositions between the free side and the roller side would originate from the difference of the cooling rate in the melt-spun technique.

Figure 5(a) and **Figure 5(b)** are depth profiles of the absorbed hydrogen of the melt-spun $Ni_{36}Nb_{27}Zr_{37}$ amorphous ribbon obtained by electrochemical charging for 0, 2 and 8 hours on the roller side (a) and on the

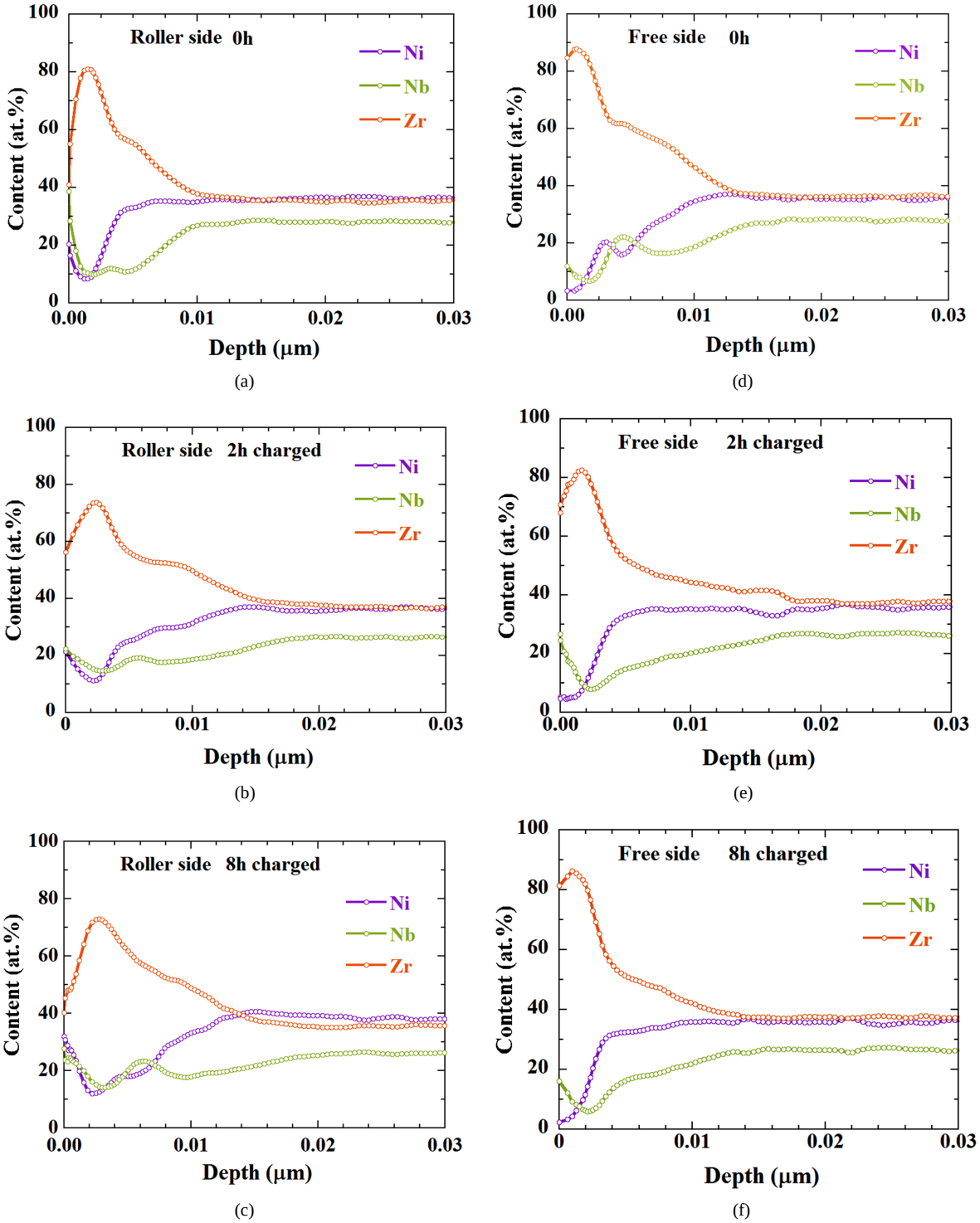
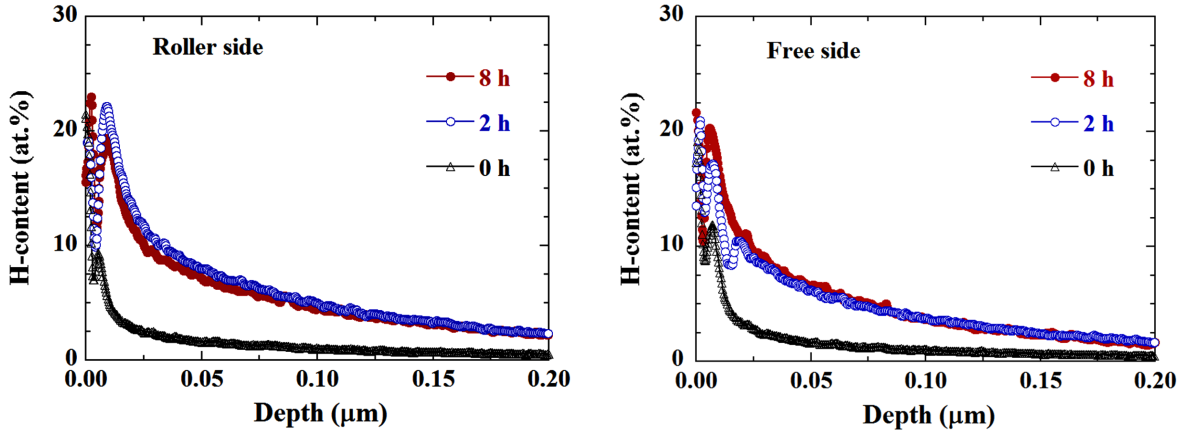


Figure 4. Depth profiles of the Ni, Nb and Zr elements for the melt-spun $Ni_{36}Nb_{27}Zr_{37}$ amorphous ribbons obtained by the electrochemically charging for 0, 2 and 8 hours on the roller side (a)-(c) and on the free side (d)-(f), respectively. The numerical values are obtained from the figures 3 and are normalized as the total value becomes 100 at%.

free side (b). They were simply extracted from the results in **Figure 3**. As mentioned above, although some amount of hydrogen as an impurity is already contained in the ribbon specimens before electrochemical charging, it is clear that a greater amount of hydrogen is actually absorbed by charging. The differences between the



(a) (b)

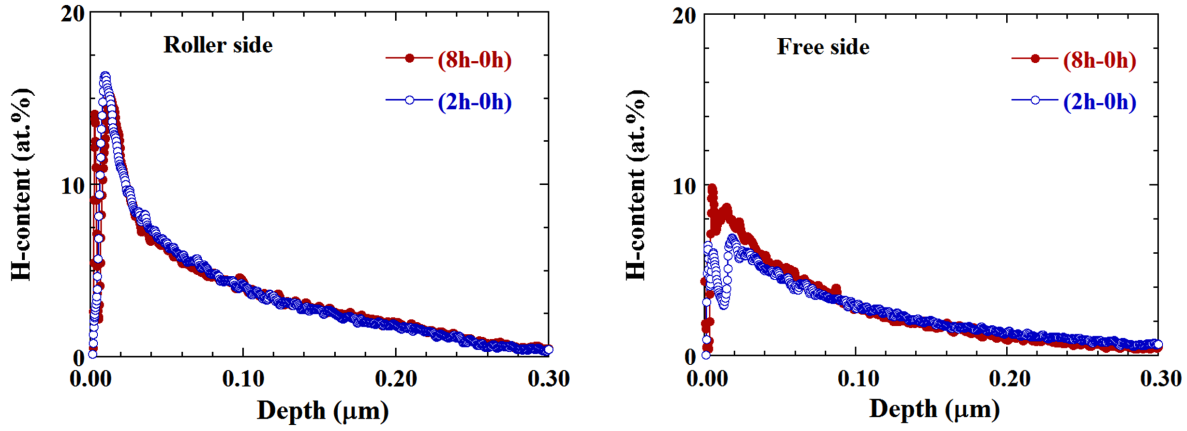
Figure 5. Depth profiles of the absorbed hydrogen of the melt-spun $Ni_{36}Nb_{27}Zr_{37}$ amorphous ribbons obtained by electrochemica charging for 0, 2 and 8 hours on the roller side (a) and on the free side (b).

depth profiles of the hydrogen content for $Ni_{36}Nb_{27}Zr_{37}$ amorphous ribbons by electrochemical charging for 8 hours and 0 hour (8 h - 0 h), and 2 hours and 0 hour (2 h - 0 h) are indicated in **Figure 6**. These profiles are real depth profiles of the absorbed hydrogen in the amorphous ribbons. It is thought that their amount does not depend on the charging time, that is, it seems to be saturated already after charging for 2 hours. However, it is significantly sensitive to depth. The content of the absorbed hydrogen in the surface on the roller side is about 17 at%, whereas it decays to several atomic percent inside the ribbon. The content of the absorbed hydrogen in the surface on the free side is about 10 at%, smaller than that on the roller side. The difference of the amount of absorbed hydrogen between on the free side and on the roller side would be due to the difference of the Zr content in the surface, as mentioned before. Kawashima *et al*. have investigated electrochemical polarization behavior of amorphous Ni-Zr alloys and concluded that the alloys with lower Zr content show higher cathodic activity, meaning higher hydrogen absorption rate [11]. The surface conditions in the present results are consistent with the previous results reported by Kawashima *et al*. although the alloy compositions of the amorphous ribbons are slightly different [6]. However, the depth profile of the absorbed hydrogen was investigated for first time in the present study, and it was clarified that the distribution of the absorbed hydrogen was not constant.

Recently, electrochemical methods have been used to investigate the diffusion coefficient. For example, Wen *et al*. discussed the diffusion coefficient of LiAl obtained by different approaches, such as the potentiostatic, galvanostatic, potentiometric, and steady-state ac methods, and showed that the results obtained by the different methods were in good agreement [12]. Sundaram *et al*. determined the diffusion coefficient of the hydrogen in some Ti-Al alloys by the galvanostatic mode [13]. They measured the electrode potential as a function of time with respect to a standard hydrogen reference electrode. The diffusion coefficient of the hydrogen in the present study cannot be precisely discussed because of the lack of the systematic investigation. It is expected roughly to be on the order of 10^{-7} cm^2/s under the assumption that the content of the absorbed hydrogen is saturated for 2 hours under the electrochemical charging. Kirchheim *et al*. have systematically investigated the diffusion coefficient of the hydrogen in Ni-Zr amorphous alloys in various compositions and reported that for amorphous $Ni_{65}Zr_{35}$ alloy at room temperature, it was on the order of 10^{-8} cm^2/s [14] [15]. They also mentioned that hydrogen diffusivity changes over two or three orders of magnitude depending on the Zr content, which results in a change of the electronic structure and of H-H interaction.

4. Conclusion

Depth profiles of the hydrogen absorption in the $Ni_{36}Nb_{27}Zr_{37}$ amorphous ribbons were analyzed by means of glow discharge optical emission spectrometry (GDOES) in order to investigate the distribution of absorbed hydrogen in Ni-Nb-Zr amorphous ribbons. From the analyses using GDOES, it was confirmed that the amounts of absorbed hydrogen, impurity oxygen and constituent elements of Ni, Nb and Zr depend on the depth. Especially, Zr content becomes rich in the surface, slightly more on the free side than that on the roller side. The amount of absorbed hydrogen is about 17 at% at the surface on the roller side and it decreases to several atomic percent.



(a) (b)

Figure 6. Difference between the depth profiles of the hydrogen content for $Ni_{36}Nb_{27}Zr_{37}$ amorphous ribbons by electrochemical charging for 8 hours and 0 hour, for 2 hours and 0 hour on the roller side (a) and on the free side (b).

The GDOES analysis clarified that the hydrogen absorbed by electrochemical charging is comparatively well-distributed in the sample surface. The amount of absorbed hydrogen on the roller side tends to be greater than that on the free side, which would correlate with the amount of the Zr content. These behaviors are similar to the previously reported results of Kawashima *et al*., even though the composition of the melt-spun ribbon is slightly different. The slight difference of the Zr content is probably due to the difference of the cooling rate between the free side and the roller side during the melt-spun technique.

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