Effect of Hydrogen Absorption on Electrical Transport Properties for $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ Amorphous Alloy Ribbons

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Electrical resistivity measurements in the temperature range from 6 to 300 K were carried out in order to investigate the effects of the hydrogen absorption on the transport properties of $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ amorphous alloy ribbon. The electrical resistivity basically behaved negative temperature dependence in all prepared specimens of $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-x}\text{H}_x$ with $0 \leq x < 15$. The absolute value of temperature coefficient of the resistivity, TCR, increased with increasing the amount of the absorbed hydrogen. In addition, it was also clear that the electrical resistivity gradually increased with the time just after electrochemically charging, and tended to saturate after about 800 ks at 300 K. The behavior of the gradual increase in the electrical resistivity with the time was explained by the model including two kinds of the relaxation times, being associated with the migration of the hydrogen from the sample surface. [doi:10.2320/matertrans.MF201305]

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1. Introduction

It has been known that Ni–Nb–Zr ternary alloys form amorphous phase in the wide concentration region.¹⁾ Yamaura *et al.* have reported the excellent hydrogen permeability of about $1.59 \times 10^{-8} \text{ mol} \cdot \text{m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$ at 673 K in melt-spun amorphous $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{50}\text{Zr}_{50}$ alloy.^{2,3)} The value of the permeability exceeds that of the Pd, thus, the Ni–Nb–Zr amorphous alloys have been thought to exhibit high potential as applicable materials. Mechanical properties of the hydrogen absorbed amorphous ribbons were also investigated by Kawashima *et al.*⁴⁾ Very recently, interesting electrical transport properties, such as ballistic-conductivity, superconductivity and the Coulomb-blockade oscillations have been found in the hydrogen absorbed $[(\text{Ni}_{0.6}\text{Nb}_{0.4})_{1-x}/100\text{Zr}_{x/100}]_{100-y}\text{H}_y$ ($30 < x < 50$, $0 < y < 20$) amorphous alloy ribbons by Fukuhara *et al.*^{5,6)} Especially for $x = 40$, it has been shown by their reports that the ballistic-conductivity, where, the electrical resistivity suddenly decreased to triple order, was observed when $y = 3.9$. The superconducting behavior whose onset is 9 K and the Coulomb-blockade oscillations were observed when $y = 5.7$ and 9.3, respectively. They have pointed out that localization effect of the hydrogen at the outside and inside space of the distorted icosahedral $\text{Zr}_5\text{Ni}_5\text{Nb}_3$ clusters plays important roles in their various electrical transport properties. That is, the unique behavior of the electrical transport properties of Ni–Nb–Zr–H amorphous alloy is thought to be very sensitive to the amount of the hydrogen absorption, thus, further studies have been required.

In our previous investigations of the temperature dependence of the electrical resistivity for $(\text{Ni}_{0.8}\text{Nb}_{0.2})_{100-x}\text{Zr}_x$ ($x = 30, 40$ and 50) glassy alloys, it has been reported that the temperature coefficient of the resistivity, TCR, tends to increase negatively in the specimens with absorbed

hydrogen.⁷⁾ It is also observed that the amount of the absorbed hydrogen is different depending on the composition of x even in the same condition of the electrochemically charging. For example, the amounts of the absorbed hydrogen of the specimens with $x = 30, 40$ and 50 after electrochemically charging for 2 h were about 4.9, 13.8 and 2.5 at%, respectively. In the specimens of $x = 40$, the absolute value of the TCR changes about three times after the hydrogen absorption. It has been pointed out that the situation of the hydrogen absorption is sensitive to the difference of the local structure of the glassy state.³⁾ Therefore, it is needed to investigate systematically the effects of the hydrogen absorption on the electrical transport properties with a fixed composition.

In the present study, we focused on the composition of $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ amorphous alloy ribbon, and measured the electrical resistivity of the specimen with electrochemically adsorbed hydrogen in order to investigate systematically the effect of the hydrogen absorption on the electrical transport properties. Furthermore, time-dependent behavior of the electrical resistivity just after the electrochemically charging was also investigated.

2. Experimental Procedures

Mother alloy of $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ was prepared by arc melting in an argon atmosphere and amorphous ribbons were made by a single roller melt-spinning technique, where the surface velocity of a copper wheel was about $50 \text{ m} \cdot \text{s}^{-1}$. The thickness and width of the fabricated ribbon were about $25 \mu\text{m}$ and 1 mm, respectively. Hydrogen absorbed specimens were made by electrochemical charging in $0.5 \text{ M H}_2\text{SO}_4 + 1.4 \text{ g} \cdot \text{L}^{-1}$ thiourea (H_2NCSNH_2) at room temperature with a current density of about $0\text{--}120 \text{ A} \cdot \text{m}^{-2}$ for 2 h. Structure was confirmed by X-ray diffraction (XRD) with using the Cu– $K\alpha$ source. The amount of the absorbed hydrogen was measured by the inert gas carrier melting-thermal conductivity method

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Fig. 1 Amount of the absorbed hydrogen as a function of the current density for $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ amorphous ribbons. The solid curve is guide to the eyes.

several times in each condition. Thermal analyzes were performed with a differential scanning calorimeter (DSC) with a heating rate of $0.33 \text{ K}\cdot\text{s}^{-1}$. Electrical resistivity was measured by a conventional four probes method in a temperature range of 6–300 K with cooling and heating rates of about $0.017 \text{ K}\cdot\text{s}^{-1}$. For the measurements of XRD, DSC and electrical resistivity, and analyzes of the hydrogen were basically carried out with the specimens, being left out at room temperature for two weeks after the electrochemically charging. Measurements of the time-dependence of the electrical resistivity were only made with the specimens just after the electrochemically charging.

3. Results and Discussion

Figure 1 indicates amount of absorbed hydrogen by electrochemical method for two hours as a function of the current density. Here, the specimens, two weeks passed after the electrochemical charging, were used for analyzing. The amount of the absorbed hydrogen increases with increasing the current density and tends to saturate. Maximum hydrogen absorption is thought to be limited up to 0.25 mass% (15 at%), because the specimens become very brittle if the specimens are charged with higher current density than $120 \text{ A}\cdot\text{m}^{-2}$.

X-ray diffraction patterns with using $\text{Cu-K}\alpha$ radiation of melt-spun ribbon for $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ and electrochemically charged specimens for 2 h with the current density of about 40 and $70 \text{ A}\cdot\text{m}^{-2}$ are shown in Fig. 2. The amount of the absorbed hydrogen corresponds to about 9.2 and 14.7 at% from the results of Fig. 1, respectively. The results show typical halo-type patterns, indicating the amorphous structure. In the figure, it is seen that the main peak around 40 degree slightly shifted to lower degree with increasing of the hydrogen absorption, indicating the volume expansion.

Figures 3(a) and 3(b) show the differential scanning calorimetry curves with a heating rate of $0.33 \text{ K}\cdot\text{s}^{-1}$ for the melt-spun amorphous ribbons and hydrogen absorbed specimens with a current density of $70 \text{ A}\cdot\text{m}^{-2}$, respectively. Here,

Fig. 2 X-ray diffraction patterns of $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ melt-spun amorphous ribbon and hydrogen absorbed specimens.

Fig. 3 Differential scanning calorimetry curves with a heating rate of $0.33 \text{ K}\cdot\text{s}^{-1}$ for some melt-spun amorphous ribbons (a) and hydrogen absorbed specimens (b).

Fig. 4 Temperature dependence of the normalized electrical resistivity, $\rho/\rho_{300\text{K}}$, for $y = 0.0, 2.0, 3.3, 9.2$ and 14.7 for $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-y}\text{H}_y$. The inset is absorbed hydrogen dependence of ratio of the resistivity, $\rho_{6\text{K}}/\rho_{300\text{K}}$. The straight line is guide to the eyes.

the amount of hydrogen for the specimens is about 14.7 at%, noted as $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{85.3}\text{H}_{14.7}$. In order to confirm the reproducibility, several measurements were performed. Although the crystallization temperature is almost same to be about 820 K in both specimens with and without hydrogen, broad endothermic reaction is clearly observed just below the crystallized temperature only in the hydrogen charged specimens. Therefore, this endothermic reaction will be due to hydrogen discharge.

Figure 4 shows temperature dependence of the normalized electrical resistivity, $\rho/\rho_{300\text{K}}$, for $y = 0, 2.0, 3.3, 9.2$ and 14.7 for $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-y}\text{H}_y$. All of the resistivity exhibits negative temperature dependence, as following the Baym-Meisel-Cote theory based on the Boltzmann transport equation for amorphous alloys with non-periodic crystal structure as follows,^{8,9)}

$$\rho = \rho_0 \exp[-2W(T)] + \rho_{\text{ph}} \left(1 - \frac{2\pi}{\Lambda q} \right) \quad (1)$$

where, ρ_0 is the residual resistivity, $\exp[-2W(T)]$ is the Debye-Waller factor, ρ_{ph} is the phonon term, Λ is the mean free path and q is the wave vector. For the amorphous and quasi-crystals with non-periodic structure, Λ is small, and consequently the second term in eq. (1) is negligible. Therefore, the electrical resistivity is governed by the temperature dependence of the Debye-Waller factor not by the electron-phonon scattering. In such case, the electrical resistivity shows T^2 -dependence in low temperature range and T -linear dependence close to the room temperature.^{10,11)} As shown in the figure, TCR, increases negatively with increasing the absorbed hydrogen, y , indicating the absorbed hydrogen effects on the electrical resistivity. The inset of Fig. 4 is ratio of the resistivity, $\rho_{6\text{K}}/\rho_{300\text{K}}$ as a function of the amount of the absorbed hydrogen. The straight line is guide to the eyes. Although it is seen that there is a linear relationship between $\rho_{6\text{K}}/\rho_{300\text{K}}$ and the amount of the absorbed hydrogen, it is somewhat difficult to clarify the origin. With regards to the origins, since there are so many possibilities, e.g., the change of the mean free path associated

Fig. 5 Time dependence of the increase of the electrical resistivity, $\Delta\rho/\rho_{t=0}$, for $y = 14.7$ in $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-y}\text{H}_y$.

to the volume expansion, change of the Debye temperature and electronic state, in addition, the existence of the scattering related to the absorbed hydrogen, we cannot make any assignment at present time. It needs further investigation.

In order to add some suggestions to the reason of the negative enhancement of the TCR, electrical resistivity as a function of the time for a specimen just after the electrochemically charging was carried out. In the previous report by Kawashima *et al.*, it has been pointed out that the morphology of the Ni-Nb-Zr amorphous alloy ribbons changed after electrochemically charging with time.⁴⁾ They showed that the ribbon specimens always curled and gradually returned to the originally straight shape. Although the behavior has been thought to be due to the homogenization of hydrogen distribution in the specimen, time-dependencies of some physical properties have not been investigated.

Time dependence of the electrical resistivity change of the specimen charged with a current density of $70 \text{ A}\cdot\text{m}^{-2}$ for 2 h is shown in Fig. 5. As shown in the figure, the resistivity first increases, gradually increases in next and tends to saturate with the time, that is, two stages of increase are observed. The behavior is similar with that of the single crystalline Nb, which is also hydrogen absorbed by the same method.¹²⁾ From the systematically investigations, Koike *et al.* have suggested that the hydrogen absorbed in the Nb exhibits two stages of diffusion caused by the different mechanisms, that is, the increase of the electrical resistivity with time is expressed as follows,^{12,13)}

$$\Delta\rho(t) = \Delta\rho_1(t) + \Delta\rho_2(t) + \Delta\rho_{\text{OX}}(t) \quad (2)$$

where,

$$\begin{aligned} \Delta\rho_1(t) &\approx \Delta\rho_1(1 - \exp(-t/\tau_1)) \\ \Delta\rho_2(t) &\approx \Delta\rho_2[1 - 0.811(\exp(-t/\tau_2) + 1/9 \exp(-9t/\tau_2))] \\ \Delta\rho_{\text{OX}}(t) &= At, \end{aligned} \quad (3)$$

here, $\Delta\rho_1$ is the first stage change, which is due to the formation of some internal sources such as dislocations, and $\Delta\rho_2$ is the second stage, which is due to the vacancy migration from the surface.^{12,14)} They explained that the last term is the correction one expressed as a linear increase with

the time in the reference. In the present case of the specimen with $y = 14.7$ in $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-y}\text{H}_y$, because the change of the resistivity seems to almost saturate over 800 ks, the experimental data was fitted by the sum of the first and second stages. From the fitting, relaxation time τ_1 and τ_2 are obtained to be about 61 and 210 ks, respectively. Since the curvature of the present data is similar to that of the Nb–H, it is suggested that the absorbed hydrogen and vacancy result in the increase of the electrical resistivity for Ni–Nb–Zr amorphous ribbon, which would be mainly due to the increase of the residual resistivity accompanied by the impurity scattering. However, in comparison with these relaxation time τ_1 and τ_2 between the present specimen and the Nb–H single crystal, it is found that τ_1 of the Ni–Nb–Zr amorphous ribbon is one order larger than that of Nb–H, even though τ_2 is comparable in the both.¹²⁾ It has been reported that the change of the electrical resistivity due to the first stage of the Nb–H single crystal composes 3/4 of the total change of the electrical resistivity. In addition, for Nb–H polycrystal specimen, most of the change of the electrical resistivity is governed by the first stage. On the other hand, the change of the electrical resistivity by the first stage for the present Ni–Nb–Zr amorphous ribbon is about 60% of the total change. These different behaviors of larger τ_1 and smaller rate of the resistivity change than those of Nb–H will be caused by the difference of the structure because the amorphous alloy is lack of the dislocations.

4. Conclusions

In conclusion, electrical transport properties in the temperature range from 6 to 300 K was investigated in order to clarify the effects of the hydrogen absorption on the electrical resistivity in $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ amorphous alloy ribbon. In addition, time-dependence of the electrical resistivity for the specimen just after the electrochemically charging was also studied. Obtained results are summarized as follows:

- (1) The amount of the absorbed hydrogen can be controlled up to about 15 at% with changing the current density of the electrochemical charging in the present $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-y}\text{H}_y$ amorphous alloy ribbons.
- (2) The electrical resistivity basically shows negative

temperature dependence in all specimens with $0 \leq y < 15$ for $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{100-y}\text{H}_y$ amorphous alloy ribbons. The temperature coefficient of the resistivity, TCR, increases negatively with increasing the amount of the absorbed hydrogen. This would be caused by the increase of the scattering of the electrons.

- (3) The electrical resistivity gradually increases with the time for the specimen just after the electrochemically charging, and it behaves to saturate after about 800 ks at 300 K. This behavior can be expressed by the model including two kinds of the relaxation times with relating to the migration of the hydrogen, being similar to the hydrogen absorbed Nb single crystal. However, the rate of the increase of the resistivity in the first stage of the present specimen is lower than that of the Nb single crystal. This difference would be come from the difference of the structure, that is, the dislocations are absent in the amorphous alloy.

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