Electrical Resistivity Studies of Hydrogenated Pd-Zr Glasses

Electrical Resistivity Studies of Hydrogenated Pd-Zr Glasses[*]

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Synopsis

The effect of hydrogen absorption on the electrical resistivity is studied for Pd-Zr glasses prepared by melt-quenching using a single roll technique. The temperature coefficients of the electrical resistivity are negative over the temperature range between 4.2 and 300 K for both as-quenched $Pd_{.35}Zr_{.65}$ and hydrogenated $Pd_{.35}Zr_{.65}H_{1.01}$ glasses. The results can be interpreted in terms of an acoustical phonon in case of $Pd_{.35}Zr_{.65}$ glass, while in $Pd_{.35}Zr_{.65}H_{1.01}$ glass an optical phonon originating from the metal-hydrogen interaction has a significant contribution to the electrical resistivity as well as an acoustic phonons.

I. Introduction

The hydrogen absorption into metallic glasses often leads to remarkable changes in physical and chemical properties of the glasses such as atomic arrangement, stability, electronic state, mechanical property and so on.

When hydrogen atoms are absorbed into metal-metal glasses including the metal atoms with strong hydrogen affinity at least as one of alloy components, an interstitial hole in the polyhedral structure unit composed of the metal atoms may be occupied by a hydrogen atom. In fact, the X-ray structure factor $S(Q)$[1] exhibits a distinguished change that the characteristic splitting of the second peak for $Pd_{.35}Zr_{.65}$ glass is diminishing due to the hydrogen absorption. The radial distribution function shows that hydrogen atoms prefer to occupy the hole in zirconium atom polyhedra[1]. These observations do not support the simple Polk's model-like discussion that hydrogen atoms

occupy at random the interstitial holes in the dense random packing of metal atoms.

The aim of this study is to measure the electrical resistivity of hydrogenated Pd-Zr glasses as a function of temperature and then to examine the drastic changes in the atomic and electronic structures expected from the chemical bond formation between hydrogen and zirconium atoms.

II. Experimental

$Pd_{.35}Zr_{.65}$ buttons were prepared as a starting materials by electron beam melting Pd(99.99% purity) and Zr($>$99.7% purity) metals. The Zr metal was purified by electron beam zone refining prior to making the buttons. $Pd_{.35}Zr_{.65}$ glass ribbons were rapidly quenched from the molten state using a single roll technique in a controlled Ar-gas atmosphere[2].

Hydrogen atoms are absorbed into the glass ribbons under 20 kg/cm^2 H_2-gas pressure at 300°C. The hydrogen-metal ratio determined by Ar-gas carrier chromatography is 1.01, which is in consistent with the result of weight change measurement.

By DTA scanning measurement, the crystallization temperature of $Pd_{.35}Zr_{.65}H_{1.01}$ glass is confirmed to be about 510°C, which is 40°C higher than that of as-quenched $Pd_{.35}Zr_{.65}$ glass (470°C).

The electrical resistivity measurement was carried out over the temperature range from 4.2 and 300 K using a conventional four-probe dc technique. Current and potential leads were connected to the glass ribbons by a conducting silver paste.

III. Results and Discussion

The magnitude of the electrical resistivities is about 240 and 270 $\mu\Omega$·cm at 300 K for $Pd_{.35}Zr_{.65}$ and $Pd_{.35}Zr_{.65}H_{1.01}$ glasses, respectively. However, the absolute values of these resistivities are not enough accurate to discuss them, because the precise measurement of the thickness of the thin ribbons is quite difficult. The temperature dependences of the resistivities normalized to the room temperature (300 K) values are shown in Fig. 1. As observed in many metallic glasses, the temperature coefficient of the resistivity (TCR) is negative over the whole temperature range investigated for the both glasses.

The electrical resistivity of metallic glass as a function of temperature $\rho(T)$ can be expressed on the basis of Ziman's diffraction model[3]
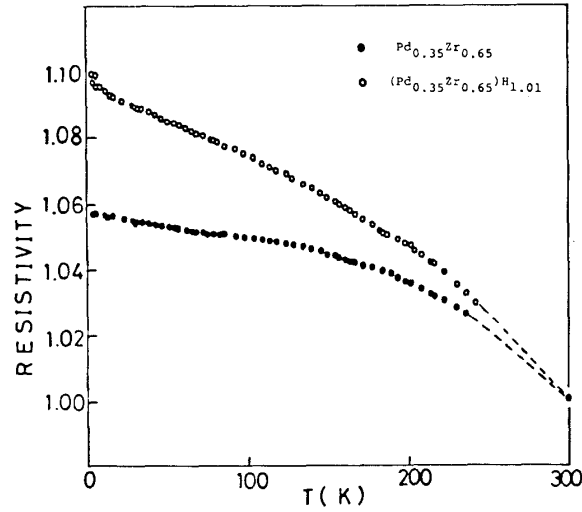
Fig. 1. Electrical resistivities of $Pd_{.35}Zr_{.65}$ (●)
and $Pd_{.35}Zr_{.65}H_{1.01}$ (○) glasses, normalized
to the resistivity at 300 K, as a function of
temperature.

$$\rho(T) = \frac{30\pi^3\hbar^3}{me^2k_F^3E_F\Omega}\sin^2[\eta_2(E_F)]\left\{1+[S_0(2k_F)-1]\ e^{-2[W(T)-W(0)]}\right\},\qquad (1)$$

where k_F and E_F are the Fermi wave vector and energy, respectively and
Ω is the atomic volume, $\eta_2(E_F)$ is the d-wave phase shift describing
the scattering of conduction electrons by the ion cores. The tempera-
ture dependence of the resistivity enters through the Debye-Waller
factor $W(T)$ which describes the modification in the structure factor
$S(Q)$ due to the vibration of ions around their equilibrium positions.
The TCR has been calculated by Nagel[4], assuming that the Debye-Waller
factor has the asymptotic form as follows,

$$W(T) = W(0) + 4W(0)\frac{\pi^2}{6}\left(\frac{T}{\theta_D}\right)^2 \qquad T \ll \theta_D \qquad (2)$$

and

$$W(T) = W(0) + 4W(0)\left(\frac{T}{\theta_D}\right) \qquad T \gg \theta_D\ , \qquad (3)$$

where θ_D is the Debye temperature and

$$W(0) = \frac{3\hbar^2k^2}{8M_ik_B\theta_D} . \qquad (4)$$

At low temperature $(T \ll \theta_D)$ the resistivity should vary as T^2, while

the resistivity should follow the linear law as T at high temperature $(T \gg \theta_D)$.

The normalized resistivities for the both glasses are plotted against a T^2 scale in Fig. 2. The temperature dependence of the resistivity for $Pd_{.35}Zr_{.65}$ glass fits well a T^2-law over the temperature range between 40 and 90 K. Based on Eq. (1), the negative TCR appears when $S_0(2k_F) > 1$. This means that the value of $2k_F$ must be located near the first peak position Q_p in the structure factor $S(Q)$. If we can assign one conduction electron for a palladium atom and two conduction electrons for a zirconium atom in the spherical Fermi surface of $Pd_{.35}Zr_{.65}$ glass, the $2k_F$ value has 2.68 A^{-1} which is quite close to $Q_p = 2.62$ A^{-1} in the experimental $S(Q)^{1,5)}$. Then we can understand the negative TCR for $Pd_{.35}Zr_{.65}$ glass. Furthermore, if it is
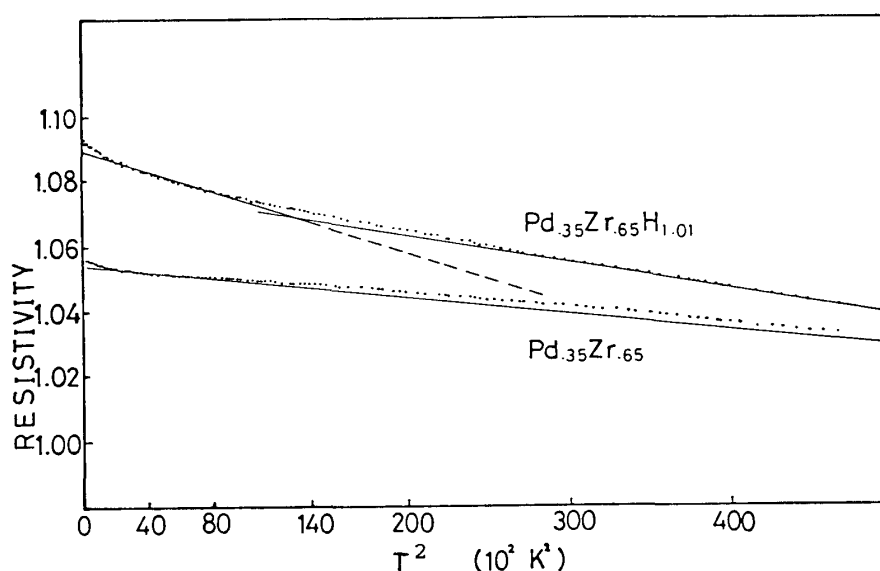

Fig. 2. Electrical resistivities of $Pd_{.35}Zr_{.65}$ and
$Pd_{.35}Zr_{.65}H_{1.01}$ glasses, normalized to the resistivity
at 300 K, plotted as a function of T^2.

assumed that M_i in Eq. (4) can be represented by an average atomic mass of palladium and zirconium atoms, the Debye temperature $\theta_D = 270$ K is obtained from the slope-fitting as shown in Fig. 2, using the experimental value $S_0(2k_F) = 2.8^{1)}$. A small deviation from the T^2-law at higher temperature (T > 100 K) may be caused by the T-law contribution which becomes predominant in high temperature range.

In $Pd_{.35}Zr_{.65}H_{1.01}$ glass, the deviation from the T^2-law becomes too much with increasing temperature to be ascribed to the T-law

contribution. This may be an indication that the onset of another scattering mechanism happens at higher temperature in $Pd_{.35}Zr_{.65}H_{1.01}$ glass. The average atomic mass(M) of metal atoms is a hundred times greater than that of hydrogen atom(m). Therefore, we can expect that an optical mode, of which frequency is propotional to $m^{-1/2}$, is separated from the acoustic mode with the frequency propotional to $M^{-1/2}$. The temperature dependence of the resistivity for the $Pd_{.35}Zr_{.65}H_{1.01}$ glass in high temperature region includes a significant contribution from the optical mode with a second Debye spectrum.

If we take that one conduction electron is donated to the conduction band in the glass by adding a hydrogen atom, the $2k_F$ value is about 2.50 A^{-1} which is again near the first peak position $Q_p=2.52$ A^{-1} in the experimental $S(Q)$ of $Pd_{.35}Zr_{.65}H_{1.01}$ glass[1]. This is the reason why $Pd_{.35}Zr_{.65}H_{1.01}$ glass still has a negative TCR. When $M_i=M$ is assumed for the acoustic mode contributing predominantly to the low temperature resistivity and $M_i=m$ for the optical mode contributing to the high temperature resistivity, $\theta_D^{acoustic}=200$ K and $\theta_D^{optic}=1100$ K are obtained from the two slopes as shown in Fig. 2, using the experimental value of $S_0(2k_F)=2.5$[1]. The Einstein spectrum must be more appropriates rather than the Debye spectrum, although the spectrum may be broadened to a wide band due to the H-H interaction in the hydrogenated glass. By fitting the Einstein spectrum to the high temperature resistivity due to the optical phonon, we find $\theta_E^{optic}=620$ K.

These results obtained in the above discussions should be compared with the vibrational data for the crystalline hydrides. The electrical resistivity of crystalline $PdH_{0.995}$[6] provides $\theta_D^{acoustic}=210$ K for the acoustic mode and $\theta_D^{optic}=1000$ K or $\theta_E^{optic}=550$ K for the optical mode. The $\theta_E^{optic}=650$ K for crystalline $PdH_{0.65}$ has been obtained by neutron scattering experiment[7]. Hydrogen atoms in $\beta-V_2H$ crystal occupy the octahedral site like in the crystalline Pd-H alloys and the optical local mode lies at about 50 meV$(\theta_E^{optic}=580$ K)[8]. The neutron scattering of fct-ZrH_2 crystal, in which hydrogen atoms occupy the tetrahedral sites, yields the optical local mode at 140 meV$(\theta_E^{optic}=1600$ K)[9].

Based on the dicussion described above, hydrogen atoms are likely to occupy the octahedral site-like positions in $Pd_{.35}Zr_{.65}$ glass. A resultant interesting problem is to define whether hydrogen atoms prefer to stay in the central hole of the octahedron consisting of Pd atoms, Zr atoms or Pd and Zr atoms. We can not find the correct answer for this problem only from the electrical resistivity measurement. Further experiments on the structure analysis by X-ray and neutron diffraction, the vibrational frequency distribution of hydrogen atoms by inelastic neutron scattering and the electronic states by photo

electron spectroscopy and γ-ray Compton scattering are in progress at the moment.

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