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Thermal relaxation of hydrogen disordering in Pd–H system irradiated with high-energy particles

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Abstract

Effects of high-energy particle irradiation on the thermal relaxation of hydrogen disordering in the Pd–H system have been studied at low temperatures. A palladium foil (1.5 μm thick) doped with hydrogen up to the atomic ratio, H/Pd, of about 0.6 is used as a specimen. First, the hydrogen disordering is induced in the $PdH_{0.6}$ specimen by the following two means; fast cooling of the specimen from 80 K to 10 K, and irradiation at 10 K with 60 MeV ^{12}C ions. Then, the thermal relaxation behavior of hydrogen disordering is observed up to 80 K by measuring the electrical resistivity as a function of temperature. From the measurements at several heating rates (1, 2, 5 and 10 K/min), we determine the activation energy of hydrogen migration in the relaxation process to the thermal equilibrium state by means of a cross-cut method. Based on the experimental results, we discuss the difference between relaxation of hydrogen disordering by fast cooling and that by ion irradiation.

Keywords: Pd–H; Hydrogen disordering; Thermal relaxation; Particle irradiation; Activation energy

1. Introduction

In the Pd–H(D) system, an extraordinary behavior in the vicinity of 50 K (what is called the '50 K anomaly') has been found in several properties such as specific heat [1], internal friction [2], Hall effect [3] and electrical resistivity [4,5]. It is well known that the anomaly is related to the order–disorder transition of hydrogen atoms in the Pd–H(D) system. Neutron scattering measurements [6–8] have shown that hydrogen atoms in the Pd–H(D) system occupy the octahedral interstitial sites of FCC Pd lattice and they tend to be in the long-range ordered state as a thermal equilibrium state below ~50 K; $I4_1/amd$ structure in PdD_x for low concentrations (x~0.64) [7] and $I4/m$ structure for higher concentrations ($x \geq 0.75$) [8]. Such a long-range ordered state disappears at higher temperatures. Therefore, slower cooling of a Pd–H(D) specimen to low temperature induces a larger number of hydrogen atoms to be in the ordered state, while fast cooling (quenching) of a Pd–H(D) specimen from above 50 K to low temperature can freeze in the high-temperature disordered state at 10 K.

Also, energetic particle irradiation can realize the disordered state of hydrogen atoms by displacing hydrogen atoms from the ordered sites. Vajda et al. [9] have shown that 0.35–0.8 MeV electrons destroy the ordered state of hydrogen atoms at 20 K, and that such an irradiation-induced hydrogen disordering is caused dominantly by secondary electrons. Therefore, it is expected that high-energy ion irradiation, which causes more secondary electrons than electron irradiation, can induce hydrogen disordering more effectively.

In the present work, high-energy ion irradiation has been performed in the Pd–H system to induce hydrogen disordering at low temperature. The difference between thermal relaxation of hydrogen disordering by fast cooling and that by ion irradiation has been studied.

2. Experimental procedure

The specimen was a Pd foil (1.5 μm thick) of 99.95% purity doped with hydrogen by the electrolysis method in 0.1N H_2SO_4 up to the atomic ratio, H/Pd, of about 0.6, which was estimated by a relative electrical resistance at room temperature [10]. First, hydrogen disordering was induced in the $PdH_{0.6}$ specimen by cooling the specimen fast (typically 7~39 K/min) from 80 to 10 K, thus freezing in the high-temperature disordered state. Then, the electri-

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cal resistivity of the specimen was measured as a function of temperature during heating to 80 K at a constant rate. We used constant heating rates of 1, 2, 5 and 10 K/min. The same measurement as mentioned above was also carried out after the ordered state of hydrogen atoms was realized at 10 K by cooling the specimen very slowly (0.5 K/min).

By subtracting the resistivity values obtained following slow cooling from those obtained following fast cooling, we could eliminate the contribution of phonon scattering, and could extract the temperature dependence of the resistivity corresponding to the thermal relaxation of hydrogen disordering.

Then, the ordered state of hydrogen atoms in the slowly-cooled specimen was destroyed by irradiation with 60 MeV ^{12}C ions at 10 K. As the projected range of the C ions was much larger than the specimen thickness, irradiating ions completely penetrated the specimen, and did not remain as impurities. We ceased the irradiation when the change in resistivity reached the same amount as that achieved by fast cooling, and the same measurements as those after fast cooling were performed. For comparison, a pure Pd specimen, which was placed adjacent to the $PdH_{0.6}$ specimen, was also ion-irradiated and the electrical resistivity was measured simultaneously.

In addition to measurements of the temperature dependence of the resistivity, we also measured the time dependence of the resistivity at 10 K after ion irradiation and after fast cooling from 80 to 10 K. For comparison, the relaxation of hydrogen disordering in the Pd–H system irradiated with 0.5 MeV electrons was also studied.

3. Results and discussion

Fig. 1 shows the change in electrical resistivity, $\Delta\rho_{irrad}$, for the $PdH_{0.6}$ and pure Pd specimens as a function of ion fluence, Φ. The resistivity change, $\Delta\rho_{irrad}$, for $PdH_{0.6}$ decreased linearly with increasing Φ. As previous studies [9] show that the electrical resistivity for the disordered state of hydrogen atoms is smaller than that for the long-range ordered state, the experimental result means that hydrogen disordering is induced by ion irradiation. We have observed the similar trend in the case of 0.5 MeV electron irradiation. The ion fluence of $\sim 3.1\times10^{16}m^{-2}$ was, however, five orders of magnitude smaller than the electron fluence of $\sim 2.7\times10^{21}m^{-2}$ for the same resistivity change due to hydrogen disordering. Thus, hydrogen disordering was induced quite effectively by ion irradiation. This result can be explained by the larger cross-sections for elastic displacements of hydrogen atoms and for production of secondary electrons in the case of ion irradiation than those of electron irradiation. As can be seen in Fig. 1, the resistivity change, $\Delta\rho_{irrad}$, for pure Pd is much smaller than that for the $PdH_{0.6}$ specimen. Therefore, the present irradiation induced hydrogen disordering, but rarely damaged the Pd lattice.

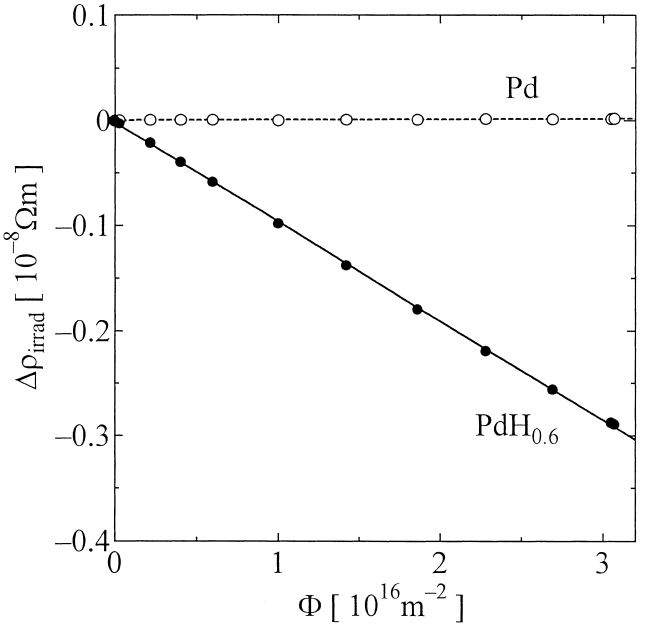

Fig. 1. Change in electrical resistivity, $\Delta\rho_{irrad}$, of $PdH_{0.6}$ and pure Pd specimens as a function of 60 MeV ^{12}C ion fluence, Φ.

Fig. 2 shows the temperature dependences of electrical resistivity, $\rho(T)$, during heating at a constant rate (2 K/min) after slow cooling, after fast cooling and after ion irradiation. The difference between $\rho(T)$ following slow cooling and that following fast cooling reflects the difference in the degree of hydrogen disordering. The higher ρ

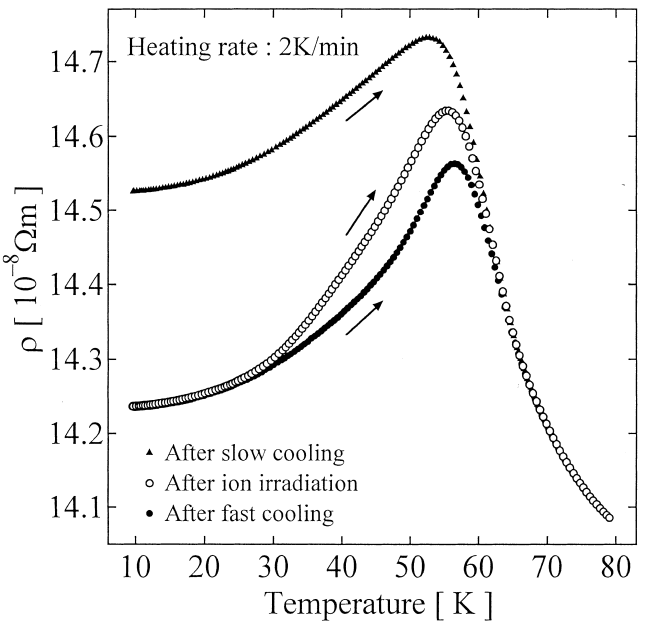

Fig. 2. Electrical resistivity of $PdH_{0.6}$ specimen, ρ, as a function of temperature during heating at 2 K/min after slow cooling, after fast cooling and after ion irradiation.

at 10 K after slow cooling relative to fast cooling indicates that a higher degree of hydrogen ordering has been achieved after slow cooling, because of the difference in time duration for the migration of hydrogen atoms in the cooling process. The temperature dependence of ρ after ion irradiation informs us that hydrogen disordering, which are induced by irradiation, can relax at lower temperature than that achieved after fast cooling.

Fig. 3 shows the thermal relaxation behavior of hydrogen disordering, i.e. the temperature dependences of the difference between electrical resistivity after ion irradiation and that after slow cooling, $\Delta\rho(T)$, and their temperature derivatives, $d(\Delta\rho)/dT$. In the figure, the relaxation curves for frozen-in disordering are also shown. Here, $\Delta\rho(T)$ corresponds to the degree of hydrogen ordering at a given temperature. The curve of $\Delta\rho$ shifts to higher temperature as the heating rate is increased. We use such a heating rate dependence later to determine the activation energy of hydrogen migration in the relaxation of hydrogen disordering. Fig. 3 clearly shows that hydrogen disordering which is frozen-in from 80 K relaxes around 55–60 K, while irradiation-induced disordering relaxes around two temperature regions; 35–40 K and 55–60 K. The relaxation process around 55–60 K for irradiation–induced disordering seems to be the same as that for frozen-in disordering.

The relaxation of irradiation-induced disordering starts at lower temperatures than that of frozen-in disordering. This trend can also be seen in Fig. 4, where the time variations of the change in resistivity at ~10 K, $\Delta\rho_{10\ K}(t)$, after ion irradiation and after fast cooling are plotted. The resistivity change, $\Delta\rho_{10\ K}(t)$, after ion irradiation increases

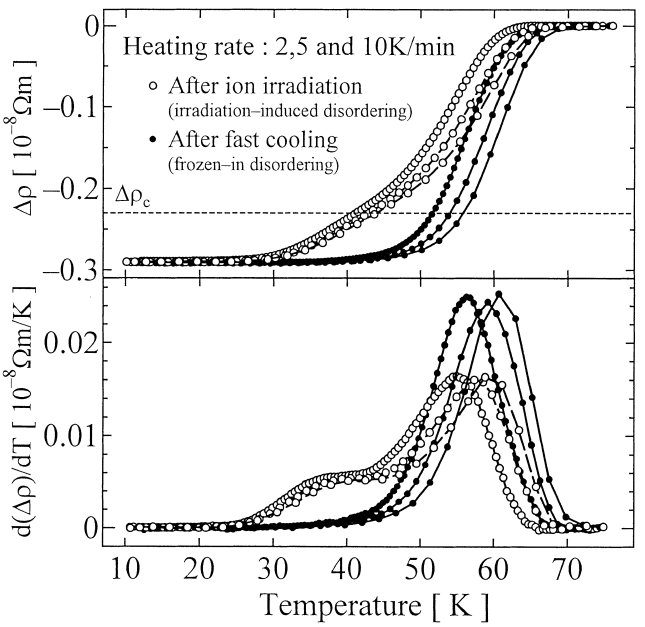

Fig. 3. Thermal relaxation behavior of hydrogen disordering after fast cooling and after ion irradiation as a function of temperature, for heating rates of 2 K/min (left curves), 5 K/min (middle curves) and 10 K/min (right curves).

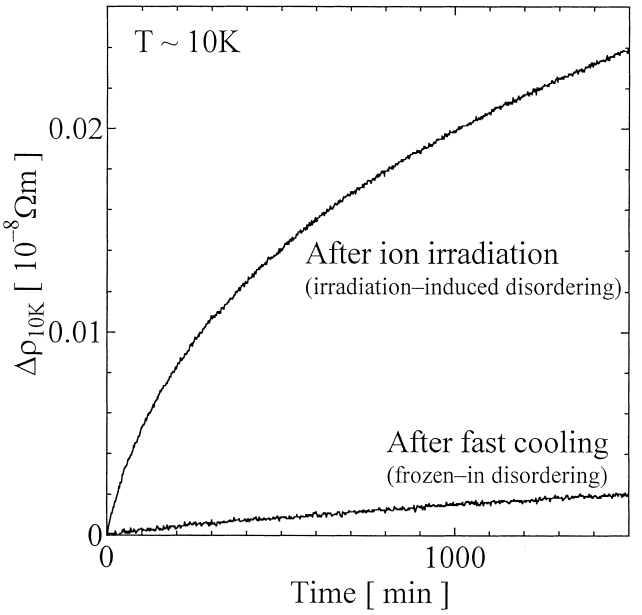

Fig. 4. Change in electrical resistivity at ~10 K, $\Delta\rho_{10\ K}$, as a function of time after ion irradiation and after fast cooling.

more swiftly than after fast cooling. This result is consistent with the results as shown in Figs. 2 and 3.

In order to derive the activation energy of hydrogen migration in the relaxation process around 35–40 K characteristic of irradiation-induced disordering, we analyzed the experimental results by means of the cross-cut method [11] in the lower temperature range, in which other relaxation processes are hardly observed. Therefore, the cross-cut resistivity, $\Delta\rho_c$, of -0.23×10^{-8} Ωm (as shown in Fig. 3) was chosen in the present analysis. Fig. 5 shows the relation between α/T_{cr}^2 and $1/T_{cr}$, where α is the constant heating rate and T_{cr} is the cross-cut temperature. The activation energy, which is determined from the slope of straight lines in Fig. 5, was 86±2 meV for both relaxation processes around 35–40 K and 55–60 K, though the relaxation temperature is quite different between the two relaxation processes.

On the analogy of the result in Ni_4Mo irradiated with electrons [12], a possible explanation is as follows; the state frozen-in from 80 K is not a completely disordered state but includes short-range order (SRO). The relaxation around 55–60 K may correspond to the transition from SRO to the long-range order (LRO). On the other hand, ion irradiation can destroy not only LRO but also SRO. Therefore, the relaxation around 35–40 K may correspond to the transition from complete disorder to SRO, which subsequently relaxes to LRO around 55–60 K. It is known that in the high-temperature SRO state hydrogen atoms occupy the octahedral sites [6]. Therefore, the agreement of the activation energy for the relaxations around 35–40 K and around 55–60 K implies that hydrogen atoms are distributed mainly on the octahedral sites also in the irradiation-induced state.

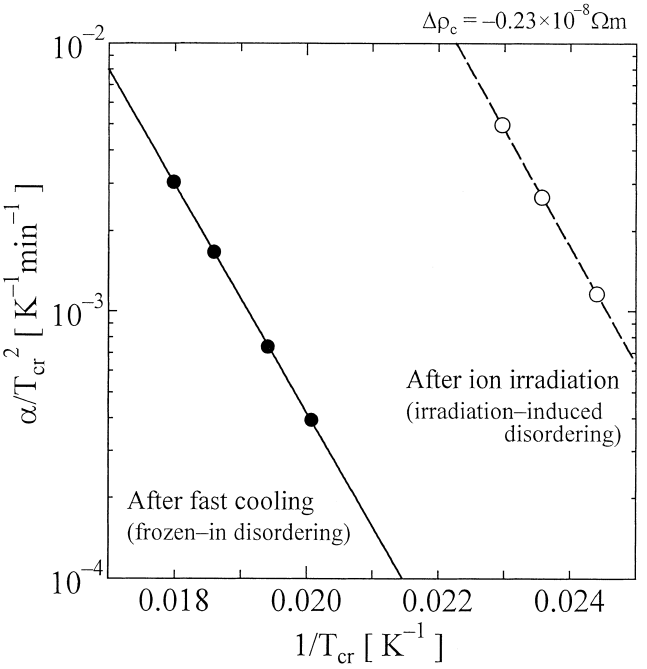

Fig. 5. Relation between α/T_{cr}^2 and $1/T_{cr}$ after ion irradiation (open circles) and after fast cooling (solid circles).

4. Summary

In order to study the effects of high-energy ion irradiation on the thermal relaxation of hydrogen disordering in the Pd–H system, the hydrogen disordering was induced in a $PdH_{0.6}$ specimen by either fast cooling from 80 K to 10 K or irradiation with 60 MeV ^{12}C ions at 10 K. The thermal relaxation behavior of hydrogen disordering was observed during heating the specimen to 80 K at several constant rates. Irradiation-induced disordering relaxes around two temperature regions, 35–40 K and 55–60 K, while disordering frozen-in from 80 K relaxes only around 55–60 K. The activation energy of hydrogen migration in the relaxation of hydrogen disordering was 86±2 meV for both relaxations around 35–40 K and around 55–60 K.

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