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LETTER TO THE EDITOR

Migration of hydrogen in rare-earth metals at the disorder–order transition

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Abstract. The migration energies, which are obtained using the hydrogen disorder–order transition, of hydrogen atoms in rare-earth metals divide into two groups, high values and low values. The high values are approximately double the low values. The cause of the discrepancy is discussed and explained as a misestimate of the order of the reaction in the rate equation for the low-value group. The high and low values of the migration energy agree well with each other on using the correct order of the reaction. The same explanation has been given for the case of Pd–H alloys.

There has been growing interest in the diffusivity of hydrogen atoms in metals. The migration energy of hydrogen at high temperatures has been determined for many metals, but the activation energy at low temperatures has rarely been determined. Therefore, the methods to obtain the energy at low temperatures have been developed using the structural disorder–order transition of the hydrogen atoms in the low-temperature range. In the following investigations, results for other hydrogen isotopes are also reported, but the situation is the same as that for the hydrogen atoms. Therefore the discussion will be limited to hydrogen atoms.

Daou *et al* [1] reported resistivity curves obtained with a constant rate of heating for quenched or electron-irradiated specimens of various lutetium–H alloys, and obtained as the order of the reaction $\gamma \sim 1$ and a migration energy of hydrogen of $E = 0.22\text{--}0.29$ eV (21.2–28.0 kJ mol⁻¹). They applied the same procedure to other rare-earth metals such as Y and Sc, and obtained nearly the same values for the migration energy of hydrogen. Their results were summarized in their review paper [2]. Swenson [3] measured the length changes of Lu–H alloy specimens during isothermal annealing and obtained $E = 0.22(1)$ and $0.31(4)$ eV (21.3 and 30.3 kJ mol⁻¹) with a combination of two processes of first-order reaction in their analyses. Jung and Lässer [4] obtained as the order of the reaction $\gamma \geq 2$ at around 160 K and a higher migration energy of hydrogen, $E = 0.45$ eV (43.4 kJ mol⁻¹), for quenched Lu–H alloys. Yamakawa and Maeta [5] determined the migration energy of hydrogen in quenched LuH_{0.06} and LuH_{0.12} alloys from a set of isothermal resistivity curves and obtained $E = 0.430$ eV (41.5 kJ mol⁻¹). They also determined the energy in YH_{0.05} by the same method and obtained $E = 0.481$ eV (46.4 kJ mol⁻¹) [6]. In their derivation of the energies, they did not need the order of the reaction to be different from that used in the analysis of Daou *et al* [1].

These values obtained for the migration energy of hydrogen divide into two groups, high values and low values (about half the high values), though the values are evaluated on the basis of the same process, namely the hydrogen disorder–order transition in rare-earth metals. The main discrepancy as regards the values obtained in these investigations is as follows. For high

values, the investigators obtained a second- (or higher-) order reaction or did not need the order of the reaction in their estimation. On the other hand, the investigators who obtained the low values used or obtained a first-order reaction in their analyses. Thus the cause of the difference between the energies becomes clear, because Daou *et al* [1] applied the following equation to determine the energies:

$$E = -\gamma k T_p^2 [d \Delta \rho(T_p)/dT] / \Delta \rho(T_p) \quad (1)$$

where T_p and $\Delta \rho$ are the peak temperature for the curve of the temperature derivative of the recovery and the resistivity (or resistance) change, respectively.

In their analysis method, the migration energy is proportional to the order of the reaction of the process. If the order of the reaction is $\gamma = 2$, the discrepancy problem for the hydrogen migration energies is resolved entirely, with good agreement with the values obtained by different methods.

Therefore, I checked the determination of the order of the reaction carried out by Daou *et al* [1] and found a misestimate in their method. They cannot determine the order of the reaction from their figure showing $\ln(-d \Delta \rho/dT)$ versus $\gamma \ln(\Delta \rho)$. For a constant rate of heating, we can get the following equation from a simple rate equation [7]:

$$E/kT + \ln(-d \Delta \rho/dT) = \ln(K_0/\alpha) + \gamma \ln(\Delta \rho) \quad (2)$$

where α is the heating rate in the relation $T = T_0 + \alpha t$. They plotted $\ln(-d \Delta \rho(T_p)/dT)$ versus $\ln(\Delta \rho(T_p))$ and stated that they obtained $\gamma \sim 1$. However, the order of the reaction cannot be derived from this plot, because a variable term, E/kT_p , is contained in equation (2) for each recovery curve.

If the order of the reaction is to be determined by means of their consideration, their analysis method must be as follows: by differentiation of the above expression, equation (2), with respect to T and using the relation $-d^2 \Delta \rho(T_p)/dT^2 = 0$, because they used the peak temperature of the derivative curve, equation (1) is derived.

Thus we can obtain the order of the reaction from E/kT_p^2 if we plot $-d \Delta \rho(T_p)/dT$ versus $\Delta \rho(T_p)$ using the data of Vajda *et al* [8]. An example is shown in figure 1 for their data for Y-H alloys, using their E -value, 0.21 eV (20.3 kJ mol⁻¹) [8], and our value, 0.481 eV (46.4 kJ mol⁻¹) [6]. From the figure, their data show accordance with $\gamma \sim 1$ and $\gamma \sim 2$ according to the value of the migration energy; i.e. in their method only the ratio E/γ can be derived and the order of the reaction cannot be decided on the basis of their data. Inconclusiveness of their value, $\gamma = 1$, has already been pointed out by Jung and Lässer [4].

In the present letter, the order of the reaction of the process is estimated from long-duration isothermal annealing experiments. In figure 2 the resistivity recovery curves are shown without correction for the heating time for 165 K isothermals for YH_{0.005} and YH_x alloys. The hydrogen concentration in the YH_x alloy was not determined, but it is inferred to be about double that for the YH_{0.05} alloy. The experimental procedure used was the same as in the earlier papers [5, 6]; the hydrogen-charged specimens were quenched into liquid nitrogen to obtain the disordered hydrogen before the annealing, and the resistivity was measured in liquid nitrogen after successive isothermal annealings.

For the isothermal annealing curves, the equation [7]

$$E/kT + \ln(-d \Delta \rho/dt) = \ln(K_0) + \gamma \ln(\Delta \rho) \quad (3)$$

is applied to determine the order of the reaction from a plot of $\ln(-d \Delta \rho/dt)$ versus $\ln(\Delta \rho)$; this is different from the case for a constant rate of heating because the term of E/kT is constant throughout the whole course of the annealing. These annealing temperatures correspond to high annealing temperatures for the hydrogen disorder-order transition in Y-H alloys. Therefore, correction for the heating time must be applied for short-time annealings for a precise analysis.

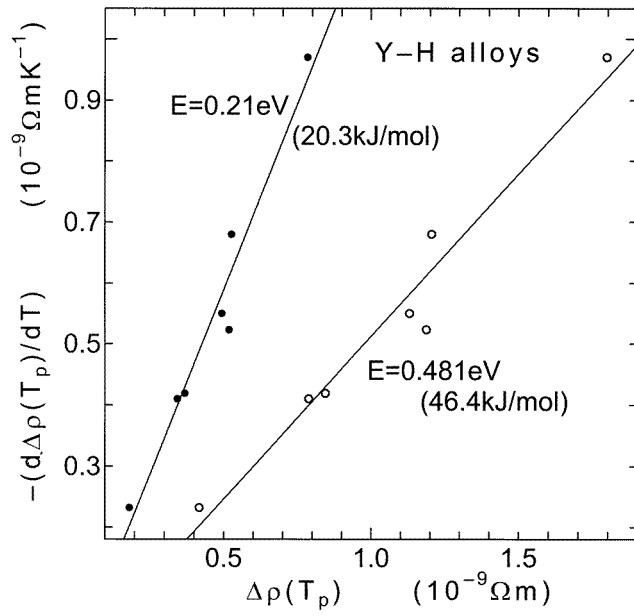


Figure 1. A logarithmic plot of the data of Vajda *et al* [8] for Y-H alloys, obtained using their migration energy, $E = 0.21$ eV (20.3 kJ mol $^{-1}$), and our value, $E = 0.481$ eV (46.4 kJ mol $^{-1}$), for the order of the reaction, γ . The slopes of the lines give $1/\gamma$. This figure shows that both values, $\gamma \sim 1$ and $\gamma \sim 2$, are permissible for the data of Vajda *et al*.

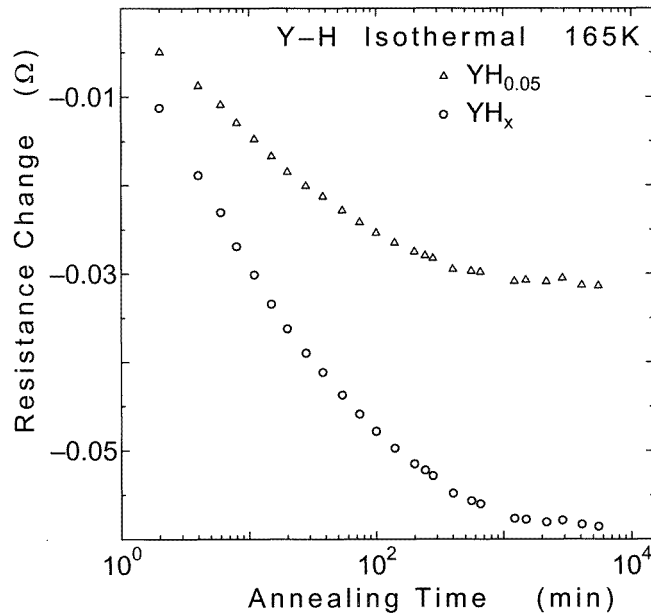


Figure 2. The isothermal annealing curves of the electrical resistance at 165 K for Y-H alloys. The specimens were quenched into liquid nitrogen from 273 K before the annealing. The hydrogen concentration in YH_x is inferred to be about double that in $\text{YH}_{0.05}$.

The correction has been applied for these isothermals as before, using the heating time and the migration energy of hydrogen that was obtained [6]. The corrected times were 0.5–0.6 min for each heating for temperatures up to 165 K. The curves of figure 2 are replotted to determine the order of the reaction from plots of $\ln(-d\Delta\rho/dt)$ versus $\ln(\Delta\rho)$ as shown in figure 3, and the slopes of the lines give the order of the reaction. The order obtained is $\gamma = 2.4$ – 2.5 (open symbols) without the heating time correction and $\gamma = 2.3$ – 2.4 (full symbols) with the correction. Some data points at the beginning and end of the isothermals were masked to determine the lines shown in the figure because other processes may affect these values.

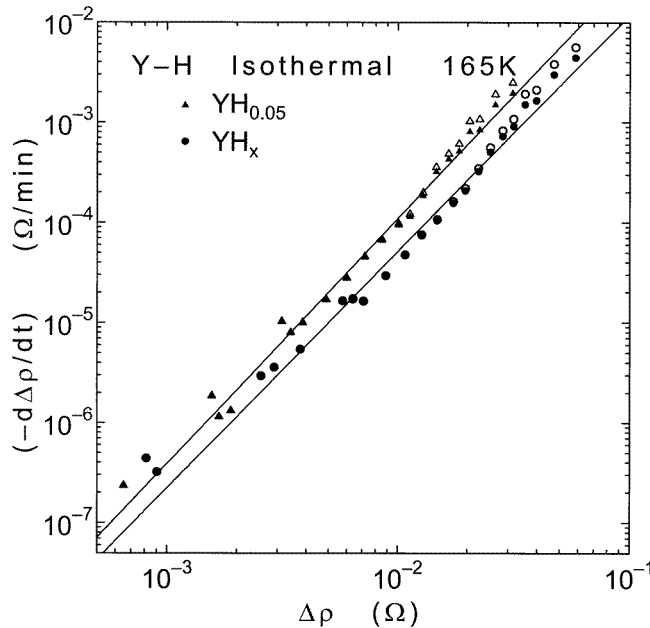


Figure 3. A logarithmic plot of the isothermal data of figure 2, used to determine the order of the reaction. The slopes of the lines give the order of the reaction. Open and full symbols show raw data points and data points with correction for the heating time, respectively.

Therefore, the order of the reaction of the process in the hydrogen disorder–order transition must be $\gamma = 2$.

Neutron diffraction results [9–11] showed that in this disorder–order transition the hydrogen atoms are paired across a metal atom and the pairs exist in ordered c -axis chains. These results suggest that the order of the reaction should be $\gamma = 2$, at least for the early part of the process, and this is in good agreement with the above values.

These features are the same, in principle, for the Pd–H case, though the resistivity change during the transformation from hydrogen disorder to order is very different from the behaviour in the rare-earth-metal–H cases. Yamakawa and Maeta [12] obtained a high migration value for quenched Pd–H alloys using the same analysis method as was used in investigating the hydrogen disorder–order transition, without using the order of the reaction. Vajda *et al* [13] obtained a low migration value and as the order of the reaction $\gamma = 1$ for quenched and electron-irradiated Pd–H alloys using their method. In the two investigations, the experimental methods were different. Therefore, Yamakawa *et al* [14] carried out similar experiments to those performed by Vajda *et al* [13] to clarify the large difference in hydrogen migration energy. They analysed the resistivity recovery data using the cross-cut method for a constant rate of

heating and using the method of Vajda *et al* [13] with $\gamma = 1$. The values obtained by the cross-cut method were double the values obtained by the method of Vajda *et al* with $\gamma = 1$, though the resistivity data were the same. These results are completely consistent with the above explanation of the discrepancy of the hydrogen migration energies.

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