ELSEVIER

Journal of Alloys and Compounds 293–295 (1999) 341–345

Journal of ALLOYS AND COMPOUNDS

Migration of hydrogen in yttrium at low temperatures

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Abstract

The migration of hydrogen atoms in yttrium ($YH_{0.05}$) is investigated by electrical resistance measurement around 150 K. The disordered hydrogen atoms are introduced by the quench from 273 K into liquid nitrogen and the hydrogen atoms are ordered by the migration of the atoms during the annealings. The activation energy of hydrogen migration is obtained from the kinetic analysis of the resistance decrease due to the ordering during the isochronal or isothermal annealings. The energy is determined more precisely by the isothermal annealings. The value, 0.481±0.005 eV (46.4±0.5 kJ/mol) is smaller than the high temperature values. The decrease of the value is caused by the tunnel effects of diffusion.

Keywords: Hydrogen migration; Order–disorder; Electrical resistivity; Low temperature; Yttrium–H alloy

1. Introduction

There has been growing interest in 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 been scarcely determined. The results show that the quantum effects in diffusion become more dominant in the low temperature range. Therefore, more measurements of the migration energy of hydrogen are desirable at a low temperature range.

Electrical resistivity of yttrium–hydrogen (or deuterium) alloys shows an anomaly around 160 K [1]. It is disclosed by neutron diffraction experiments that this anomaly is caused by the ordering of hydrogen isotopes which are dissolved in interstitial sites (*T*-sites) of the yttrium lattice in this temperature range [2]. In the Y–H(D) alloys, the electrical resistance decreases with the ordering of hydrogen isotopes and increases with the disordering. The migration energies of hydrogen isotopes in metal–H(D) alloys can be determined by using the electrical resistance change due to the ordering of hydrogen isotopes because the ordering is caused by migration of hydrogen isotopes [3–6]. Vajda et al. reported the migration energies, which are obtained by the electrical resistance change due to the ordering, of hydrogen isotopes in Y–H(D) alloys around 160 K [1]. In their analysis the order of reaction, which is difficult to obtain, and the temperature derivative at the peak temperature of the decay were used to determine the migration energy of hydrogen isotope. This is a convenient and general method for analyzing the reaction process in materials at low defect concentration. However, in the present case it contains questionable assumptions such as proportionality between the amount of hydrogen disorder and the resistivity change and no temperature dependence of disordered resistivity. The assumption of proportionality is suspected due to the high concentration of hydrogen atoms in the specimen. Furthermore, one can not guarantee that the electrical resistance change by hydrogen ordering follows a kinetic equation with a simple order of reaction.

In the present work, the behavior of hydrogen in Y–H alloys has been investigated by the measurement of the electrical resistance change due to the ordering of hydrogen. The analysis has been done for isochronal and isothermal annealing curves without using the above questionable assumptions. The results obtained from isothermal annealing have been compared with those from isochronal annealing.

2. Experimental details

The specimens were prepared from thin polycrystalline foil (100 μm in thickness) which was purchased from Goodfellow Metals Ltd. The nominal purity of the foil was 99.9%. The foil was cut into thin strips which were

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0925-8388/99/$ – see front matter
PII: S0925-8388(99)00397-7

annealed at 1220–1270 K in ultrahigh vacuum (10^{-6} Pa) longer than 2 h to degas gaseous impurities and to reduce dislocation density. The specimens were the thin strips to which were spot-welded four thin platinum leads. The hydrogen atoms were introduced into the specimen by electric current heating the specimen in a hydrogen gas atmosphere. The amount of hydrogen in the specimen was determined as $YH_{0.05}$ by using the data of resistivity at 273 K after the hydrogen charging and before charging [1].

After the hydrogen charging, the specimens were set on a specimen holder and were quenched into liquid nitrogen from 273 K after holding at 273 K for 10 min to obtain disordered hydrogen atoms. Then isochronal annealing curves of electrical resistance were obtained for heating-up and cooling-down with various rates of temperature change. The isothermal annealing curves at various temperatures were also obtained after the same quenching procedure above mentioned. The specimen without hydrogen charging after annealing in an ultrahigh vacuum, hereafter, is called the vacuum-annealed specimen.

In the present experiment, the same specimens are used to obtain a set of isochronal and of isothermal curves because the same disordered state of hydrogen is obtained by heating-up to 273 K. For the isochronals the heating rates were from 10 K/1 min to 10 K/5600 min. The temperatures on the isothermal annealing ranged between 137.5 and 170 K.

The specimens were quenched into liquid nitrogen after each isochronal or isothermal annealing to maintain the annealed state during measurement and to reduce the temperature dependent resistance and therefore the electrical resistance was always measured in liquid nitrogen by the standard four-probe method.

3. Experimental results and discussion

The values of electrical resistance of the specimen at 77 K are shown in Fig. 1 against various cooling rates. In these cooling procedures the specimens were held for 10 min at 273 K and then cooled down to low temperature from 273 K with constant cooling rates between 0.1 K/min and 2×10^4 K/min. The highest rate (2×10^4 K/min) corresponds to the quenching from 273 K into liquid nitrogen. At higher cooling rates the rate could not hold to the constant rate. Therefore, the mean rate around 180 K is taken for the higher cooling rate because the hydrogen atoms order in this temperature range. The measured resistance increases almost linearly against the logarithm of cooling rate. This fact shows that the quenched-in resistance is related to the thermally excited process.

The isochronal curves of the electrical resistance for Y–H alloy are shown in Fig. 2 for heating-up and cooling-down together with the curves of the vacuum-annealed specimen. The isochronal curves of the vacuum-annealed specimen scarcely change for the whole temperature range of the annealing. On the other hand, the curves of hydrogen-charged specimen show an abrupt decrease around 160 K and again increase around 200 K for heating-up and show a decrease around 240 K and saturation to the constant value for cooling-down. Therefore it is concluded that the observed change of electrical resistance is caused by hydrogen atoms charged. The stage of abrupt decrease which appears in isochronal curve of heating-up, shifts to higher temperatures with increasing rate of heating as shown in Fig. 3. From the shift of the stage in these isochronal curves, the activation energy of hydrogen migration is obtained by the method of constant heating rate.

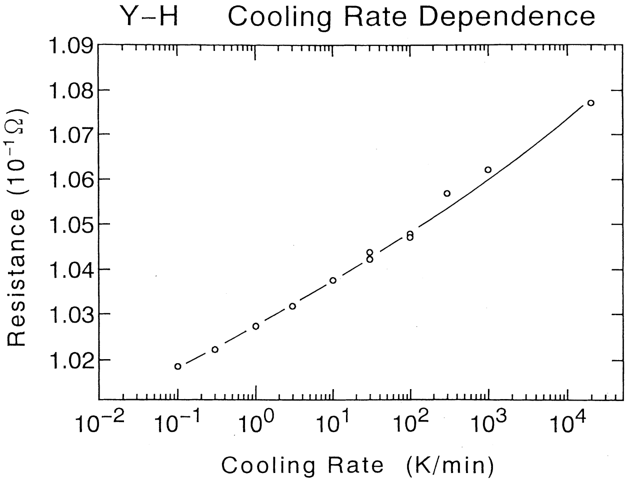

Fig. 1. The values of electrical resistance at 77 K against cooling rate. At higher cooling rates, the mean rates around 180 K are shown.

The saturated value of the resistance at a low temperature range in the cooling-down curve decreases with decreasing of cooling rate of the specimen. This is caused

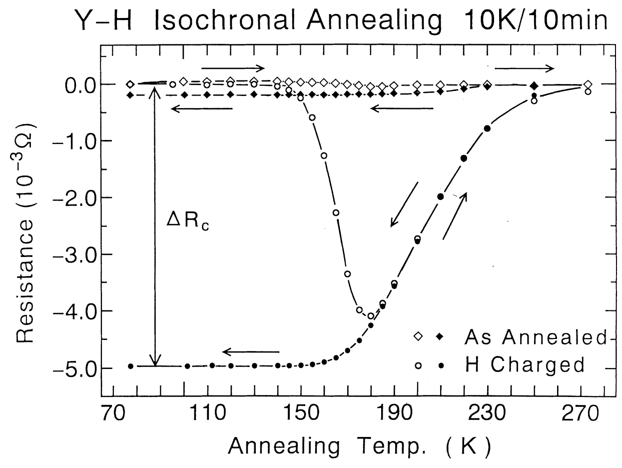

Fig. 2. The isochronal curves of electrical resistance for heating-up (open marks) and cooling-down (full marks) at the heating rate 10 K/10 min together with those of as vacuum-annealed specimen. The total resistance change ΔR_c is defined as in the figure.

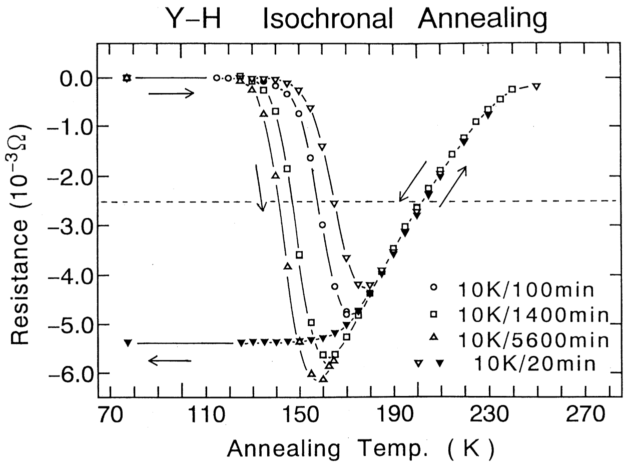

Fig. 3. The isochronal curves of electrical resistance for heating-up (open marks) and cooling-down (full marks) at various annealing times. The decay stage around 160 K shifts to lower temperature with decrease of heating rate.

by the difference of time duration at which hydrogen atoms are able to migrate to order.

The quenched-in resistance decreases during the isothermal annealing as shown in Fig. 4. The resistance change ΔR on the isothermal annealing curves is normalized by the amount of the total resistance change ΔR_c which is defined as shown in Fig. 2 on the isochronal curve for 10 K/10 min. Each isothermal curve shifts parallel to the region of shorter annealing time with increasing annealing temperature. This fact shows that the process of the hydrogen ordering is a thermally activated process.

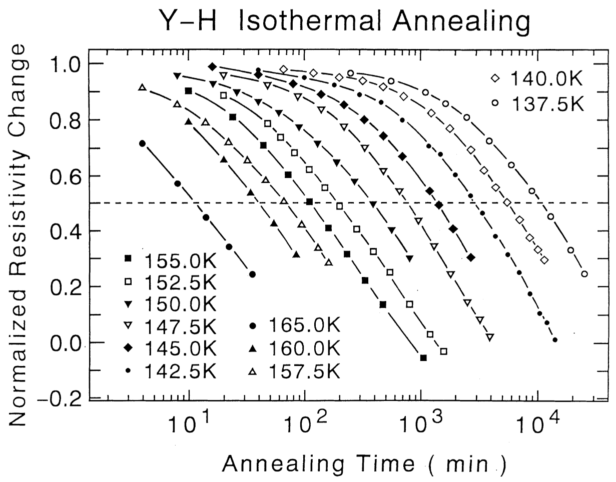

Fig. 4. The isothermal curves of electrical resistance at various annealing temperatures. The resistance decay shifts to shorter annealing time with higher annealing temperature. The resistance decrease is normalized by ΔR_c which is defined in Fig. 2.

It is assumed that the electrical resistance change due to hydrogen ordering, ΔR is a function of the amount, n, of hydrogen disordering. A rate equation for the thermally excited process is shown as any function, $F(n)$, of the amount,

$$-\,\mathrm{d}n/\mathrm{d}t = K_0 F(n)\exp(-E/kT) \tag{1}$$

where K_0, E and k are reaction constant, migration energy of hydrogen isotope and Boltzmann's constant, respectively [7].

By integration on the condition of constant rate of heating $T = \alpha t$ and $E/kT \gg 1$, the following relation is obtained:

$$\ln(\alpha_2 T_1^2/\alpha_1 T_2^2) = E/k(1/T_1 - 1/T_2) \tag{2}$$

where T_1 and T_2 are the temperatures at which identical amount n are achieved at heating rates α_1 and α_2, respectively [7].

For isothermal annealing curves, by integration of the rate equation on the condition of isothermal annealing,

$$\ln(t_1/t_2) = E/k(1/T_1 - 1/T_2) \tag{3}$$

where t_1 and t_2 are the annealing times at which identical amount n are achieved at the annealing temperatures T_1 and T_2, respectively [7].

By both methods one can easily determine the migration energy without using the order of reaction and the assumption of proportionality between the electrical resistance change and amount of disordering of hydrogen. From Eqs. (2) or (3) the migration energy is obtained as the slope of the line for the graph of $\ln(T^2/\alpha)$ vs. $1/T$ for isochronal annealing curves and $\ln(t)$ vs. $1/T$ for isothermal annealing curves. Though these methods are troublesome because of the necessity of obtaining many isochronal or isothermal curves, the correct value of migration energy must be obtained.

The annealing temperature to attain the same resistance decrease is estimated from Fig. 3 as the crossing point with the broken line and the isochronal curve. Though the number of data points in this stage of the resistance decrease on the isochronal curve is not sufficiently high, the temperature is determined for each isochronal curve. The value $\ln(T^2/\alpha)$ from each isochronal curve is plotted in Fig. 5 against the reciprocal of the annealing temperature. A straight line is obtained at slow heating rates for a set of the curves with the same specimen. Deviation at high heating rates from the straight line at slow heating rates is caused by the following reasons. In these isochronal curves the heating-up time to the annealing temperature is not taken into consideration. By the heating-up time correction the value of T^2/α increases at high heating rates and the data points become closer to the line extrapolated from the slow heating rates. The value of migration energy of hydrogen is estimated from the slope of the line at the slow heating rates as 0.458 ± 0.008 eV (44.2 ± 0.8 kJ/mol).

The migration energy of hydrogen in Y–H alloys is obtained from the time intervals needed to the same resistance decrease at various isothermal annealing tem-

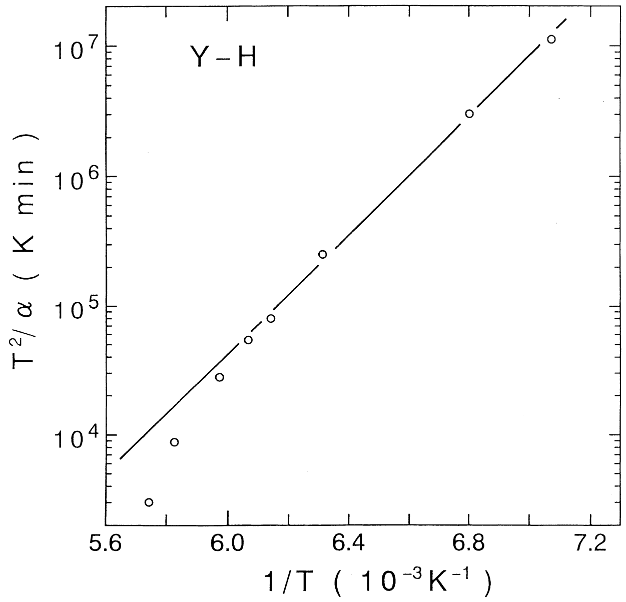

Fig. 5. Logarithm of T^2/α against the reciprocal of the annealing temperature. The symbol T is the annealing temperature at which the same resistance decrease is attained at heating rate α. The slope of the line shows the migration energy of hydrogen atoms.

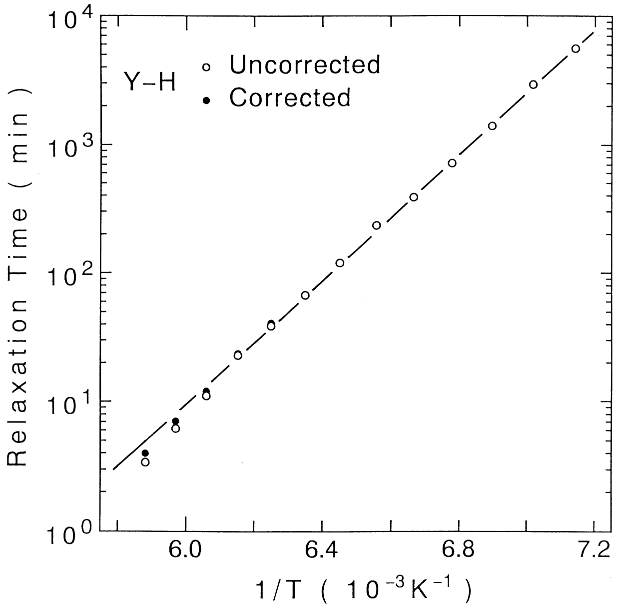

Fig. 6. Logarithm of the relaxation time for the process against the reciprocal of the annealing temperature. The slope of the line shows the migration energy of hydrogen atoms. The open marks show raw data and the full marks show the data corrected for heating-up time.

peratures. The annealing time interval to attain the same normalized resistance decrease is estimated from Fig. 4 as the crossing point with the broken line and the isothermal curve. The time interval is defined as the relaxation time of the process. The relaxation time corresponds to the time required for the migration of hydrogen because the resistance decrease is caused by the migration of hydrogen to induce the hydrogen ordering. The logarithm of the uncorrected relaxation time on the isothermal annealing is plotted against the reciprocal of the annealing temperature with open marks as shown in Fig. 6. A straight line is obtained for the specimen at a low temperature range and it bends downward at a high temperature range. The migration energy of hydrogen is estimated from the slope at the low temperature range as 0.481±0.005 eV (46.4±0.5 kJ/mol). At high annealing temperatures each annealing time is from few minutes to several minutes. In these cases the time needed to heat-up the specimen to the annealing temperature becomes an interval of the same order to the annealing time. The time to heat-up is neglected on the isothermal curves in Fig. 4. However, for the determination of the migration energy at high temperature range the time can not be ignored. Each heating-up time at high temperature range is converted to the equivalent time at the annealing temperature by using the measured heating-up rate, heating-up time and obtained migration energy of hydrogen. The equivalent time is added to the annealing time. At low temperatures, the annealing time is not affected by the heating-up time because each annealing time is sufficiently long. The corrected relaxation times are also plotted in Fig. 6 with full marks.

It must be noted that the migration energy of hydrogen which is obtained by the above two different methods (by the isochronal annealing or isothermal annealing) shows similar value. This fact suggests that the process is analyzed correctly by these methods. The disagreement between the values obtained from both methods is caused by following reasons. For the isochronal annealing curves the heating-up time correction is not done. The number of data points at the stage in the isochronals is too few to determine the temperature precisely. Constant heating rate required by the calculation is approximated with step like annealing rate in the experiment. Therefore, the value from isothermal curves is recommended as a more precise value for the migration energy of hydrogen than that from isochronal curves. Vajda et al. [1] obtained very smaller value, 0.200±0.020 eV (19.3±1.9 kJ/mol) by the measurement of electrical resistance change comparing with the present value. It is caused by their no good assumptions as mentioned in the introduction.

The present values are clearly smaller than the high temperature value [8,9]. Anderson et al. [8] and Lichty et al. [9] investigated hydrogen diffusion in Y–H alloys by quasi-elastic neutron scattering between 590 K and 700 K and nuclear magnetic resonance around 500 K, respectively. They obtained hydrogen migration energy of 0.6 eV (58 kJ/mol) and 0.51 eV (49.2 kJ/mol), respectively. In many metal–H systems the diffusivity of hydrogen atoms has been measured and the diffusivity at low temperatures in M–H systems such as Ni–H, Ta–H and Nb–H has been higher than those extrapolated from the value obtained at high temperatures [10,11]; i.e., the migration energies of hydrogen decrease with decreasing of the temperature. The values determined by hydrogen ordering in Pd–H and Lu–H alloys also decrease at low temperatures [3–6]. This phenomenon is interpreted by the tunnel effects of diffusion which become more important at low temperatures and small mass of diffusing atoms. Therefore the smaller value is caused by the tunnel effects of diffusion.

Acknowledgements

We gratefully acknowledge Dr. E. Hashimoto, Hiroshima University for heat treatment of the specimens in ultrahigh vacuum to reduce lattice defects such as gaseous impurities and dislocations. This work has been supported by the JAERI-University Research Cooperation.

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