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Effect of hydrogen on the electrical resistance of palladium

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Abstract

A four-point constant-current technique was used to determine the change in resistivity with time at 298 K for Pd-wires which had been annealed for 20 h at 1000 K in both argon and hydrogen atmospheres. A large resistivity decrement was discovered in the H_2-annealed wires which was not obtained in the case of the Ar-annealed specimens. The resistivity decrement has been related to recrystallization effects concomitant with the production of H-induced vacancies in the Pd-lattice.

Keywords: Palladium; Electrical resistance hydrogen absorption

1. Introduction

The electrical resistance, *R*, of hydrogenated palladium has been the subject of experimental studies for a long period of time going back to the work of Graham [1] in 1869. Much of the early work on the variation of *R* with H-content (θ) and temperature was concerned with the dependence of *R* upon the phases (α and β) present in the Pd–H system [2]. In the work to be discussed in the present paper we will restrict our observation and interpretation to effects measured in the single phase region (i.e., small θ-values) so as to avoid such complications.

The object of the resistivity measurements was to study the effect upon *R* that is expected to ensue from the generation of H-induced vacancies in the Pd lattice. The generation of large vacancy concentrations in Pd and Ni was first observed by Fukai and Okuma in their measurements of the lattice parameter of the metals after exposure to H_2-gas at high pressure (5 GPa) [3]. Similar studies by Fukai and Okuma [4,5] were followed by a series of experimental studies in which H-induced vacancy formation was observed indirectly by measuring the rapid diffusion rates of lattice atoms in order–disorder reactions in H-containing Pd-based binary substitutional solutions [6–10].

This experimental activity provided the impetus for a study of H-induced vacancy formation in Pd in which the statistical methods derived previously [11] were combined with the effective medium estimates of the ε_{bi}, the H-vacancy binding energies, [12] in order to calculate the vacancy concentration in hydrogenated Pd [13]. Recently, Maroevic and McLellan have developed a cell model based upon Fermi–Dirac statistics to calculate the vacancy concentration in hydrogenated Pd [14]. These calculations showed that at 1000 K the vacancy concentration in Pd would increase more than 3 orders of magnitude as θ, the atomic ratio of H/Pd, increased from 0→0.1. It is obvious that H-induced vacancy enhancement should lead to a substantial increase in the mobility of lattice atoms migrating by a vacancy-exchange process [15].

Such a degree of H-induced vacancy concentration and associated microstructural changes, such as grain growth, grain boundary reconstruction, and dislocation density reduction, due to the enhanced mobility of lattice atoms, may lead to a change in electrical resistivity of palladium. In the present report, the electrical resistance of palladium after hydrogen gas charging at different temperatures and different times has been measured by means of a four-point technique and the possible mechanisms associated with the change in electrical resistance have been discussed.

2. Experimental procedure

Palladium wires of purity 99.994% with diameter d= 0.25 mm, were purchased from Johnson Matthey Co. The Pd wires were ultrasonically cleaned using acetone and

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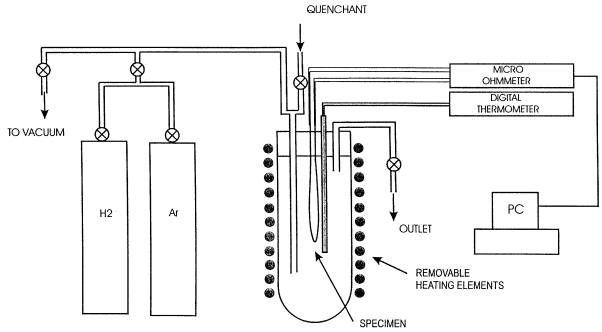

Fig. 1. Schematic of the experimental setup developed for in situ measurement of electrical resistance.

methanol, followed by an annealing in a vacuum furnace of 10^{-5} Pa at 1100 K for 20 h.

A schematic of an experimental setup developed for in situ measurement is shown in Fig. 1. The electrical resistance of the specimen before hydrogenation was measured is designated R_o. The resistance of the Pd specimen during H-charging, R_t, was measured in situ. After hydrogenation, the specimen was quenched to room temperature and then annealed at room temperature in atmosphere. The electrical resistance measurements were carried out by the four-point constant-current technique and was recorded by a personal computer. The resistance, R_f, obtained after annealing for long time (more than 70 h) where no more resistance change was observed, was used to calculate the increment or decrement of resistance in Fig. 3. The online temperatures were displayed by a digital thermometer.

3. Results

The wires were equilibrated at 1000 K with H_2-gas at atmosphere pressure for 20 h. This treatment results in an H-concentration in equilibrium of $\theta=9\times10^{-3}$ [16] where θ is the H/Pd atomic ratio. After this gas charging treatment, the wires were quenched and the resistance measured as a function of time at 298 K. The ratio R_t/R_o decreases in the manner shown in Fig. 2 (Plot (a)). The data obtained for

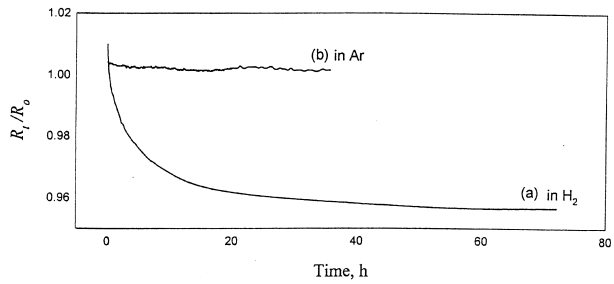

Fig. 2. Relative resistance, R_f/R_o, vs. time of annealing in atmosphere at 295 K. Plot (a), after the specimens were H_2-gas charged at 1000 K for 20 h and then quenched. Plot (b) shows the data after the specimen were Ar-gas treated at 1000 K for 20 h and then quenched.

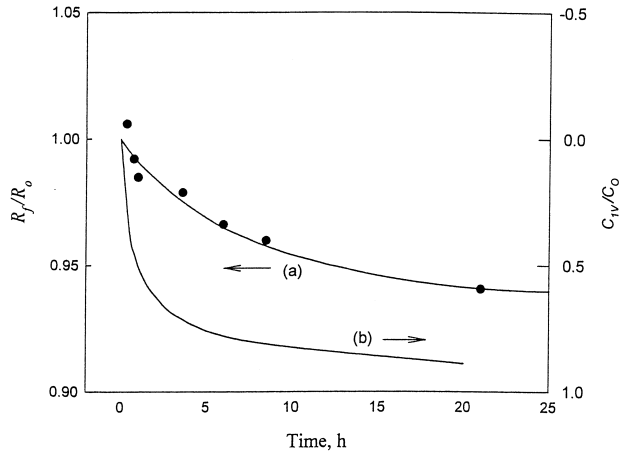

Fig. 3. Plot (a), Relative resistance, R_f/R_o, and plot (b), relative vacancy concentration, C_{1V}/C_O, as a function of H_2-charging time.

the four sets of measurements were coincidental to within ±12.5% and the lower curve in Fig. 2 represents the arithmetic mean of the data sets. The Plot (b) in Fig. 2 show the results obtained under identical conditions (i.e., 20 h at 1000 K, followed by the quench) except that the 1000 K treatment was carried out in an argon atmosphere instead of H_2. The decrease in resistivity with time observed in the argon-annealed wires is clearly not observed.

In a second set of experiments, H_2-gas charging at 1000 K was carried out for successive times, the wires quenched, and the final value of R_f/R_o determined after a steady state resistance had been reached at 273 K in air. Each wire was monitored for at least 70 h in order to determine R_f The results are shown in Plot (a) of Fig. 3. It is clear that the final resistivity decrement increases with equilibration time.

4. Discussion

The observed decrease in electrical resistance of Pd after hydrogen charging at 1000 K is an interesting phenomenon. This experiment involves three procedures, that is, introduction of hydrogen, high temperature exposure, and quench. All these procedures could affect the electrical resistance of Pd wire and need to be carefully considered. Introduction of hydrogen will increase the electrical resistance. High temperature exposure can cause grain growth and quenching can freeze the equilibrium vacancy concentration generated at high temperature. Both of these mechanisms could have effects on the measured electrical resistance. However, the experimental results shown in Fig. 2 obtained from the specimen treated in the argon atmosphere indicate that the change in electrical resistance possibly caused by high temperature exposure at 1000 K/20 h and quench from 1000 K to room temperature were not significant.

This conclusion is strengthened by direct measurements of the average grain size in which it was found that the average grain size was ~15 μm for the specimens after the treatments under the two different experimental conditions.

In regard to the contribution of quenched-in vacancies to the resistivity, we must first estimate the vacancy concentrations produced in the H_2 and Ar annealing processes. If equilibrium is achieved in 20 h at 1000 K, the Ar-anneal will result in a vacancy concentration C_{1V} given by,

$$C_{1V} \cong \exp\left[1 - \frac{H^f_{1V}}{kT}\right] \quad (1)$$

where we have set, arbitrarily, the vacancy formation entropy at $S^f_{1V} = k$ and H^f_{1V} is the vacancy formation enthalpy. The best value for H^f_{1V} is 1.5 eV (144.7 kJ mol^{-1}) [13]. Eq. (1) gives $C_{1V} = 7.5 \times 10^{-8}$. For the hydrogenated Pd containing the equilibrium H-concentration [16], the value of C_{1V} (H) can be calculated from the relations developed previously [13] and the ε_{bi}-values from the effective medium calculations [12]. The result is C_{1V} (H) 2.5×10^{-7}.

It should perhaps be noted that the ratio C_{1V} (H)/C_{1V} increases very rapidly as the temperature decreases [13] and this remains true when the usual Maxwell–Boltzmann statistics are replaced by the more accurate Fermi–Dirac expressions [14,17].

The remaining question relates to the attainment of the equilibrium values of C_{1V} (H) and C_{1V}. If the conservative assumption is made that the surface of the solid acts as an 'infinite' (i.e., non-depleted) vacancy source, then the time (t)–distance (x) profiles for the vacancy concentration are given by the appropriate solution of Fick's Second Law, i.e.,

$$C_{1V}(x, t) = C_{1V}(0)\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{D_{1V}t}}\right)\right] \quad (2)$$

where $C_{1V}(O)$ is the surface concentration and D_{1V} is the monovacancy diffusivity given by,

$$D_{1V} = a_o^2 \nu \exp\left(-\frac{H^m_{1V}}{kT}\right) \exp\left(\frac{S^m_{1V}}{k}\right) \quad (3)$$

where a_o is the cube edge length, ν is the attempt frequency, and $H1^m_V$ and S^m_{1V} are the vacancy motion enthalpy and entropy. The best value of H^m_{1V} is 1.75 ev (121 kJ mol^{-1}) [18]. Setting $S^m_{1V} = 0$ and using the Debye frequency for ν enables reasonable penetration profiles to be calculated. For $t = 7.2 \times 10^4$ s (20 h), $C_{1V}(x)/C_{1V}(O) \approx$ 0.9 for $x = 0.5$ mm. Thus even neglecting the generation of vacancies at internal discontinuities, there is no doubt that the equilibrium vacancy concentrations are achieved during the annealing 20 h periods. If this is the case, then the different behavior (H_2 vs. Ar) revealed in Fig. 2 is a consequence of the effect of the generation of 'extra' vacancies due to the presence of dissolved H-atoms. However, at 1000 K $C_{1V}(H)/C_{1V}$ is only ~3.3, and furthermore, the absolute values of vacancy concentration are small.

An accurate description of the electron transport in the metal–hydrogen system, such as Pd–H, is a tedious problem, especially if the resistivity measurements are to be used in search for such microscopic changes in metal as hydrogen induced vacancies, hydrogen defects itself, and possible recrystallization exhibited through either grain growth, grain boundary reconstruction, or dislocation density reduction. Theoretical descriptions of the electron scattering in metals [19,20] are generally complex even for much simpler systems than this one and do not provide results which would enable a quantitative elucidation of the results of Fig. 2 to be made. We will thus attempt to explain the results found using simple description and estimates of orders of magnitude.

Firstly, we will assume that the phonon contribution to R is independent of the concentration of lattice defects. This assumption is valid provided the concentration of defects is small. The decrease in R seen in the lower curve of Fig. 2 is due to the out-migration of H-atoms. Curve fitting of the shape of the plot for small annealing time to the expression for the out-gassing of a semi-infinite cylinder gives resulting values for the H-diffusivity in Pd which are close to measured diffusivity at low temperatures [21]. The final value of R, or the resistivity decrement, is due to the effect of H-induced vacancies.

A simple description of the contribution of vacancies and dislocations to the electrical resistivity has been given by Tsivinskii [22]. In his model R is proportional to the vacancy concentration and to the dislocation density. Although the metal Pd was not specifically treated, order-of magnitude comparison with metals neighboring Pd in the Periodic Table are certainly in order. A more elaborate theory of dislocation scattering in metals was given by Hunter and Nabarro [23] and same measurements performed by Buck et al. [24]. The effect of grain structure on resistivity is usually simplified using the average grain diameter as a parameter. A model was proposed by Mayadas and Shatzkas [25] and applied to the resistivity of thin films [26]. The resistivity is inversely proportional to the average gram size.

Now the resistivity of Pd ranges from 10^{-8} Ωm to 10^{-7} Ωm in the temperature range 100–1000 K [27]. Vacancies increase the resistivity with a contribution proportional to C_{1V}, but the proportionality constant is ~10^{-6} Ωm as calculated using Tsivinskii's model [22] so that the resistivity decrements found in this work are clearly not due to the frozen-in vacancies. The references given in this section indicate, qualitatively, that the dislocation scatting would contribute 10^{-12}~10^{-14} Ωm to R for high dislocation density of 10^{11}~10^{13} m^2 and a grain boundary contribution of ~10^{-11} Ωm corresponding to the microscopically observed average grain size of ~10 μm. Thus, of all the possible mechanisms which could account for the resistivity decrement found, the effects of reducing dislo-

cation density and grain boundary reorganization are the largest, but can not be quantitatively attributed to the measured effects. The atomistic details of the recrystallization process are not understood but it is clear that the 'extra' vacancy concentration generated by the H_2-anneal at 1000 K is sufficient to produce the recrystallization during the 20 h charging period.

The recrystallization kinetics are reflected in the data of Fig. 3. The resistivity decrement is small for short charging times. Values of $C_{1V}(x, t)/C_{1V}(O)$ calculated from Eq. (2) and Eq. (3), for x set at the radius of the wire, are given in Plot (b) of Fig. 3 (right-hand scale). Saturation of the wire with H-induced vacancies occurs as the charging time approaches 20 h.

5. Conclusions

Resistivity decrements found after the annealing of Pd wires in H_2-atmospheres for up to 20 h at 1000 k and subsequent quenching are not due to the presence of residual H-atoms or frozen-in vacancies, but to a recrystallization process accelerated by H-induced vacancy formation. The atomistic nature of the recrystallization process is not known at this time, but the elimination or reorganization of sub-grain boundaries and the reduction of the dislocation density are viable candidates.

Acknowledgements

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References

[1] T. Graham, Proc. Roy. Soc. 17 (1869) 212.
[2] F.A. Lewis, The Palladium/Hydrogen System, Academic Press, New York, 1967.
[3] Y. Fukai, N. Okuma, Jap. J. Appl. Phys. 32 (1993) 1256.
[4] Y. Fukai, N. Okuma, Phys. Rev. Lett. 73 (1994) 1640.
[5] Y. Fukai, J. Alloys Comp. 231 (1995) 35.
[6] H. Noh, J.D. Clewley, T.B. Flanagan, Scripta mater. 34 (1996) 665.
[7] H. Noh, T.B. Flanagan, Y. Sakamoto, Scripta metall. mater. 29 (1993) 445.
[8] K. Watanabe, N. Okuma, Y. Fukai, Y. Sakamoto, Y. Hayashi, Scripta mater. 34 (1996) 551.
[9] T.B. Flanagan, H. Noh, J. Alloys Comp. 231 (1995) 1.
[10] H. Noh, T.B. Flanagan, Y. Sakamoto, J. Alloys Comp. 231 (1995) 10.
[11] R.B. McLellan, J. Phys. Chem. Solids 49 (1988) 1213.
[12] P. Nordlander, J.K. Norskov, F. Besenbacher, S.M. Myers, Phys. Rev. B 40 (1989) 1990.
[13] R.B. McLellan, L. Yang, Acta. metal. mater. 43 (1995) 2463.
[14] P. Maroevic, R.B. McLellan, Equilibrium Vacancy Concentration in Pd-H Solid Solutions, Acta materialia - in press.
[15] R.B. McLellan, Acta. mater. 45 (1997) 1995.
[16] C. Labes, R.B. McLellan, Acta metall. 26 (1978) 893.
[17] P. Maroevic, R.B. McLellan, J. Phys. Chem. Solids 58 (1996) 403.
[18] D. Zang, R.B. McLellan, Scripta mater. 1207 (1997) 36.
[19] J.M. Ziman, Electrons and Phonons, Claredon Press, Oxford, 1960.
[20] V.F. Gantmakher, Y.B. Levinson, Carrier Scattering in Metals and Semiconductors, North Holland, Amsterdam, 1987, pp. 241–252.
[21] R. Kirchheim, R.B. McLellan, J. Electrochem. Soc. 127 (1980) 2419.
[22] S.V. Tsivinskii, Phys. Stat. Sol. (a) 80 (1983) 439.
[23] S.C. Hunter, F.R.N. Nabarro, Proc. Roy. Soc. 220A (1953) 542.
[24] O. Buck, D. Schumacher, A. Seeger, Phys. Stat. Sol. 60 (1973) 707.
[25] A.F. Mayadas, M. Shatzkes, Phys. Rev. B 1 (1970) 1382.
[26] J.W.C. De Vries, Thin Solid Films 167 (1988) 25.
[27] G.T. Dyos, T. Farrell, Elecrical Resistivity Handbook, London, 1992, pp. 472–473.