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Electrical resistance measurements as a function of composition of palladium–hydrogen(deuterium) systems by a gas phase method

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Abstract. The simultaneous measurement of both the relative electrical resistance and the equilibrium hydrogen and deuterium pressure as a function of composition of Pd–H and Pd–D systems have been carried out at temperatures between 273 and 323 K at H₂(D₂) pressures up to about 3.3 MPa. The relative resistance, R/R_0 , in the $(\alpha + \beta)$ two-phase region for the absorption processes shows a very small and almost linear increase with increasing H(D) content, especially for the Pd–H system, compared to the larger changes previously observed by the electrolysis method. The resistance behaviour is quite similar to the shape of p – c isotherm relationships. The relative resistance increments per unit change of H(D)/Pd content at 298 K, $\Delta(R/R_0)/\Delta r$, in the $(\alpha + \beta)$ two-phase region are about 1.5 and 2.1 times larger for the Pd–H and Pd–D systems, respectively, compared to the changes in the relative lattice parameters with H(D)/Pd content, $\Delta(a/a_0)/\Delta r$, within the two-phase region, where a_0 is the lattice parameter of H(D)-free Pd and r is the atom ratio. On the other hand, the resistance increment in the α single solid solution phase and β single phase, except for the higher-H(D)-content region, is significantly larger compared to the changes of the lattice expansion due to dissolved hydrogen and deuterium. Thus, the variation in resistance with hydrogen and deuterium content in the $(\alpha + \beta)$ two-phase region may be mainly associated with an incoherent formation of β hydride within the α phase. The relative resistance for the subsequent desorption processes from the absorption up to about 3.3 MPa at 298 K in both Pd–H and Pd–D systems exhibits almost the same maximum as that of the absorption processes, i.e. $(R/R_0)_{H,\max} \simeq 1.87$ at about H/Pd = 0.76 and $(R/R_0)_{D,\max} \simeq 2.07$ at about D/Pd = 0.75, and then the R/R_0 values decrease gradually with decreasing H(D) content up to the β_{\min} phase boundary composition; on entering the $(\alpha + \beta)$ two-phase region, the R/R_0 values remain almost constant, i.e. $(R/R_0)_{(\alpha+\beta)} \simeq 1.76$ for the Pd–H system and $(R/R_0)_{(\alpha+\beta)} \simeq 1.89$ for the Pd–D system. This large hysteresis of resistance can be attributed to the creation of ‘lattice strain deformations’ accompanied by dislocation formation from β hydride (deuteride) formation and by further highly dissolved hydrogen and deuterium in the β phase region.

1. Introduction

A number of investigations of the electrical resistance of the palladium–hydrogen and palladium–deuterium systems have been carried out mainly by an electrolytic charging method and/or by absorption of hydrogen by the specimens directly from hydrogen-saturated and stirred acidic solutions [1–8] or using a high-pressure device [9–12]. More recently, with regard to ‘cold-fusion’ experiments, the resistance of the Pd wire electrodes with D has been remeasured [13, 14], in comparison with that of the Pd–H system, because the resistance measurement is a simple and useful way of obtaining the H(D) contents of the Pd electrode as the electrolysis proceeds.

It has been shown [2] that in the Pd–H and Pd–D systems, two phases, α and β (α') with low and high hydrogen (deuterium) concentrations, respectively, exist in equilibrium below the critical temperature; the octahedral interstitial sites of the fcc Pd lattice are occupied for both the α and β phases. The previously observed relationships between the electrical resistances of the Pd–H and Pd–D systems (298 K) and the H(D) contents have appeared to be not associated with the $(\alpha + \beta)/\beta$ phase boundary.

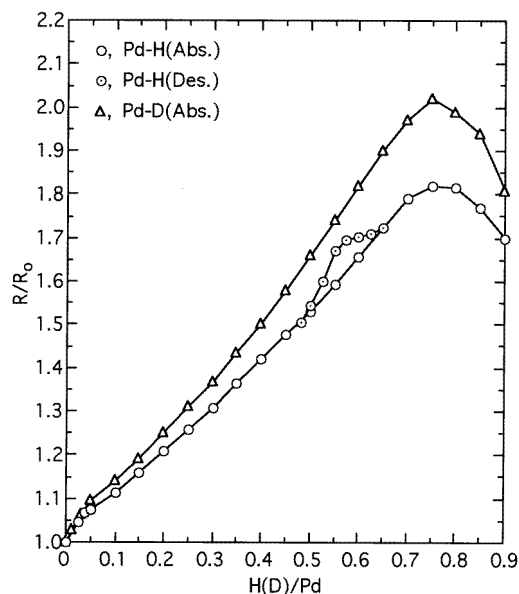


Figure 1. The previously reported relative resistance, R/R_0 , against H(D)/Pd content at 298 K in Pd–H and Pd–D systems measured mainly by the electrolysis method [1–5, 8, 9, 13, 14]. \circ , absorption for the Pd–H system; \odot , desorption for the Pd–H system; \triangle , absorption for the Pd–D system.

Figure 1 shows the previously reported relative electrical resistance, R/R_0 (298 K) as a function of H/Pd and D/Pd content [1–5, 8, 9, 13, 14], where R_0 is the resistance of the initially H(D)-free sample. The relationships between R/R_0 and the H(D)/Pd content have almost the same shape for both the Pd–H and Pd–D systems but, at the same H(D) content, the resistance is somewhat larger for the Pd–D system, in particular in the high-H(D)-content region. The relative resistance in the α phase region of both systems increases almost linearly with increasing H(D) content up to about the α_{\max} phase boundary composition. Even in the $(\alpha + \beta)$ two-phase region from α_{\max} to about H(D)/Pd = 0.6, near the β_{\min} phase boundary composition, the resistance increases relatively strongly with increasing H(D) content, although the rate of increase is smaller than that in the α phase region. With further increase of the H(D) content, the rate of increase gradually decreases and R/R_0 reaches a maximum at around H(D)/Pd = 0.75. In the higher-H(D)-content region, the resistance again decreases (figure 1). The decrease in the high-concentration region has been confirmed using high pressure devices [9–12].

The interpretation of Bambakidis *et al* [6, 7] of the shape of the R/R_0 –H(D)/Pd curves is based on the gradual filling of the d-band holes for H(D)/Pd < 0.55, and the presence of an NaCl type structure for H(D)/Pd > 0.55; they did not take into account the presence of the $(\alpha + \beta)$ two-coexistent phase, i.e. the irreversible ‘plastic deformation (lattice strains)’

accompanied by the dislocations introduced by the β hydride formation [15, 16]. They assumed that the hydrogen is screened from the conduction electrons by the highly localized palladium d band for $H(D)/Pd < 0.36$ [17]. For $0.36 < H(D)/Pd < 0.55$, the hydrogen electrons enter increasingly into s states, resulting in a decrease in the screening effect and consequently a more rapid increase in R/R_0 as $H(D)/Pd$ increases from 0.36 to 0.55. Above 0.55, vacancies in the stoichiometry of the NaCl type lattice are filled by hydrogen and the R/R_0 value goes through a maximum near 0.75 and then decreases to approximately one at $H(D)/Pd = 1$. Fletcher *et al* [8] have shown that the behaviour of the resistance in the two-phase region with either the hydrogen or deuterium concentration may be explained on the simple basis that the observed resistance is an approximate average between the resistances at the α_{\max} and β_{\min} phase boundary compositions. Baranowski *et al* [10, 12] explained qualitatively the observed resistances of Pd–H and Pd–Ag–H systems under high-pressure conditions, based on the assumption of partial occupation of both octahedral and tetrahedral sites by hydrogen after filling the d-band vacancies.

The previously employed electrolytic charging method for electrical resistance measurements is a convenient way of determining the resistance as a function of H and D contents, however, the method may be sensitive to the accumulation of some cathodically deposited impurities that may influence the absorption or desorption rates, and may consequently influence the H(D) contents absorbed or desorbed, at least during a long electrolysis time in the high-H(D)-content region.

In this study, in order to avoid the difficulty in measuring the resistance and H(D) contents during electrolysis, the electrical resistances of Pd have been measured in the temperature range 273–323 K by means of a four-point technique, while simultaneously the pressure–composition isotherms have been determined.

2. Experimental details

The experimental set-up for measurement of electrical resistance by the gas phase method is shown in figure 2, where (a) is a conventional pressure (p)–composition (c) isotherm measurement apparatus constructed of all stainless steel tubes and vessels with VCR couplings, Swagelok tube fittings and weldings. Pressures were measured by two pressure gauges: one is a $0\text{--}10^3$ Torr pressure transducer (MKS) for relatively low-pressure measurements and the other is a $0\text{--}2.5 \times 10^4$ Torr (about 3.3 MPa) (MKS). The system is also capable of evacuation up to about 4×10^{-5} Pa. The enclosure with dotted lines in the figure is a constant-temperature chamber enclosing the dosing tube with the gas reservoir and the pressure transducers. (b) is the reaction vessel (outer diameter 1/2 in \times 150 mm, SUS 316 tube), for which the bottom is welded and the feed-through in the upper is sealed by Varian ‘Torr-Seal’.

6.0077 g of fully annealed Pd foil (99.99 wt%, a bench mark specimen supplied by Tanaka Kikinzoku Kogyo KK for research projects of NHE) of thicknesses 50–60 μm cut into about 2 mm \times 5 mm pieces was used in the reaction vessel as a sample for p – c isotherm measurements; the sample for electrical resistance measurement had dimensions of about 120 μm \times 2 mm \times 20 mm, and had been spot-welded with Ni lead wires (0.3 mm \varnothing). As an electrical insulation for the Ni-lead wires, appropriate glass tubes were used, and, in order to diminish the dead space of ‘connection tube’ volume a glass rod was inserted in the tube. V_c and V_s are the volumes of the ‘connection’ tube and ‘sample (reaction) vessel’, respectively, and they were calibrated as accurately as possible by taking into consideration the volumes of the glass rod, tubes and lead wires. V_R is a reaction valve. Before inserting the Pd specimens into the vessel, they were chemically etched with a solution of 2:2:1

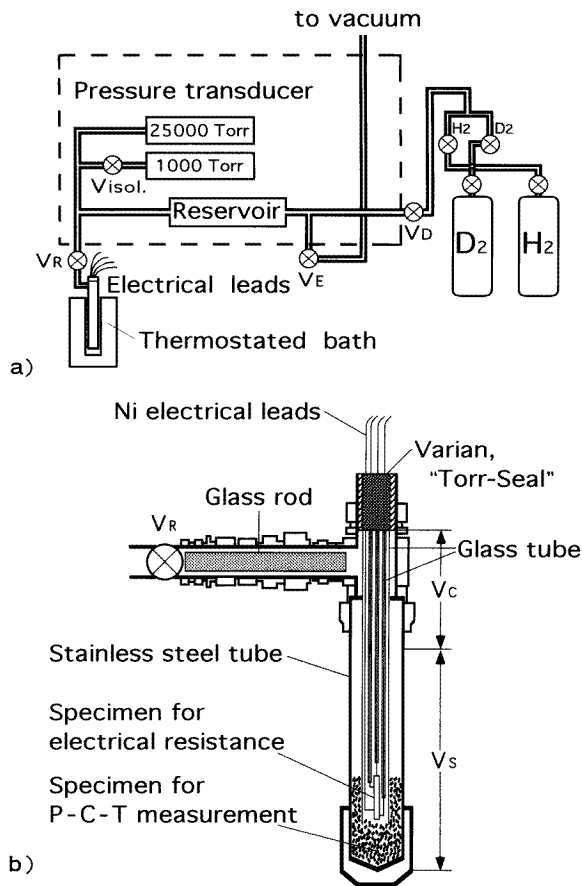


Figure 2. Experimental set-up for measurement of electrical resistance by a gas phase method: (a) pressure (p)-composition (c) isotherm measurement apparatus; (b) the reaction vessel.

$H_2SO_4:HNO_3:H_2O$ mixture in order to remove any oxides from the surfaces. In order to obtain a highly active state for the p - c isotherm measurements and resistometry, the vessel was completely outgassed at 573 K and about 4×10^{-5} Pa, and then the samples were exposed to hydrogen gas of $p_{H_2} \approx 0.1$ –3 MPa for 10 min. Subsequently, the vessel was slowly cooled down into ice-water, and dehydriding by evacuating and reheating to 573 K was then accomplished. This hydriding-dehydriding treatment was repeated more than 10 times.

The electrical resistance measurements were carried out at the following temperatures: 273, 298 and 323 K (± 0.1 K) and at pressures up to $p_{H_2(D_2)} \approx 3.3$ MPa by the four-point-constant-current reversal technique with 50 mA. After attaining equilibrium pressures, the electrical resistances were measured and the hydrogen and deuterium concentrations in the sample were determined, from the pressure changes following each absorption or desorption in the known volumes, and are expressed as $r = H(D)/Pd$, i.e. as the ratio of the number of hydrogen (deuterium) atoms to the number of Pd atoms. In the determination of $H(D)/Pd$ contents at higher pressures, $p_{H_2(D_2)} > 0.4$ MPa, in order to avoid the difficulties in determining $H(D)/Pd$ values [18], they were calculated using the extrapolation formula of

the Wicke–Nernst p - c isotherms [19], i.e. $\log p_{\text{H}_2(\text{D}_2)} = -A(T) + B(T) \text{H(D)}/\text{Pd}$ for both Pd–H and Pd–D systems by measuring the initial and final equilibrium pressures during the absorption and desorption processes [18].

In the experiments for the Pd–D system, about 1.5 kg of granular $\text{Fe}_{0.94}\text{Ti}_{0.96}\text{Zr}_{0.04}\text{Nb}_{0.04}$ alloy was used as a D_2 storage system in a 1000 ml 316 stainless steel cylinder vessel. After absorption of D_2 gas by the alloy material at 273 K and up to about 1.5 MPa, the required D_2 pressures could be obtained by electrical heating of the vessel.

The initial resistance of the H(D)-free Pd sample, R_0 , used in this study before a series of experiments of Pd–H and Pd–D systems at the individual temperatures was about $4.2682 \pm 0.1067 \text{ m}\Omega$ at 273 K, $4.6523 \pm 0.1163 \text{ m}\Omega$ at 298 K and $5.0710 \pm 0.1268 \text{ m}\Omega$ at 323 K; after each experiment the R_0 values returned to the resistance values within about 2–3% on degassing the samples at 573 K for more than 3 h *in vacuo*.

3. Results and discussion

The relationships between the relative resistance, R/R_0 , and the H/Pd content at temperatures of 273, 298 and 323 K for the Pd–H system are shown in figures 3–5, respectively, together with the p - c isotherms. Figures 6–8 show the corresponding relationships for the Pd–D system. The insets in the same figures are enlarged versions of the plots of the respective R/R_0 against H(D)/Pd. As shown in figures 4, 5, 7 and 8 for the experiments at 298 and 323 K, the relative resistance was measured for the subsequent desorption processes (\odot), together with the desorption isotherm measurements (\square); however the desorption processes are incomplete because the kinetics were sluggish.

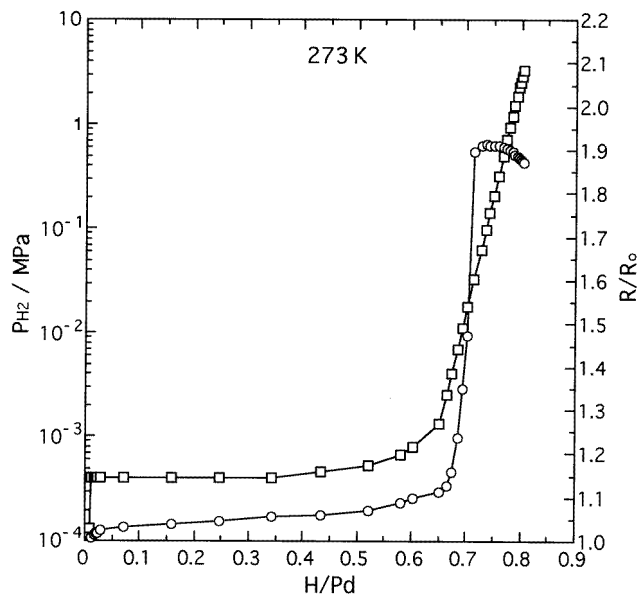


Figure 3. Relative resistance, R/R_0 , as a function of H/Pd content at 273 K for absorption, along with the p - c isotherm. \circ , R/R_0 , against H/Pd; \square , p_{H_2} against H/Pd.

It can be seen that in the α single (solid solution) phase region of both systems, the R/R_0 values increase with increasing H(D) content up to about α_{max} composition. In the $(\alpha + \beta)$

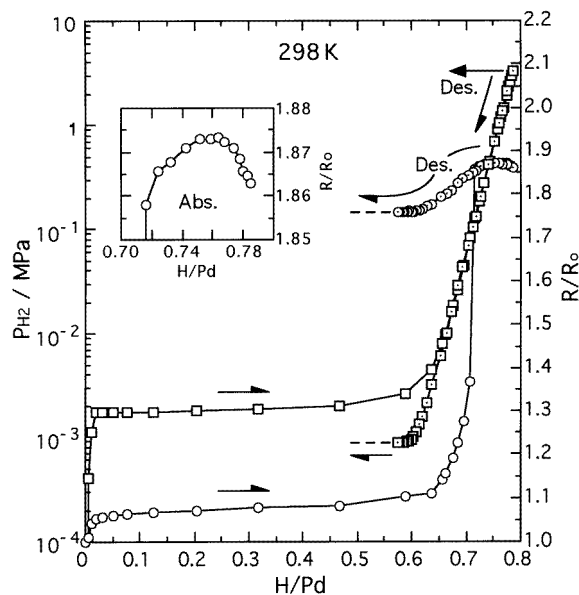


Figure 4. Relative resistance, R/R_0 , as a function of H/Pd content at 298 K for absorption–desorption processes, along with the p – c isotherm. \circ , R/R_0 against H/Pd for absorption; \odot , R/R_0 against H/Pd for desorption; \square , p_{H_2} against H/Pd for absorption; \square , p_{H_2} against H/Pd for desorption. The arrows indicate the directions of absorption and desorption processes.

two-phase region, compared to the previously reported results (figure 1) [1–5, 8, 9, 13, 14], the R/R_0 values show only a small increase from α_{\max} up to about the β_{\min} composition, especially for the Pd–H system. The behaviour of R/R_0 against H(D) content is quite similar to the shape of the p – c isotherms. On entering the β single solid solution phase region, the resistance increases abruptly, reaching a maximum; e.g., the $(R/R_0)_{H,\max} \approx 1.87$ at around H/Pd = 0.76 and $(R/R_0)_{D,\max} \approx 2.07$ at D/Pd ≈ 0.75 (298 K). After passing through the maximum with further increase of the H(D) content, the resistance decreases due to an approach to the stoichiometry of NaCl type lattice, i.e. to an increase of the ordering. In the β phase region of both systems, the R/R_0 maximum values tend to decrease with increasing temperature. This temperature dependence in the β phase region is the opposite to that in the α and $(\alpha + \beta)$ phase regions.

It has been found [20, 21] that in the α single-phase region of Pd and Pd solid solution alloys, the resistance increases almost linearly with hydrogen content up to about H/Pd = 0.015, where the hydrogen was introduced by electrolysis with a short current pulse, e.g., at 301 K the resistance increment per unit change of hydrogen concentration in pure Pd, $d(R - R_0)/R_0/dr$ is about 3.7 [20]. This resistance increment is in good agreement with that of the present result.

The R/R_0 values at the α_{\max} and β_{\min} phase boundary compositions at 298 K in both systems obtained from the extrapolation of the R/R_0 values from the relatively low-H(D)/Pd-content region for the absorption results are $(R/R_0)_{\alpha_{\max},H} = 1.06 \pm 0.01$ at $r_{\alpha_{\max}} \approx 0.015$, $(R/R_0)_{\beta_{\min},H} = 1.11 \pm 0.02$ at $r_{\beta_{\min}} \approx 0.61$ for the Pd–H system: the former $(R/R_0)_{\alpha_{\max},H}$ value is in agreement with that observed by the electrolytic charging method [3]; and for the Pd–D system $(R/R_0)_{\alpha_{\max},D} = 1.08 \pm 0.01$ at $r_{\alpha_{\max}} \approx 0.02$, $(R/R_0)_{\beta_{\min},D} = 1.15 \pm 0.02$ at $r_{\beta_{\min}} \approx 0.6$. Thus, the relative resistance increment per unit change of H(D)/Pd content

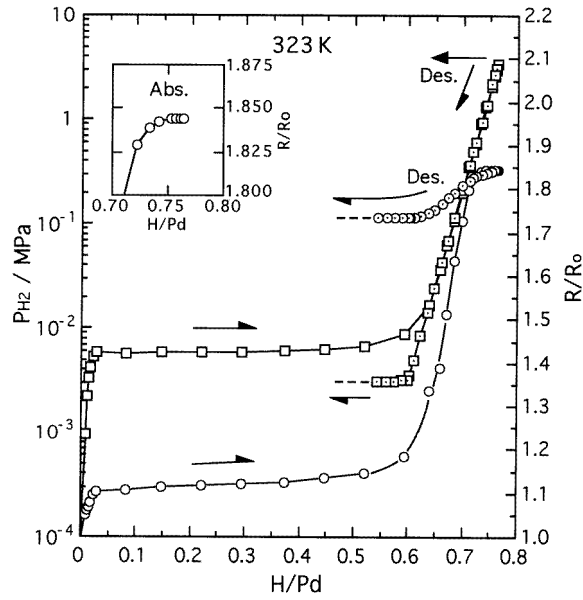


Figure 5. Relative resistance, R/R_0 , as a function of H/Pd content at 323 K for absorption-desorption processes, along with the p - c isotherm. \circ , R/R_0 against H/Pd for absorption; \odot , R/R_0 against H/Pd for desorption; \square , p_{H_2} against H/Pd for absorption; \square , p_{H_2} against H/Pd for desorption. The arrows indicate the directions of absorption and desorption processes.

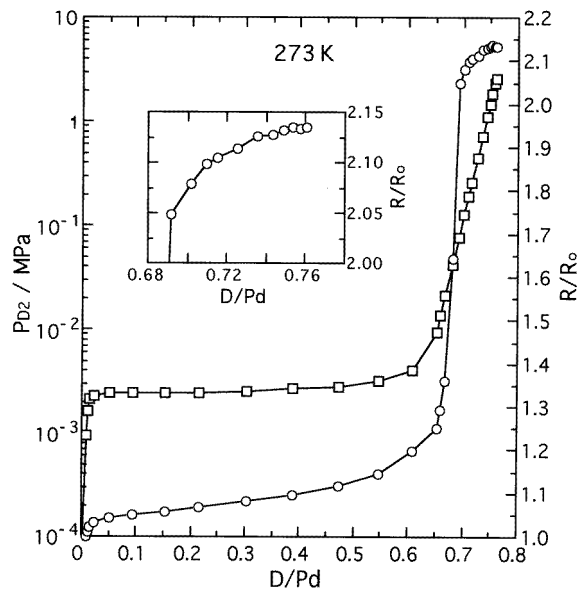


Figure 6. Relative resistance, R/R_0 , as a function of D/Pd content at 273 K for absorption, along with the p - c isotherm. \circ , R/R_0 against D/Pd ; \square , p_{D_2} against D/Pd .

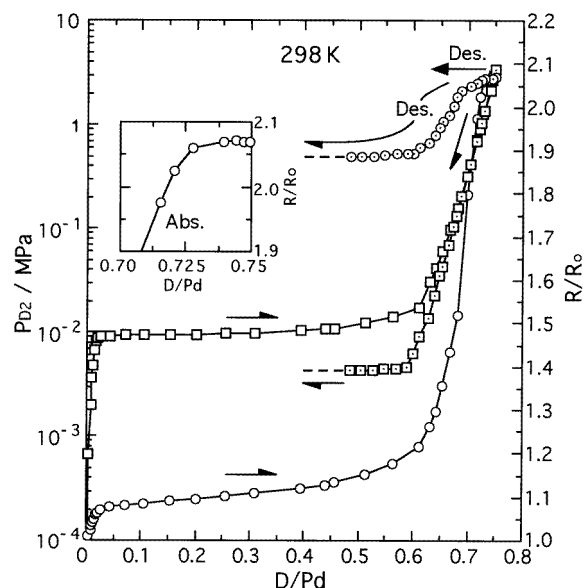


Figure 7. Relative resistance, R/R_0 , as a function of D/Pd content at 298 K for absorption–desorption processes, along with the p – c isotherm. \circ , R/R_0 against D/Pd for absorption; \odot , R/R_0 against D/Pd for desorption; \square , p_{D_2} against D/Pd for absorption, \square , p_{D_2} against D/Pd for desorption. The arrows indicate the directions of absorption and desorption processes.

within the $(\alpha + \beta)$ two-phase region at 298 K is $\Delta(R/R_0)/\Delta r_{(\alpha+\beta)} \simeq 0.084$ for the Pd–H system and $\Delta(R/R_0)/\Delta r_{(\alpha+\beta)} \simeq 0.12$ for the Pd–D system.

It has been shown that the lattice parameters at the α_{\max} and β_{\min} phase boundary compositions for the Pd–H system are $a_{\alpha_{\max},H} = 0.3895$ nm at H/Pd $\simeq 0.015$, and $a_{\beta_{\min},H} = 0.4025$ nm at H/Pd $\simeq 0.61$, respectively, at 298 K [22, 23]. Similarly, for the Pd–D system the lattice parameters at the α_{\max} and β_{\min} phase boundary compositions are $a_{\alpha_{\max},D} = 0.3893$ nm at D/Pd $\simeq 0.01$, and $a_{\beta_{\min},D} = 0.4022$ nm at D/Pd $\simeq 0.6$ [23, 24].

The relative resistance increment per unit change of H(D)/Pd content at 298 K, $\Delta(R/R_0)/\Delta r_{(\alpha+\beta)}$ is about 1.5 and 2.1 times larger for Pd–H and Pd–D systems, respectively, than the changes in the relative lattice parameters with H(D)/Pd content, i.e. $\Delta(a/a_0)/\Delta r$, between the α_{\max} and β_{\min} phase boundary compositions, where a_0 is the lattice parameter of H(D)-free Pd, i.e. 0.3890 nm. However, the resistance increment in the α single solid solution phase and β single phase, except for the high-H(D)-content region with H(D)/Pd $\gtrsim 0.72$, is significantly larger compared to the changes in the lattice expansion due to dissolved hydrogen and deuterium; the changes in the relative lattice parameters with H(D)/Pd content in the α single-phase region are $\Delta(a/a_0)/\Delta r \simeq 0.085$ for the Pd–H system [22, 23] and $\Delta(a/a_0)/\Delta r \simeq 0.077$ for the Pd–D system [23, 24], and the changes of the lattice parameters in the β single-phase region of both systems are $\Delta(a/a_0)/\Delta r \simeq 0.046$ in the composition range $0.8 < r < 0.98$ [25] at a temperature of 77 K.

Thus, the formation of β hydride, i.e. the initiation and growth in the two-phase region, may be regarded as incoherent between the two phases, because the relative resistance increment per unit change of H(D)/Pd content is almost the same order of magnitude to the changes in the relative lattice parameter with H(D)/Pd content. However, the steep increase

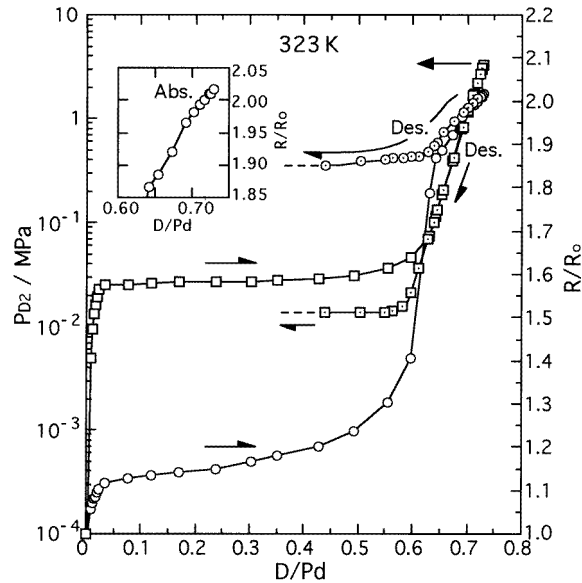


Figure 8. Relative resistance, R/R_0 , as a function of D/Pd content at 323 K for absorption–desorption processes, along with the p – c isotherm. \circ , R/R_0 against D/Pd for absorption; \odot , R/R_0 against D/Pd for desorption; \square , p_{D_2} against D/Pd for absorption; \square , p_{D_2} against D/Pd for desorption. The arrows indicate the directions of absorption and desorption processes.

of resistance in the α single solid solution region and in the β single-phase region up to the maximal R/R_0 values seems to be mainly related to the scattering of conduction electrons due to the lattice expansion, in particular the steep increase in the β phase region may be due to the creation of plastic deformation by further highly dissolved hydrogen (deuterium), because the macro-lattice strains, i.e. the changes in lattice parameters in the β phase region [25], are smaller than those in the α phase region. At almost the same H(D) contents in the α and $(\alpha + \beta)$ two-phase regions, the R/R_0 values have a tendency to increase with increasing temperature due to a thermal effect.

As can be seen from figures 4, 5, 7 and 8, the relative resistance for the subsequent desorption processes from the high-H(D)-content region exhibits a similar behaviour to that of the absorption processes, and then the R/R_0 values decrease gradually with decreasing H(D)/Pd content up to about the β_{\min} phase boundary composition, and on entering the $(\alpha + \beta)$ two-phase region the R/R_0 values have a tendency to remain almost constant, e.g., at 298 K $R/R_{0(\alpha+\beta)} \simeq 1.76$ for the Pd–H system and $R/R_{0(\alpha+\beta)} \simeq 1.89$ for the Pd–D system. The constant R/R_0 values in the $(\alpha + \beta)$ two-phase region did not quite change even if the system was degassed at the same temperature, 298 K for 3 h *in vacuo*.

In order to obtain more detailed information about the resistance behaviour for desorption, resistance measurements were also carried out at 298 K during the subsequent desorption following absorption to about 0.13 MPa. Figures 9 and 10 show the relationships between the relative resistance, R/R_0 , and H(D)/Pd content at 298 K for Pd–H and Pd–D systems, respectively, together with the corresponding p – c isotherms. It can be seen by comparison with the results shown in figures 4 and 7 that there is a good reproducibility for the resistance behaviour in the absorption processes up to about 0.13 MPa. On the subsequent desorption for the Pd–H system the resistance increases slightly initially, and

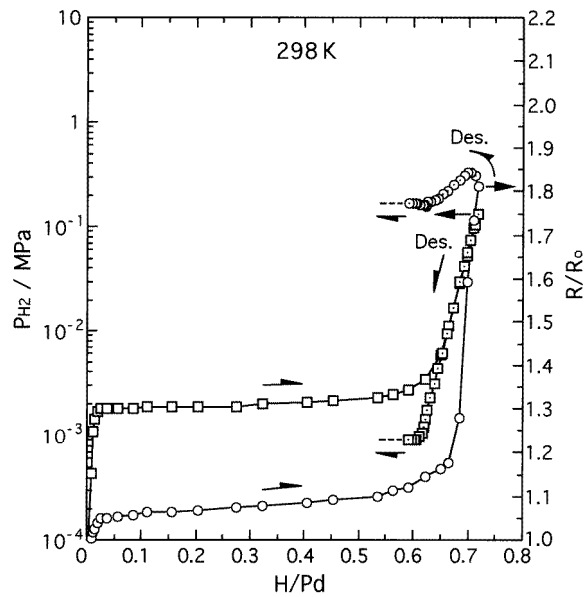


Figure 9. Relative resistance, R/R_0 , as a function of H/Pd content at 298 K for absorption–desorption processes up to about $p_{H_2} = 0.13$ MPa, along with the p - c isotherm. \circ , R/R_0 against H/Pd for absorption; \odot , R/R_0 against H/Pd for desorption, \square , p_{H_2} against H/Pd for absorption; \square , p_{H_2} against H/Pd for desorption. The arrows indicate the directions of absorption and desorption processes.

then the R/R_0 values decrease gradually with decreasing H/Pd content in a rather similar way to those shown in figure 4; on entering the $(\alpha + \beta)$ two-phase region the R/R_0 values also remain constant. The constant R/R_0 value is almost the same as observed for the subsequent desorption experiments from the absorption processes up to higher pressures of about 3.3 MPa (figure 4).

In the case of desorption following absorption up to about 0.13 MPa for the Pd–D system, the R/R_0 value unexpectedly increases steeply initially with decreasing D/Pd content down to about D/Pd = 0.6, and then attains a small maximum. After that, the resistance again decreases with decreasing D/Pd content, and on entering the $(\alpha + \beta)$ two-phase region, the resistance also tends to remain constant at about $R/R_0 = 1.59$ (figure 10). The initial increase in resistance during the desorption process has been similarly observed for Pd alloy–hydrogen systems: Pd–Ni–H [26], Pd–Rh–H [26, 27] and Pd–Pt–H [28]. Its origin is unknown; it may however be associated with the formation of micro-lattice strains and distortions due to the hydride (deuteride) decomposition. The subsequent decrease of R/R_0 value before reaching an almost constant value may be due to the lattice relaxation by desorbed deuterium.

The small increase in resistance shown in figures 4 and 7 during the subsequent desorption following absorption up to higher pressure (about 3.3 MPa) may be due to the formation of vacancies in the stoichiometry of the NaCl type lattice. Judging from the resistance results of the subsequent desorption following low-pressure absorption in the Pd–D system (figure 10), the steep increase in resistance during high-pressure absorption (figures 4 and 7) in the β phase regions of both systems may also be attributed to the creation of dislocations caused by further higher-content hydride (deuteride) formation, because there

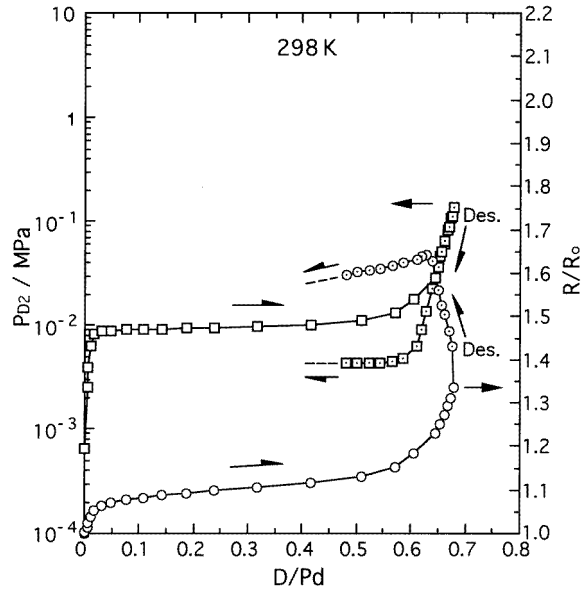


Figure 10. Relative resistance, R/R_0 , as a function of D/Pd content at 298 K for absorption-desorption processes up to about $p_{D_2} = 0.13$ MPa, along with the p - c isotherm. \circ , R/R_0 against D/Pd for absorption; \odot , R/R_0 against D/Pd for desorption; \square , p_{D_2} against D/Pd for absorption; \square , p_{D_2} against D/Pd for desorption. The arrows indicate the directions of absorption and desorption processes.

is a large hysteresis in the resistance. These results mean that the micro-lattice strains and distortions can be formed by both the high-pressure absorption and the subsequent desorption from relatively low-pressure absorption. Therefore, the large hysteresis loops of the resistance can be attributed to the 'plastic deformation (lattice strains)' accompanied by the dislocations caused by the β hydride (deuteride) formation and by further dissolving of hydrogen and deuterium in the β phase region.

The discrepancy between the present data using the equilibrium gas phase method and the results previously observed by the electrolytic charging method may be due to the circumstance that the latter method is affected by the introduction of 'lattice strain deformations' near the electrode surface during the initial charging due to the formation of β hydride (deuteride) which corresponds to hydrogen (deuterium) pressure of about $p_{H_2(D_2)} = 0.1$ MPa (1 atm) and also by the micro-lattice strains introduced by dissolved hydrogen and deuterium at large contents.

It should be noted that prior to the electrical resistance measurements by the electrolysis method, even if the electrode sample is palladized (Pd black) in order to obtain a sufficient catalytic active surface with high current density and prepared by electrolytic anodization in electrolyte to remove hydrogen absorbed during the palladizing that, unless the electrode sample is annealed at a high temperature, e.g., about 1073 K *in vacuo*, the electrode will already contain 'lattice strain deformations' accompanied by dislocations due to formation of the β hydride during the palladization, in particular near the electrode surface; these may significantly affect the electrical resistance, especially in the $(\alpha + \beta)$ two-phase region. It is therefore important to specify the prehistory of the samples for the electrical resistance measurements and this was usually not done in the earlier work.

It seems that the effect of palladium deformed by the α/β phase change or cold work is not very sensitive to the relationship between electrode potential and hydrogen content compared to the influence on the resistometry, except for the hydrogen solubility enhancement in the low-hydrogen-content α -phase region [15, 16], because there is an interdependence of the relationships between electrode potential and hydrogen content and the p - c - T relationships obtained by the gas phase method [2, 3, 4, 15, 16].

At present further electrical resistance measurements by the gas phase method are in progress on the investigation of the resistance behaviour in the α single and $(\alpha + \beta)$ two-phase regions during cyclic absorption-desorption processes, together with that in the β phase regions with different hydrogen contents.

4. Conclusions

The relative resistance, R/R_0 , in the α phase region of both Pd-H and Pd-D systems increases significantly with increasing H(D) contents up to the α_{\max} composition. On entering into the $(\alpha + \beta)$ two-phase region the R/R_0 value shows a small increase with increasing H(D) content up to about the β_{\min} composition because of the incoherent formation of β hydride within the α phase. In the β single-phase region, the resistance increases steeply, reaching a maximum at 298 K, $(R/R_0)_{H,\max} \simeq 1.87$ at about H/Pd = 0.76 and $(R/R_0)_{D,\max} \simeq 2.07$ at D/Pd = 0.75. The steep increase in resistance in the α and β single-phase regions may be attributed to the scattering of conduction electrons due to the lattice expansion; in particular the steep increase in the β phase region is due to the micro-lattice strains and distortions caused by highly dissolved hydrogen and deuterium. In the higher-H(D)-concentration region, the resistance decreases again due to the approach to the stoichiometric NaCl type lattice. If compared at almost the same H(D) content in the α and $(\alpha + \beta)$ two-phase regions, the R/R_0 values have a tendency to increase with increasing temperature, while in the β phase region of both systems the R/R_0 values, e.g., the maximum values, tend to decrease with increasing temperature.

The relative resistance at 298 K during the subsequent desorption after absorption up to about 3.3 MPa in both systems exhibits a similar maximum at H(D)/Pd $\simeq 0.75$ – 0.76 ; then the R/R_0 values decrease gradually with decreasing H(D) content up to the β_{\min} phase boundary composition, and on entering into the $(\alpha + \beta)$ two-phase region, the R/R_0 values remain almost constant, i.e. $(R/R_0)_{(\alpha+\beta)} \cong 1.76$ for the Pd-H system and $(R/R_0)_{(\alpha+\beta)} \cong 1.89$ for the Pd-D system. This large resistance hysteresis can be attributed to the creation of ‘lattice strain deformations’ accompanied by dislocations due to β hydride (deuteride) formation and from the additional dissolved hydrogen and deuterium in the β -phase region.

The discrepancy between the present data obtained by an equilibrium gas phase method and the previously observed results obtained by the electrolytic charging method may be that the latter method introduces ‘lattice strain deformations’ near the electrode surface due to the formation of β hydride (deuteride) from the initial charging stage and/or the micro-lattice strains and distortions which had been caused by dissolved hydrogen and deuterium.

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