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# Hysteresis behaviour of electrical resistance of the Pd–H system measured by a gas-phase method

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Abstract. The hysteresis behaviour of electrical resistance during the absorption-desorption processes in the  $\alpha$ -,  $(\alpha + \beta)$ - and  $\beta$ -phase regions of the Pd-H system, respectively, have been investigated at 323 K by a gas-phase method. A small extent of hysteresis in relative electrical resistance  $R/R_0$  over the cyclic absorption–desorption processes in the  $\alpha$  single-phase region has been observed, showing slightly larger  $R/R_0$ -values for desorption processes than for absorption processes, where  $R_0$  is the initial resistance of a hydrogen-free sample. In cyclic desorption-absorption scans commencing from the absorption branch of p-c isotherms in the  $\alpha + \beta$  two-phase plateau region, similar hysteresis loops to those of p-c isotherms have been observed for plots of  $R/R_0$  versus [H]/[Pd]. On the other hand, for cyclic desorptionabsorption scans starting from absorption pressures, corresponding to hydrogen concentrations near the  $\beta_{min}$ -phase boundary composition,  $R/R_0$ -values do not return to those of desorption plateau in the  $\alpha + \beta$  two-phase region. Values of relative resistance over subsequent desorptions from absorption pressures with  $p_{H_2}$  > 4.7  $\times$  10<sup>-2</sup> MPa decrease gradually with decreasing H content down to  $\beta_{min}$ -phase boundary compositions and exhibit almost the same values as those observed for the absorption processes and, on entering the  $\alpha + \beta$  two-phase region, the  $R/R_0$ -values remain almost constant with decreasing [H]/[Pd], i.e. at  $(R/R_0)_{(\alpha+\beta)} \simeq 1.73$  at 323 K. The large hysteresis of resistance relationships can be attributed to creations of lattice strains accompanied by dislocation formation arising from  $\alpha \rightarrow \beta$ -phase hydride transitions and by further highly dissolved hydrogen in the  $\beta$ -phase region.

### 1. Introduction

Recently, simultaneous measurements of both electrical resistance and pressureconcentration isotherms for the Pd–H(D) system have been carried out at temperatures between 273 and 323 K at H<sub>2</sub>(D<sub>2</sub>) pressures of up to about 3.3 MPa [1]. As examples, relationships between relative resistance  $R/R_0$  and hydrogen-to-palladium ratio [H]/[Pd] at 323 K for the Pd–H system are shown in figure 1, together with the p-c isotherm. Similar forms of results have also been obtained for the Pd–D system [1]. The inset in figure 1 is an enlarged version of the plot of  $R/R_0$  against [H]/[Pd] on absorption in the higher [H]/[Pd] region. Here, the open circles represent  $R/R_0$  against [H]/[Pd] for absorption and the open circles with dots represent  $R/R_0$  against [H]/[Pd] during desorption. The open squares and the open squares with dots represent the corresponding  $p_{H_2}$ -values against [H]/[Pd] for the absorption and desorption, respectively. The desorption isotherm is incomplete, because the kinetics were sluggish.

It can be seen from figure 1 that the relative resistance  $R/R_0$  in the  $\alpha$  (solid-solution) single-phase region during the absorption process increases with increasing [H]/[Pd] up to about the  $\alpha_{max}$ -phase boundary composition. Compared with the previously reported results

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**Figure 1.** Example in the Pd–H system of changes in the relative electrical resistance  $R/R_0$  as a function of [H]/[Pd] at 323 K during absorption–desorption processes, together with the corresponding p-c isotherm:  $\bigcirc$ ,  $\bigcirc$ ,  $R/R_0$  during absorption and desorption, respectively.  $\Box$ ,  $\Box$ , corresponding  $p_{H_2}$  during absorption and desorption, respectively. The arrows indicate the directions of respective absorption and desorption processes [1].

measured mainly by the electrolytic charging method and/or by absorption of hydrogen by the specimens from hydrogen-saturated acidic solutions [2–10],  $R/R_0$ -values show only a small increase from the  $\alpha_{max}$ -phase to  $\beta_{min}$ -phase boundary compositions, and the form of  $R/R_0$  against [H]/[Pd] is quite similar to the shape of the p-c isotherm. On entering the  $\beta$ -phase region, the resistance increases abruptly with increasing [H]/[Pd], before reaching a maximum. It thus can be seen that the resistance behaviour is closely related to the phase relationship. After passing through maximum values with further increase in [H]/[Pd],  $R/R_0$  tends to decrease again with further increase of [H]/[Pd] due to an approach to the stoichiometry of the NaCl-type lattice, i.e. to an increase in ordering, as [H]/[Pd]  $\rightarrow 1$ [11, 12]. This trend of decrease in  $R/R_0$  in the high [H]/[Pd] region has been observed to be more pronounced at lower temperatures [1].

Over the subsequent desorption process following absorption to about  $p_{H_2} = 3.3$  MPa,  $R/R_0$  exhibits a reversal of similar behaviour to that of absorption over the high-[H]/[Pd] region, and the  $R/R_0$ -value gradually decreases with decreasing [H]/[Pd] down to about the  $\beta_{min}$ -phase boundary composition and, on entering the  $\alpha + \beta$  two-phase region,  $R/R_0$ -values have a strong tendency to remain almost constant. Similar sequences of relationships have been observed between  $R/R_0$  and [D]/[Pd] for the Pd–D system [1]. The large hysteresis loop of  $R/R_0$  in the  $\alpha + \beta$  two-phase region may be attributed to 'lattice strains' accompanied by dislocations associated with  $\beta$ -hydride formation and further dissolution of hydrogen in the  $\beta$ -hydride phase [13, 14].

A similar rapid increase or decrease in  $R/R_0$  corresponding to the formation or decomposition of the  $\beta$ -hydride phase, respectively, have been observed for a series of nickel alloy–hydrogen systems by the high-pressure technique of Baranowski [12] as a function of pressure at 25 °C, e.g. for Ni–Fe–H(D) [15, 16], Ni–Co–H(D) [17], Ni–Mn–H [18], Ni–V–H(D) [19], Ni–Si–H(D) [19] and Ni–Cr–H [20] systems. However, for pure nickel a sharp decrease in the  $R/R_0$ -value takes place because of the increase in ordering, as [H]/[Ni]  $\rightarrow$  1 at about 6.3 kbar which corresponds to the formation of the  $\beta$ -hydride phase [15].

Discrepancies between the present data obtained with the equilibrium gas-phase method [1] and the results previously observed by the electrolytic charging method and/or absorption of hydrogen by the specimen directly from hydrogen-saturated acidic solutions [3–10] may be due to the circumstance that the latter methods are affected by the introduction of 'lattice strains' near electrode surfaces during the relatively initial charging state owing to the formation of  $\beta$ -hydride which corresponds to the relatively high-pressures, e.g. up to about  $p_{H_2} = 0.1$  MPa (1 atm) and thus by the microlattice strains introduced by dissolved hydrogen at high contents. Alternatively, for some of the latter methods there may be influences on the resistance of some hydroxide and/or oxide formation in interfaces between the sample electrode surface and the electrolyte.

The purpose of the present research has been to investigate the hysteresis behaviour of electrical resistance for the Pd–H system in more detail during the cyclic absorption–desorption processes in the  $\alpha$ -, ( $\alpha + \beta$ )- and  $\beta$ -phase regions by a gas-phase method.

#### 2. Experimental details

The experimental apparatus for measurement of electrical resistance by the gas-phase method which is combined with a conventional pressure p-concentration c isotherm measurement apparatus constructed of all stainless steel tubes and vessels was the same as described before [1]. Pressures were measured by two pressure gauges: one is a  $0-10^3$  Torr pressure transducer (MKS) for relatively low-pressure measurements and the other is a  $0-2.5 \times 10^4$  Torr (about 3.3 MPa) instrument (MKS). The sample for p-c isotherm measurements consisted of 6.0077 g of fully annealed Pd foil (purity, 99.99 wt%) of thicknesses 50-60  $\mu$ m cut into about 2 mm  $\times$  5 mm pieces. This was inserted in the reaction vessel, together with the sample for electrical resistance measurement which had dimensions of about 120  $\mu$ m  $\times$  2 mm  $\times$  20 mm and had been spot welded with Ni-leading wires (0.3 mm diameter). Appropriate glass tubes were used as electrical insulation for the Ni-leading wires. In order to diminish the dead space of the 'connection tube' volume, a glass rod was inserted in the tube. The volumes of the 'connection' tube and 'sample (reaction) vessel' were calibrated as accurately as possible by taking into consideration the volumes of the glass rod, tubes and of the lead wires. Before inserting the Pd specimens into the vessel, they were chemically etched with a solution of 2:2:1H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub>:H<sub>2</sub>O mixture in order to remove any oxides from their surfaces. In order to sustain a highly active state for resistometry and the p-c isotherm measurements, the vessel was completely outgassed at 573 K and about  $4 \times 10^{-5}$  Pa, and then samples were exposed to hydrogen gas with  $p_{H_2} = 0.1-3$  MPa for 10 min. Subsequently, the vessel was cooled by immersion in ice-water, and the dehydriding was accomplished by evacuating and reheating to 573 K. This hydriding-dehydriding treatment was repeated more than ten times.

The electrical resistance measurements were carried out at  $323 \pm 0.1$  K and at pressures of up to  $p_{H_2} \simeq 3.3$  MPa by the four-point constant-current reversal technique with a current of 50 mA. In the determination of [H]/[Pd] contents at higher pressures  $p_{H_2} > 0.4$  MPa, in order to avoid the difficulties in determining [H]/[Pd]-values [21], they were calculated by using the extrapolation formula of the Wicke–Nernst [22] p-c isotherms, i.e. log  $p_{H_2} =$ -A(T) + B(T). [H]/[Pd] from measurements of the initial and final equilibrium pressures during the absorption and desorption processes.

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Before a series of experiments, the initial resistance  $R_0$  of the H-free Pd sample used in this study was about  $(5.0710 \pm 0.1268) \times 10^{-3} \Omega$  at 323 K. After each experiment the  $R_0$ -values returned to the initial resistance values within about 2–3% after degassing of the samples *in vacuo* at 573 K for more than 3 h.



**Figure 2.** Changes in the relative electrical resistance  $R/R_0$  as a function of [H]/[Pd] at 323 K during two-cycle absorption–desorption processes in an  $\alpha$  single-phase region, together with the p-c isotherms;  $\bigcirc$ ,  $\bigcirc$ ,  $R/R_0$  during the first absorption and desorption stages, respectively;  $\square$ ,  $\square$ ,  $p_{H_2}$  values of the corresponding first absorption and desorption, respectively;  $\triangle$ ,  $\triangle$ ,  $R/R_0$  of the subsequent second absorption and desorption, respectively;  $\Diamond$ ,  $\Diamond$ ,  $p_{H_2}$  during the corresponding second absorption and desorption, respectively. The arrows indicate the directions of respective absorption and desorption processes.

#### 3. Results and discussion

# 3.1. Resistance behaviour during cyclic absorption–desorption processes in the $\alpha$ single-phase region

The effects of cyclic absorption–desorption on the resistance behaviour in the  $\alpha$  single-phase region were examined at 323 K by two repetitions of hydrogen absorption up to a pressure  $p_{H_2} \simeq 4.6 \times 10^{-3}$  MPa, corresponding to [H]/[Pd] =  $2.1 \times 10^{-2}$  and then by desorption down to about  $p_{H_2} \simeq 1.6 \times 10^{-4}$  MPa, corresponding to about [H]/[Pd]  $\simeq 4 \times 10^{-3}$ . Figure 2 shows the relationship between relative electrical resistance,  $R/R_0$ , and [H]/[Pd], together with the p-c ([H]/[Pd]) isotherms.

In general, during the absorption,  $R/R_0$  increases with increasing [H]/[Pd], owing to the scattering of conduction electrons by the lattice expansion, and conversely  $R/R_0$  decreases with decreasing [H]/[Pd] during desorption. However, figure 2 shows a small hysteresis in  $R/R_0$  during the cyclic absorption–desorption processes, showing slightly larger  $R/R_0$ -values during the desorption process than during the absorption process, although, as has been observed, the corresponding p-c isotherms do not show any hysteresis during the cyclic absorption–desorption processes. This could be attributable to formation of some lattice defects such as dislocations introduced during the first absorption process since, on each increment in the amount of hydrogen gas, the gas pressure initially rises and, particularly in the surface of the Pd, a higher concentration region is formed and instantaneous initiation of

 $\beta$ -hydride nuclei occurs at least near to the sample surface, leading to the formation of some lattice defects, but then the hydrogen diffuses into the bulk of the samples. Consequently, during the cyclic process, the hysteresis of resistance would occur even in the  $\alpha$ -phase region. It also seems relevant that the  $R/R_0$ -values during the first absorption (open circles) and desorption (opencircles with a dot) processes almost coincide with those of the subsequent second absorption (open triangles) and desorption (open triangles) with a dot) processes, respectively. This result suggests that dislocations introduced in the hydrogen dosing may move around as the hydrogen content changes, but not so much as to change the total hydrogen content at a given pressure.

### 3.2. Resistance hysteresis in the $\alpha + \beta$ two-phase region

In order to examine the hysteresis behaviour of resistance during the desorption-absorption processes in the  $\alpha + \beta$  two-phase plateau region, two examples of cyclic desorption-absorption scans were performed at 323 K, each commencing from the absorption branch of the hysteresis loop of a p-c ([H]/[Pd]) isotherm in the two-phase region. One of these followed after an initial absorption up to [H]/[Pd]  $\simeq 0.19$ , and the other followed after initial absorption up to [H]/[Pd]  $\simeq 0.384$ .



**Figure 3.** Changes in the relative resistance  $R/R_0$  as a function of [H]/[Pd] at 323 K during cyclic desorption–absorption scans in the  $\alpha + \beta$  two-phase plateau region, together with complementary p-c isotherms:  $\bigcirc$ , subsequent desorption and reabsorption  $R/R_0$  following an initial absorption up to [H]/[Pd]  $\simeq 0.19$ ,  $\Box$ , corresponding  $p_{H_2}$ ;  $\odot$ , subsequent desorption and reabsorption  $R/R_0$  following the initial absorption up to [H]/[Pd]  $\simeq 0.38$ ;  $\Box$ , corresponding  $p_{H_2}$ ; values. The arrows indicate the directions of respective absorption and desorption processes.

Figure 3 shows the results of the  $R/R_0$  against [H]/[Pd] for the two examples of cyclic desorption-absorption scans, together with the corresponding p-c isotherms. As indicated, the  $R/R_0$ -values following the initial absorption up to [H]/[Pd]  $\simeq 0.19$  and subsequent desorption to reabsorptions are represented by open circles, and the corresponding p-c isotherm is represented by open squares. In the experiments following the initial absorption up to [H]/[Pd]  $\simeq 0.38$ , the subsequent  $R/R_0$  on desorption to re-absorptions are represented



Figure 4. (a) Changes in the relative resistance  $R/R_0$  as a function of [H]/[Pd] at 323 K for a desorption process (O), subsequent to the initial absorption process (O) at pressures up to  $p_{H_2} \simeq 8.0 \times 10^{-3}$  MPa, and then for reabsorption (O) up to  $p_{H_2} \simeq 4.7 \times 10^{-2}$  MPa, together with the p-c isotherms:  $\Box$ , corresponding  $p_{H_2}$  for the initial absorption and then for the reabsorption processes;  $\boxdot$ , corresponding  $p_{H_2}$  for the desorption. The arrows indicate the directions of the absorption and desorption processes, respectively. (b) Changes in the relative resistance  $R/R_0$  as a function of [H]/[Pd] content during the desorption ( $\odot$ ), subsequent to absorption up to  $p_{H_2} = 4.7 \times 10^{-2}$  MPa, and for a subsequent reabsorption process (O) up to  $p_{H_2} \simeq 1.35 \times 10^{-1}$  MPa, together with the corresponding p-c isotherms:  $\Box$ ,  $\Box$ , corresponding  $p_{H_2}$  for the subsequent desorption and further reabsorption respectively. The arrows indicate the directions of absorption and desorption processes, respectively. (c) Changes in the relative resistance  $R/R_0$  as a function of [H]/[Pd] during desorption ( $\odot$ ), subsequent to absorption up to  $p_{H_2} \simeq 1.35 \times 10^{-1}$  MPa, and for reabsorption (O) up to  $p_{H_2} \simeq 3.3$  MPa and a further redesorption ( $\Phi$ ) from the higher pressure:  $\Box$ ,  $\Box$ ,  $\Box$ , corresponding p-c isotherms for the desorption, further reabsorption and further subsequent redesorption processes, respectively. The arrows indicate the directions of absorption and desorption processes, respectively.



Figure 4. (Continued)

by open circles with a dot, and the corresponding p-c isotherm by open squares with a dot.

In comparison with the previously determined data shown in figure 1, there is a good reproducibility of the resistance behaviour over the initial absorption processes up to  $[H]/[Pd] \simeq 0.19$  (open circles) and  $[H]/[Pd] \simeq 0.38$  (open circles with a dot), respectively, and similar hysteresis loops to those of the p-c isotherm are observed for those of the corresponding plots of  $R/R_0$  against [H]/[Pd]. The broken lines in figure 3 represent predicted  $R/R_0$ - and  $p_{H_2}$ -values for the desorption plateau pressures and it seems that the resistance hysteresis for the cyclic desorption-absorption scans commencing from the absorption branch in the  $\alpha + \beta$  two-phase region is smaller than that observed previously for a cycle of complete conversion to the  $\beta$ -phase such as illustrated in figure 1; measurements of the complete hysteresis loop (figure 1) show that, on desorption,  $R/R_0$  is about 1.55 higher than on absorption whereas, if the plateau is only partly traversed, switching to desorption actually reduces  $R/R_0$ , about 0.97–0.98 times lower than on absorption. This indicates a smaller production of 'lattice strains' accompanied by dislocations caused by  $\beta$ -hydride formations within the  $\alpha + \beta$  two-phase region, and on desorption the lattice strains break off up to those of desorption plateaux in the two-phase region. It may thus be expected that a relation such as  $R/R_0 = f_{\alpha}(R/R_0)_{\alpha_{max}} + f_{\beta}(R/R_0)_{\beta_{min}}$  holds for the  $\alpha + \beta$  two-phase region, especially for absorption processes, where  $(R/R_0)_{\alpha_{max}}$  and  $(R/R_0)_{b_{min}}$  are relative resistances at the respective phase boundary compositions, and  $f_{\alpha}$  and  $f_{\beta}$  are fractions of each phase present. Therefore, as has been discussed [1] from the changes in the relative lattice expansions with [H]/[Pd] ([D]/[Pd]), the  $R/R_0$ -value in the two-phase region would increase with increase in  $f_{\beta}$  owing to the lattice strains due to the accommodation of the  $\alpha_{max}/\beta_{min}$ -phase boundary mismatch at the phase boundaries. However, going fully into the  $\beta_{min}$  boundary composition produces more lattice strains.

The  $R/R_0$ -value in the two-phase region is flatter than in the previous measurements of electrolytic charging methods [3–10], since each dose pressure, i.e. hydrogen incremental content during the absorption process for the present gas-phase method, is relatively small. In other words, in the case of the electrolytic charging method, very high instantaneous

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concentrations are produced in the surface region, especially with a galvanostatic technique, so that the equivalent isotherm in the two-phase region will also be steeper in such measurements. Alternatively, as described before for the electrolytic charging methods and/or absorption of hydrogen by the specimen directly from hydrogen-saturated acidic solutions [3–10] there may be influences of some hydroxide and/or oxide formation on the resistance between the sample electrode surface and the electrolyte.

#### 3.3. Resistance hysteresis in the $\beta$ single-phase region

The behaviour of resistance hysteresis during absorption–desorption processes in the  $\beta$  single-phase region was also examined at 323 K by an analogous series of experiments. The initial absorption of hydrogen was up to  $p_{H_2} \simeq 8.0 \times 10^{-3}$  MPa which corresponds to [H]/[Pd]  $\simeq 0.585$  near to the  $\beta_{min}$ -phase boundary composition. The subsequent desorption measurements were carried out down to about the desorption plateau pressure, and reabsorption measurements were then performed up to about  $p_{H_2} = 4.7 \times 10^{-2}$  MPa. Figure 4(a) shows plots of both  $R/R_0$  and  $p_{H_2}$  against [H]/[Pd], where open circles represents  $R/R_0$  against [H]/[Pd] over the initial absorption and subsequent reabsorption, and open circles with a dot represent  $R/R_0$ -values over the desorption process. Open squares represent the corresponding plots of  $p_{H_2}$  against [H]/[Pd] content over the initial absorption and reabsorption and reabsorption, while open circles with a dot represent the corresponding  $p_{H_2}$  values for the desorption process.

It can be seen that the resistance behaviour for the desorption subsequent to absorption up to near the  $\beta_{min}$ -phase boundary composition is dissimilar to that observed for the cycle processes within the  $\alpha + \beta$  two-phase plateau region (figure 3). The resistance tends to decrease gradually with decreasing [H]/[Pd], retaining relatively high  $R/R_0$ -values corresponding to the  $\beta_{min}$ -phase boundary composition; the  $R/R_0$ -values do not return to those of desorption plateaux in the  $\alpha + \beta$  two-phase region, and even during reabsorption within the two-phase region the resistance increases only slightly with increasing [H]/[Pd]. The resistances of reabsorption (open circles) are a little larger than those of desorption (open circles with a dot) within the  $\alpha + \beta$  two-phase region. This resistance behaviour can be attributed to a relatively large creation of 'lattice strains' accompanied by dislocation formations from  $\beta$ -hydride formations near the  $\beta_{min}$ -phase boundary composition [13, 14]. However, on re-entering the  $\beta$ -phase region the resistance increases abruptly because of larger formations of lattice strain deformations and reaches a value of  $R/R_0 = 1.76$  at  $p_{H_2} = 4.7 \times 10^{-2}$  MPa. From comparison with the previously measured data shown in figure 1, it may be seen that the difference in magnitude of  $R/R_0$ -values at the same [H]/[Pd] in the  $\beta$ -phase region may arise because the specimen in the present experiments has already been subjected to the cyclic desorption-absorption process from  $p_{H_2} = 8.0 \times 10^{-3}$  MPa.

Figure 4(b) shows relationships between  $R/R_0$  and [H]/[Pd] during the desorption (open circles with a dot) subsequent to an initial  $p_{H_2} = 4.7 \times 10^{-2}$  MPa down to the desorption plateau pressure, together with the desorption p-c isotherm represented by open sqares with a dot. Figure 4(b) also shows  $R/R_0$  versus [H]/[Pd] relationships (open circles) during subsequent reabsorption up to  $p_{H_2} \simeq 1.35 \times 10^{-1}$  MPa, together with the corresponding  $p_{H_2}$  versus [H]/[Pd] relationships represented by open squares. It can be seen in the subsequent desorption process that the  $R/R_0$ -values decrease gradually with decreasing [H]/[Pd] down to about the  $\beta_{min}$ -phase boundary composition. Again as observed in figure 1, at the beginning of the  $\alpha + \beta$  two-phase region, the  $R/R_0$ -values show a tendency to remain almost constant at about  $R/R_{0(\alpha+\beta)} = 1.73$ . Subsequently, during reabsorption up to  $p_{H_2} = 1.35 \times 10^{-1}$  MPa,  $R/R_0$ -values follow almost the same route as the preceding

Figure 4(c) shows plots of  $R/R_0$  against [H]/[Pd] during the subsequent desorption represented by open circles with a dot, from  $p_{H_2} = 1.35 \times 10^{-1}$  MPa down to the desorption plateau pressure, together with the corresponding desorption p-c isotherm represented by open squares with a dot. Figure 4(c) also shows plots during the further subsequent reabsorption up to  $p_{H_2} = 3.3$  MPa, where open circles represent the  $R/R_0$  versus [H]/[Pd] data and the open squares represent the corresponding  $pH_2$  versus [H]/[Pd] data for the reabsorption process. Also, data of  $R/R_0$  (open circles with a vertical line) and  $p_{H_2}$ (open squares with a vertical line) against [H]/[Pd] during the further redesorption from  $p_{H_2} = 3.3$  MPa down to the desorption plateau pressure are shown in figure 4(c).

It can be seen that  $R/R_0$ -values during the desorption (open circles with a dot) from  $p_{H_2} = 1.35 \times 10^{-1}$  and then on reabsorption (open circles) and further redesorption (open circles with a vertical line) from  $p_{H_2} = 3.3$  MPa have almost the same forms as those observed during the desorption-absorption processes commencing from about  $p_{H_2} = 4.7 \times 10^{-2}$  MPa illustrated in figure 4(b); there is no large hysteresis between the  $R/R_0$  for the desorption and absorption processes within either the  $\alpha + \beta$  two-phase or the  $\beta$ -phase regions, which is also in agreement with the previously measured data of figure 1. For the subsequent desorption from high-H-content regions,  $R/R_0$  decreases gradually with decreasing [H]/[Pd] down to about the  $\beta_{min}$ -phase boundary composition and, on reaching the  $\alpha + \beta$  two-phase region,  $R/R_0$ -values remain thereafter almost constant at about  $R/R_{0(\alpha+\beta)} = 1.73$ , and the resistance behaviour is almost a repetition during the subsequent reabsorption processes.

### 4. Conclusions

During cyclic absorption–desorption processes in the  $\alpha$ -phase region, a small extent of hysteresis in the relative resistance  $R/R_0$  has been observed, corresponding to slightly larger  $R/R_0$ -values during desorption processes compared with those during absorption processes. During the cyclic desorption-absorption scans commencing from the absorption branch in the  $\alpha + \beta$  two-phase plateau region, a similar hysteresis loop to that of the p-c isotherm has been observed for plots of  $R/R_0$  versus [H]/[Pd]. This is mainly attributed to creations of lattice strains due to the accommodation of the  $\alpha_{max}$ - $\beta_{min}$ -phase boundary mismatch at the phase boundaries. On the other hand, during cyclic desorption-absorption scans from an absorption pressure corresponding to hydrogen concentrations near  $\beta_{min}$ -phase boundary compositions,  $R/R_0$ -values do not return to those for the desorption plateau in the  $\alpha + \beta$  two-phase region. On the subsequent desorptions from absorption pressures of about  $p_{H_2} > 4.7 \times 10^{-2}$  MPa,  $R/R_0$  follows almost the same values as during absorption with  $R/R_0$ -values decreasing gradually with decreasing H content down to  $\beta_{min}$ -phase boundary compositions. On further decrease in [H]/[Pd] into the  $\alpha + \beta$  two-phase region,  $R/R_0$ -values remain almost constant, i.e. at  $(R/R_0)_{(\alpha+\beta)} \simeq 1.73$  at 323 K. Hysteresis of resistance could be attributed to the creations of lattice strains accompanied by dislocation formation from  $\beta$ -phase hydride transitions and additional solutions of hydrogen in the  $\beta$ -phase regions.

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## References

- [1] Sakamoto Y, Takai K, Takashima I and Imada M 1996 J. Phys.: Condens. Matter 8 3399
- Brüning H and Sieverts A 1933 Z. Phys. Chem. A 163 409 Sieverts A and Danz W 1937 Z. Phys. Chem. B 38 46
- [3] Lewis F A 1967 *The Palladium-Hydrogen System* (New York: Academic)
- [4] Lewis F A, McFall W D and Witherspoon T C 1979 Z. Phys. Chem., NF 114 239
- [5] Flanagan T B and Lewis F A 1959 Trans. Faraday Soc. 55 1400
- [6] Flanagan T B 1961 J. Phys. Chem. **65** 121
- [0] Flanagan I B 1901 J. Phys. Chem. 05 121
- [7] Flanagan T B and Lewis F A 1961 Z. Phys. Chem. 27 104
- [8] Barton J C, Lewis F A and Woodward I 1963 Trans. Faraday Soc. 59 1201
- [9] Bambakidis G, Smith R J and Otterson D A 1969 Phys. Rev. 177 1044
- [10] Smith R J and Otterson D A 1970 J. Phys. Chem Solids 31 187
- [11] Szafranski A W and Baranowski B 1972 Phys. Status Solidi a 9 435
- [12] Baranowski B 1978 Hydrogen in Metals II (Top. Appl. Phys. 29) ed G Alefeld and J Völkl (Berlin: Springer) p 180
- [13] Flanagan T B, Lynch J F, Clewley J D and Von Turkovich B 1976 J. Less-Common Met. 49 13
- [14] Lynch J F, Clewley J D, Curran T and Flanagan T B 1977 J. Less-Common Met. 55 153
- [15] Baranowski B and Filipek S 1973 Rocz. Chem. 47 2165
- [16] Filipek S and Baranowski B 1979 Polish J. Chem. 53 951
- [17] Filipek S, Baranowski B and Yoneda M 1977 Rocz. Chem. 51 2243
- [18] Krukowski M and Baranowski B 1976 J.Less-Common Met. 49 385
- [19] Filipek S M, Szafranski A W, Warsa M and Majchrzak S 1989 Z. Phys. Chem., NF 163 483
- [20] Filipek S M, Bauer H J, Majchrzak S and Yamamoto H 1989 Z. Phys. Chem., NF 163 485
- [21] Sakamoto Y, Imoto M, Takai K, Yanaru T and Ohshima K 1996 J. Phys.: Condens. Matter 8 3229
- [22] Wicke E and Nernst G H 1964 Ber. Bunsenges. Phys. Chem. 68 224