

## Variation of Resistance with Composition in the $\beta$ -Phase of the H–Pd System at 298 K

By S. Crouch-Baker\*, M. C. H. McKubre and F. L. Tanzella

SRI International, Menlo Park, CA 94025, USA

(Received January 25, 1997)

### *Hydrogen-palladium / Resistance ratio / Loading / Pressure-composition isotherm*

Measurement of electrical resistance is a convenient method for the determination of composition in a number of metal–hydrogen systems. For the  $\beta$ -phase of the H–Pd system, pertinent data from the literature are employed in order to construct a complete resistance-loading function at 298 K.

### 1. Introduction

In the study of the bulk properties of metal–hydrogen systems, two synthetic techniques are commonly employed [1, 2]: Reaction of the metal with hydrogen gas, if necessary at elevated pressures, and the electrochemical insertion of hydrogen into the metal, which is usually carried out at atmospheric pressure. These techniques share a common problem: that of the convenient, reliable *in situ* measurement of the hydrogen/metal atomic ratio. In the case of the system of interest in this work, the H–Pd system, measurement of the electrical resistance of the sample has long been known to provide a solution to this problem, at least for H/Pd atomic ratios (“loadings”) up to approximately 0.75, for which the necessary resistance-loading functionality has been obtained by a variety of analytical methods [2]. However, in the case of more highly-loaded compositions, as well as palladium alloy-hydrogen systems for which the sample resistance is known to vary with composition (e.g. [3–8]), the detailed results of a direct experimental determination of the resistance-loading function at room temperature are not available.

---

\* Corresponding author.

At 298 K, the  $\beta(\alpha')$ -phase of the H–Pd system extends from a loading of approximately 0.61 to (at least) unity. Despite the wealth of published data and analysis which are available for the  $\alpha$ - and two-phase regions in the H–Pd system, relatively fewer studies have been reported for the  $\beta$ -phase. This is particularly so for more highly loaded compositions (with H/Pd in excess of 0.8), for which the chemical potential of dissolved hydrogen increases rapidly with increasing concentration such that, in the case of loading from the gas phase at 298 K, a hydrogen partial pressure of 1 bar is sufficient to achieve H/Pd = 0.72 [9–11], whereas a pressure in excess of 12 kbar is required to reach H/Pd = 1 [12] (n.b. in most gas-loading experiments, the system pressure is indistinguishable from the hydrogen partial pressure; this latter quantity will henceforth be referred to here as “pressure” unless further clarification is required). The attainment by electrochemical means of such elevated chemical potentials of dissolved hydrogen, with the resulting high loadings, is a subject of continued interest (e.g. [13, 14]). At this point, we should emphasize that the pressure-composition data quoted above refer to samples with low surface area to volume ratios. As the particle size decreases, the presence of increasing quantities of chemisorbed hydrogen, as well as the involvement of sub-surface hydrogen, serve to modify the pressure-composition isotherms. This subject has been discussed by Wicke [15].

Although the qualitative form of the resistance-loading function for the  $\beta$ -phase of the H–Pd system has been described previously (e.g. [16, 17]) and is not under discussion here, several differing *quantitative* descriptions have been employed in earlier studies (e.g. [3, 13, 14]). In order to clarify this situation and facilitate the study of the H–Pd system at high loadings, here we review briefly relevant data taken from the literature and employ selected results in order to construct the resistance-loading function at 298 K.

## 2. Derivation of resistance-loading function

At 298 K, the variation of electrical resistance ratio ( $R/R^0$ , where  $R$  denotes the sample resistance and  $R^0$  is that of the hydrogen-free metal at the outset of the experiment) of  $\beta$ -phase H–Pd samples with imposed pressure, up to 25 kbar, has been determined [3, 4, 7, 8, 18]; the results of two of these studies [4, 8] are shown in Fig. 1. As the pressure increases above approximately 10 bar, the resistance falls, eventually achieving values which are actually less than that of the hydrogen-free metal at the outset of the experiment. For compositions within the  $\beta$ -phase, measurements made during both absorption and desorption of hydrogen exhibited negligible hysteresis, as is commonly observed if the extensive formation of compositions within the  $\alpha + \beta$  two-phase region is avoided during cycling.

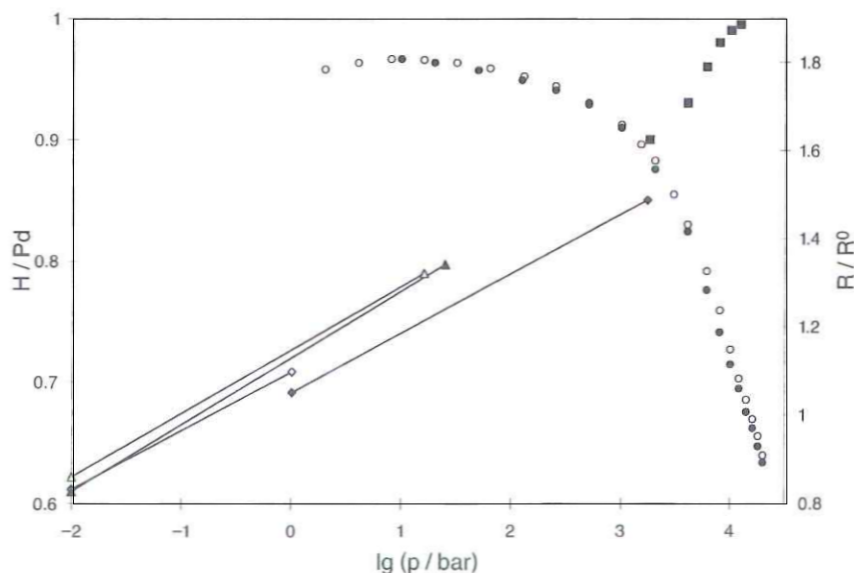
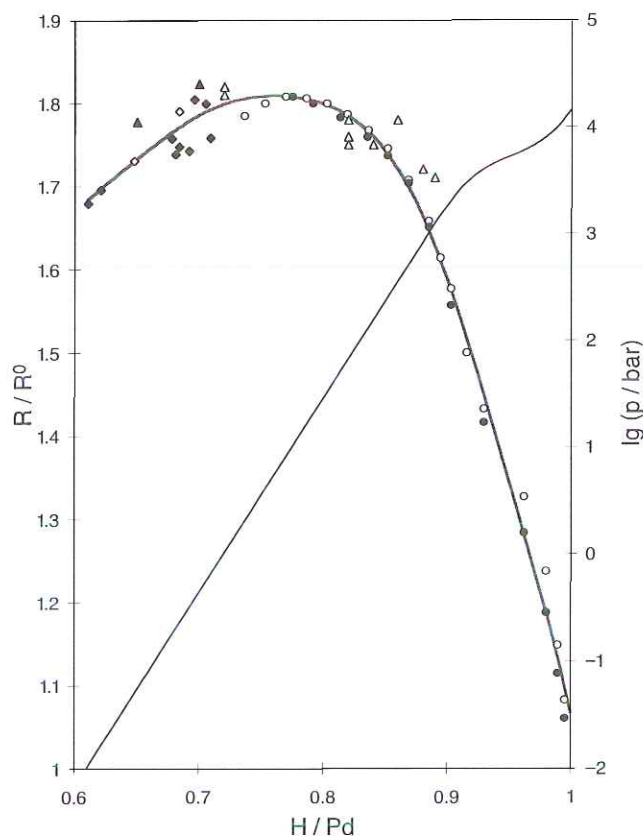


Fig. 1. Variation of loading ( $H/Pd$ ) and resistance ratio ( $R/R^0$ ) with the (common) logarithm of hydrogen partial pressure ( $p$ ) in the  $\beta$ -phase of the H-Pd system, at 298 K unless otherwise stated.  $\blacklozenge$  Loading data from Ref. [19] (290 K);  $\diamond$  Loading data from Ref. [10] (298 K, interpolation of original data);  $\blacktriangle$  Loading data from Ref. [9] (298 K, interpolation of original data);  $\triangle$  Loading data from Ref. [11];  $\blacksquare$  Loading data from Ref. [12];  $\circ$  Resistance data from Ref. [4];  $\bullet$  Resistance data from Ref. [8].

In order to make use of the resistance data shown in Fig. 1 for the determination of loading, we require the pressure-composition isotherm for the  $\beta$ -phase of the H-Pd system at 298 K. Several experimental data sets bear on this matter [9–12, 19]; unfortunately, only one relates to loadings in excess of 0.9, and, even at lower loadings, not all are consistent, Fig. 1. At lower loadings, the loading is seen to increase linearly with the logarithm of the pressure, an observation which has been the subject of extensive theoretical discussion [20]. The data of Perminov *et al.* [19] are significant in that, although clearly offset in loading from the other results shown in Fig. 1, their slope is similar and, most importantly, they indicate that the linear variation in fact extends to quite high pressures.

Since, for hydrogen at 298 K, pressure and fugacity are effectively indistinguishable up to pressures of approximately 100 bar, the observed linear variations of loading with the logarithm of pressure shown in Fig. 1 are equivalent to the statement that the loading varies linearly with the chemical potential of hydrogen in the  $\beta$ -phase, at least over a certain range of composition. Some authors have chosen to extrapolate this latter relation in order



**Fig. 2.** Variation of resistance ratio and the (common) logarithm of hydrogen partial pressure with loading in the  $\beta$ -phase of the H-Pd system at 298 K.  $\blacklozenge$  Measured resistance data from Ref. [21];  $\diamond$  measured resistance data from Ref. [22];  $\blacktriangle$  measured resistance data from Ref. [8];  $\triangle$  measured resistance data from Ref. [23];  $\circ$  calculated from data in Ref. [4];  $\bullet$  calculated from data in Ref. [8]; — summary resistance ratio function; — logarithm of hydrogen partial pressure.

to calculate the resulting loadings at *all* pressures consistent with the existence of the  $\beta$ -phase, via determination of the hydrogen fugacity corresponding to a given pressure (e.g. [3, 4]). The loading data of Perminov *et al.*, however, show a linear variation with the logarithm of pressure, rather than chemical potential, up to approximately 1700 bar at 290 K. In addition, the assumption of a linear variation of loading with chemical potential has been shown to be inapplicable to the experimental data of Tkacz and Baranowski for loadings greater than 0.9 [12].

With these considerations in mind, we have elected to adopt the results given by Frieske and Wicke [9] as representative of the more recent data



**Table 1.** Variation of resistance ratio with composition for the  $\beta$ -phase of the H–Pd system at 298 K.

H/Pd	$R/R^0$	H/Pd	$R/R^0$
0.61	1.683	0.81	1.793
0.62	1.696	0.82	1.785
0.63	1.708	0.83	1.774
0.64	1.720	0.84	1.760
0.65	1.733	0.85	1.742
0.66	1.744	0.86	1.721
0.67	1.755	0.87	1.694
0.68	1.767	0.88	1.664
0.69	1.777	0.89	1.628
0.70	1.786	0.90	1.588
0.71	1.793	0.91	1.544
0.72	1.799	0.92	1.497
0.73	1.803	0.93	1.448
0.74	1.806	0.94	1.396
0.75	1.808	0.95	1.345
0.76	1.809	0.96	1.293
0.77	1.808	0.97	1.241
0.78	1.806	0.98	1.188
0.79	1.803	0.99	1.132
0.80	1.799	1.00	1.067

sets shown in Fig. 1 in order to interconvert hydrogen pressure and loading, by extrapolation where necessary, over the *entire* loading range 0.61 to 0.9 at 298 K. Further, we note: (i) The data of Frieske and Wicke give 0.72 as the loading at 1 bar; this value is an acceptable average of the more recent values reported in the literature, and (ii) when extrapolated, these data are consistent with the first data point of Tkacz and Baranowski (at H/Pd = 0.9 in Fig. 1) [12]. This latter agreement must be regarded as somewhat fortuitous, however, since this particular loading was itself determined by an extrapolation procedure based on the low pressure data of Wicke and Nernst [10]. Nonetheless, the remainder of the loading data determined by Tkacz and Baranowski [12] were determined experimentally as *differences* in loading, measured relative to this initial point.

Based on the considerations of the prior paragraph, and interpolating the data of Tkacz and Baranowski where necessary, the pressure-composition isotherm used in this work for the  $\beta$ -phase at 298 K is illustrated in Fig. 2. Using this isotherm, the resistance-pressure results shown in Fig. 1 may be converted to resistance-loading data for the  $\beta$ -phase at 298 K; these are plotted in Fig. 2. Also shown in Fig. 2, and described in detail in Table 1, is a single resistance-loading function which is designed to summarize the various available data sets. In obtaining this result, it was necessary to em-

ploy additional data from the literature [8, 21–23] in order to define better the resistance-loading curve in the vicinity of the resistance maximum. These additional data, which are derived mostly from electrochemically-loaded specimens, are also plotted in Fig. 2.

### 3. Discussion

In the summary resistance-loading function shown in Fig. 2, the maximum occurs at a loading of 0.76 (corresponding to a pressure of approximately 5 bar in a gas-loading experiment) and a resistance ratio of approximately 1.81. Especially in the vicinity of this point, there is noticeable scatter in the resistance ratio values corresponding to a given loading for the various data sets shown in Fig. 2. This must be borne in mind when employing the summary resistance-loading function detailed in Table 1; in particular, these resistance data are quoted to three decimal places for future convenience in plotting, rather than as an indicator of reproducibility between different palladium samples. Similarly, the function given in Table 1 necessarily refers to samples in internal compositional equilibrium; thus, it may not apply to specimens undergoing rapid changes in loading, for which significant internal compositional gradients may be expected, leading to a variable average sample resistance for a given total loading.

The data at high loadings shown in Figs. 1 and 2 were obtained by gas-loading at elevated pressures. Electrochemical loading, on the other hand, is usually undertaken at a hydrostatic pressure in the vicinity of one atmosphere. If, for the moment at least, we ignore the effects of internal microstructural variables on the measured resistance of a bulk  $\beta$ -phase sample, this quantity may be taken as a function of temperature, composition and hydrostatic pressure. For a number of compositions, the magnitude of the rate of change of resistance ratio with hydrostatic pressure, at constant temperature, has been determined to be on the order of  $10^{-6}$  bar $^{-1}$  [3, 4, 7]. Thus, the resistance-loading function shown in Fig. 2 will vary negligibly depending on the hydrostatic pressure entailed by the method of sample synthesis.

It should be emphasized that the resistance of compositions within the  $\beta$ -phase, rather than the resistivity, is shown in Figs. 1 and 2. Data for the variation of resistivity with loading, up to values in the vicinity of unity, are available [16, 17]; unfortunately, these data are not easily compared with those discussed here due to uncertainties associated with the corrections necessary as a result of changes in sample dimension as a function of loading. In addition, the resistivity data of Smith and Otterson [16] were obtained at 273 K. This temperature is sufficiently far removed from that employed here, 298 K, to require appropriate correction of the measured

data for comparative purposes, using the temperature coefficient of resistance at constant composition. It appears, however, that values of this latter quantity are not available at high loadings [21].

While it is evident that a number of possible uncertainties have entered into the derivation of the pressure-composition isotherm shown in Fig. 2, mostly arising from the paucity of experimental data for loadings in excess of 0.8, its form warrants further comment. In the gas-loading procedure employed by Tkacz and Baranowski [12], the system pressure is indistinguishable from the partial pressure of hydrogen. Under these circumstances, for the two-component H–Pd system, constancy of pressure over a range of composition is indicative of the presence of two phases. Although such behaviour is certainly not clearly evident in the data shown in Figs. 1 and 2, the partial arrest in the rate of change of pressure with composition for loadings in the vicinity of 0.95 is intriguing in this respect. Further, corresponding data obtained over a range of temperatures [12] exhibit similar arrests. It is to be understood, however, that such data were obtained under exacting experimental conditions.

While, in the absence of further data, any discussion of this aspect of the phase behaviour at very high loadings must be regarded as speculative, we note that binary phases in the H–Pd system with loadings greater than unity have been described [24–27], although under different preparative circumstances from those involved here. In addition, the (slight) change in the slope of the variation of resistance with pressure observed at approximately 10 kbar, Fig. 1, has been interpreted in terms of the occupation by hydrogen of a significant fraction of the tetrahedral sites within the palladium structure [4], although it is unclear whether loadings in excess of unity are achieved under these conditions. Finally, we note that single crystal neutron diffraction studies of the  $\beta$ -phase up to a loading of 0.92 showed no evidence for other than octahedral site occupancy [28].

### Acknowledgements

The authors acknowledge gratefully the partial financial support provided by the Institute for Applied Energy (Japan), and DARPA under Contract No. N66001-96-C-8634. In addition, we would like to thank Prof. B. Baranowski, Polish Academy of Sciences, and Prof. E. Wicke, University of Münster, for providing helpful criticism.

### References

1. B. Baranowski, *Plat. Met. Rev.* **16** (1972) 10.
2. F. A. Lewis, *The Palladium Hydrogen System*, Academic Press, London 1967.
3. B. Baranowski and R. Wisniewski, *Phys. Status Solidi* **35** (1969) 593.
4. A. W. Szafranski and B. Baranowski, *Phys. Status Solidi (a)* **9** (1972) 435.
5. A. W. Szafranski, *Phys. Status Solidi (a)* **19** (1973) 459.



6. B. Baranowski, S. Majchrzak and T. B. Flanagan, *J. Phys. Chem.* **77** (1973) 35.
7. A. W. Szafranski, *Pol. J. Chem.* **55** (1981) 2413.
8. B. Baranowski, F. A. Lewis, W. D. McFall, S. Filipek and T. C. Witherspoon, *Proc. R. Soc. London A* **386** (1983) 309.
9. H. Frieske and E. Wicke, *Ber. Bunsenges. Phys. Chem.* **77** (1973) 48.
10. E. Wicke and G. H. Nernst, *Ber. Bunsenges. Phys. Chem.* **68** (1964) 224.
11. T. B. Flanagan, W. Luo and J. D. Clewley, *J. Less-Common Met.* **172–174** (1991) 42.
12. M. Tkacz and B. Baranowski, *Pol. J. Chem.* **50** (1976) 2159.
13. M. C. H. McKubre, S. Crouch-Baker, A. M. Riley, R. C. Rocha-Filho, M. Schreiber, S. I. Smedley and F. L. Tanzella, in *Proc. Symp. On Hydrogen Storage Materials, Batteries and Electrochemistry*, edited by D. A. Corrigan and S. Srinivasan, pp. 269–286, Electrochemical Society, Pennington, New York 1992.
14. T. A. Green and T. I. Quickenden, *J. Electroanal. Chem.* **368** (1994) 121.
15. E. Wicke, *Z. Phys. Chem. N.F.* **143** (1985) 1.
16. R. J. Smith and D. A. Otterson, *J. Phys. Chem. Solids* **31** (1970) 187.
17. J. P. Burger, D. S. MacLachlan, R. Mailfert and B. Souffaché, *Solid State Commun.* **17** (1975) 277.
18. B. Baranowski and R. Wisniewski, *J. Phys. Chem. Solids* **29** (1968) 1275.
19. P. S. Perminov, A. A. Orlov and A. N. Frumkin, *Dokl. Akad. Nauk SSSR* **84** (1952) 749.
20. E. Wicke and H. Brodowsky, in *Hydrogen in Metals II*, edited by G. Alefeld and J. Völkl, *Top. Appl. Phys.* Vol. 29, pp. 73–155, Springer-Verlag, Berlin 1978.
21. T. B. Flanagan and F. A. Lewis, *Z. Phys. Chem. N.F.* **27** (1961) 104.
22. J. C. Barton, F. A. Lewis and I. Woodward, *Trans. Faraday Soc.* **59** (1963) 1201.
23. J. C. Barton and F. A. Lewis, *Z. Phys. Chem. N.F.* **33** (1962) 99.
24. Y. Fukai and N. Okuma, *Phys. Rev. Lett.* **73** (1994) 1640.
25. Y. Fukai and N. Okuma, *Jap. J. Appl. Phys.* **32** (1993) L1256.
26. R. V. Baranova, Y. P. Khodyrev, R. M. Imamov and S. A. Semiletov, *Sov. Phys. Crystallogr.* **25** (1980) 736.
27. S. A. Semiletov, R. V. Baranova, Y. P. Khodyrev and R. M. Imamov, *Sov. Phys. Crystallogr.* **25** (1980) 665.
28. M. H. Mueller, J. Faber, H. E. Flotow and D. G. Westlake, *Acta Crystallogr.* **A31** (1975) S99.