

Palladium-Rare Earth Alloys

THEIR ORDER-DISORDER TRANSFORMATIONS AND BEHAVIOUR WITH HYDROGEN

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Despite considerable research activity, palladium-based alloys still represent the only known metallic systems which show appreciable permeability to hydrogen gas at moderate temperatures, without forming a discrete second phase. Solutions of rare-earth metals such as yttrium, cerium, and gadolinium in palladium permeate hydrogen readily and are of interest as possible alternatives to the palladium-silver alloys currently used as hydrogen diffusion membranes.

The unusual alloying behaviour of the rare-earth metals with palladium, that is their unexpected solid solubility, their structural changes and their very open lattice structures have made these systems of great physical and metallurgical interest.

These materials also offer the opportunity of studying the equilibrium and kinetic behaviour of hydrogen in very expanded metal environments and thus provide useful tests of thermodynamic and diffusion models.

The Metallurgy of Palladium-Rare Earth Alloys

The solid solubilities of rare-earth (R) metals in palladium were first investigated by Harris and Norman (1, 2) and Thompson (3) for the rare-earth metals lanthanum, cerium, praseodymium, yttrium, gadolinium and the actinide thorium. They found that, while lanthanum and praseodymium were virtually insoluble in palladium, cerium, yttrium, gadolinium and thorium were soluble up to about 12, 12, 11 and 16 per cent solute content, respectively. (Later Speight found praseodymium soluble up to 2 per cent in palladium (4).) (All compositions given in this paper are in atomic per cent.) This solid solubility is despite the fact that the nominal size factor of these

atoms with respect to palladium is considerably in excess of the Hume-Rothery size limit of 15 per cent. In fact, cerium, yttrium and gadolinium are all approximately 30 per cent larger than the palladium atom and, on solution, expand the palladium lattice to a far greater extent than do noble metal substitutional additions.

The variation of room temperature lattice spacings of some palladium-rare earth solid solution alloys with increasing solute content are compared to the increase produced by corresponding silver and thorium additions in Figure 1. It was noted that the expansion of the palladium lattice occurred to a larger extent for additions of thorium than for yttrium and gadolinium, despite the closely similar atomic diameters of these metals, which are 3.596 Å (thorium), 3.602 Å (yttrium) and 3.589 Å

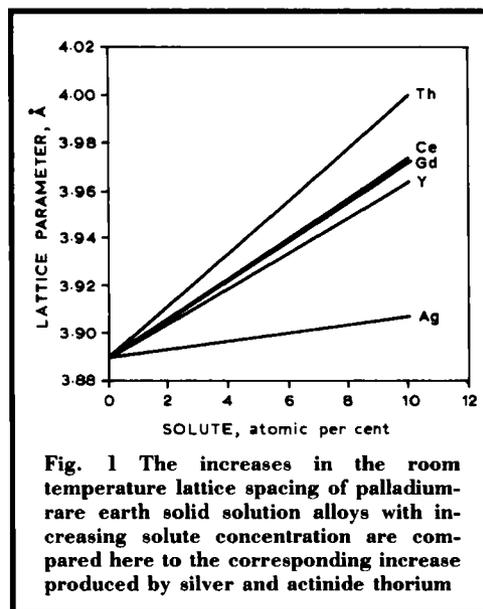


Fig. 1 The increases in the room temperature lattice spacing of palladium-rare earth solid solution alloys with increasing solute concentration are compared here to the corresponding increase produced by silver and actinide thorium

(gadolinium) (2). In the same way, despite having a substantially smaller atomic diameter 3.422 \AA cerium produced a larger lattice expansion than did yttrium or gadolinium. This value of 3.422 \AA refers to cerium with an effective valency of close to four, as suggested by Harris and Norman for cerium in palladium-cerium solid solutions (1). These effects were attributed by Harris and Norman to an additional expansion due to the more rapid filling of vacant Pd 4d states by the tetravalent thorium and cerium atoms as compared to the trivalent yttrium and gadolinium atoms (5).

Hardness measurements of palladium-cerium, palladium-yttrium, palladium-gadolinium and palladium-europium solid solutions up to their solubility limits showed that the hardness did not vary with increasing rare-earth concentration in a simple way (6, 7). Inflections appeared in the hardness versus composition variations at cerium contents around 6 per cent and at yttrium, gadolinium and europium contents around 8 per cent. It was shown subsequently that these plateau regions in the hardness measurements were sensitive to the thermal history of the alloys, and a quenching procedure increased substantially the hardness values of the alloys in these regions, as seen in Figure 2 for the palladium-cerium alloys (8). In the quenched condition the hardness data exhibited the normal $C^{1/2}$ dependence, where C is the solute concentration. These observations were attributed to a degree of short range order (S.R.O.) in these alloys which was removed by the quenching process. The large atomic mismatch in palladium-rare earth binary alloys makes them good candidates for S.R.O., with the strain energy associated with two widely different sized atoms being relieved by forming an ordered or a partly ordered structure. The presence of order in these alloys was also suggested by the further observations that all these palladium-rare earth solid solutions are succeeded by a stable, congruent, Pd_3R ordered phase with the $L1_2$ (Cu₃Au type) structure (9, 10).

Electrical resistivity measurements on a quenched palladium-6.5 per cent cerium alloy

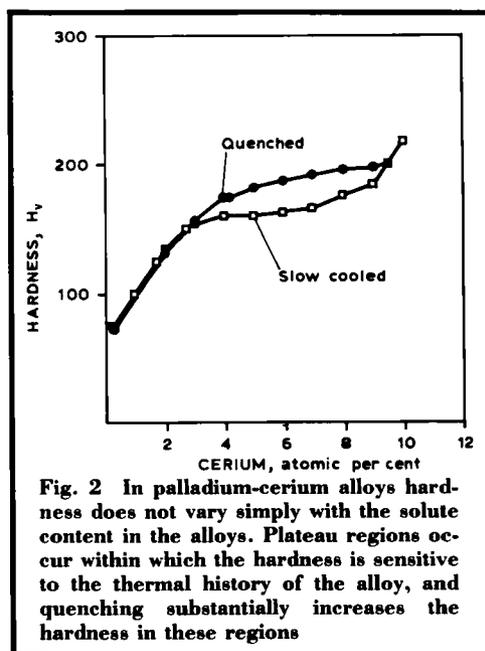
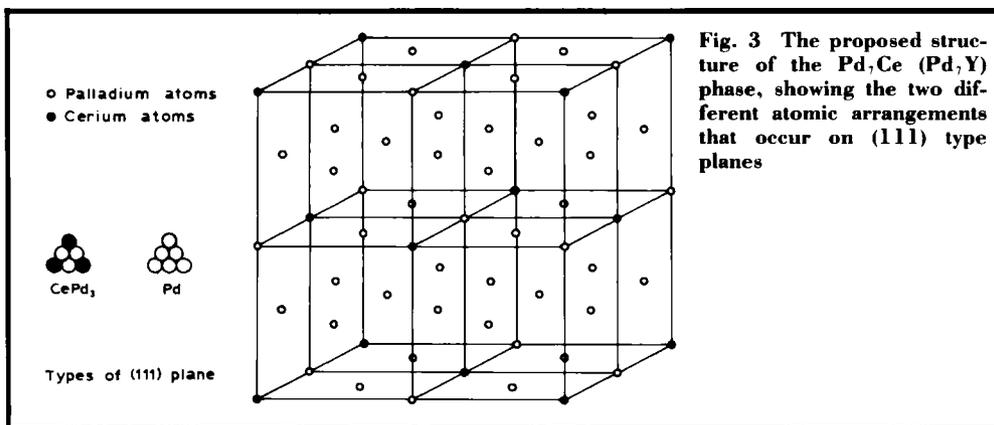


Fig. 2 In palladium-cerium alloys hardness does not vary simply with the solute content in the alloys. Plateau regions occur within which the hardness is sensitive to the thermal history of the alloy, and quenching substantially increases the hardness in these regions

showed a large decrease at an annealing temperature of about 300°C (11) consistent with there being appreciable S.R.O. present in the alloy. Electron microscope observations of planar slip in a lightly deformed palladium-9.4 per cent cerium alloy also suggested S.R.O. in this material (11).

The thermal expansion and magnetic susceptibility behaviours of some palladium-cerium and palladium-yttrium alloys have been examined (12). It was found that palladium-cerium alloys, with cerium contents greater than 3 per cent, and all of the palladium-yttrium alloys, showed anomalous thermal expansion behaviour in the temperature range 20 to 700°C . The plots of thermal expansion as a function of temperature showed two distinct linear regions with a much greater expansion rate in the higher temperature range. The temperature at which these changes in expansion behaviour occurred were $310 \pm 10^{\circ}\text{C}$ for the palladium-cerium and $360 \pm 10^{\circ}\text{C}$ for the palladium-yttrium alloys. Magnetic susceptibility measurements on a quenched palladium-6.5 per cent cerium alloy subjected to a series of isochronal anneals showed a dip in



susceptibility at an annealing temperature of 300°C, analogous to the dip in resistivity previously observed for the same alloy (11). Room temperature magnetic susceptibility measurements were performed on palladium-5.75 per cent cerium alloys subjected to three different treatments: (i) vacuum annealed at 450°C and slow cooled, (ii) vacuum annealed and quenched from 450°C and (iii) slow cooled in hydrogen from 450°C. This study revealed that slow cooling of the alloy in hydrogen and subsequent removal of the hydrogen at low temperatures produced a susceptibility higher than could be achieved by slow cooling in a

vacuum, and close to the "quenched" value. This result suggested that the hydrogen absorbed into the palladium-cerium alloy inhibited the proposed ordering process on cooling from 450°C.

The evidence obtained in this laboratory for ordering in these palladium-rare earth systems was all rather indirect until electron microscopical examinations were made on the palladium-cerium system close to the solubility limit at palladium-12.5 per cent cerium (13, 14). Bright superlattice spots, situated halfway between the fundamental reflections, in their diffraction patterns were observed, indicating

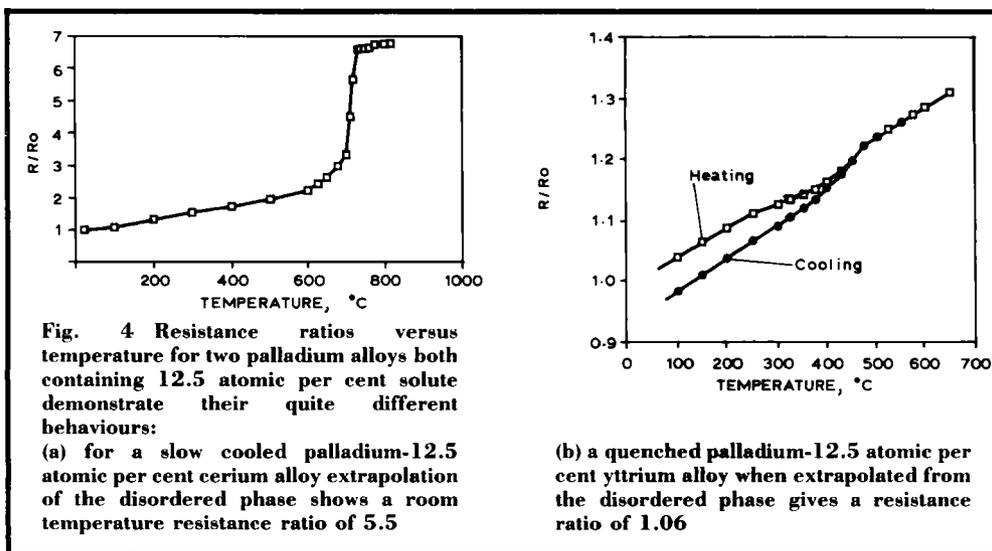


Fig. 4 Resistance ratios versus temperature for two palladium alloys both containing 12.5 atomic per cent solute demonstrate their quite different behaviours:

(a) for a slow cooled palladium-12.5 atomic per cent cerium alloy extrapolation of the disordered phase shows a room temperature resistance ratio of 5.5

(b) a quenched palladium-12.5 atomic per cent yttrium alloy when extrapolated from the disordered phase gives a resistance ratio of 1.06



Fig. 5(a) The (001) type electron diffraction pattern for a palladium-12.5 atomic per cent yttrium alloy aged for one week at 475°C shows the superlattice reflections corresponding to a highly ordered structure

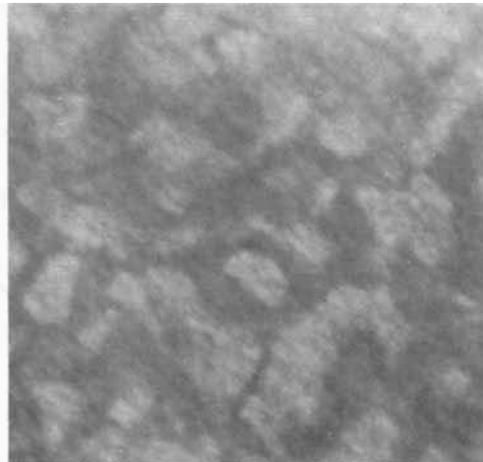


Fig. 5(b) The ordered domains and antiphase domain boundaries in a palladium-12.5 atomic per cent yttrium alloy aged for four weeks at 475°C

magnification $\times 68,000$ approx.

the presence of a long-range ordered Pd,Ce structure. It was proposed that the Pd,Ce structure, shown in Figure 3, is a derivative of the Cu₃Au-type, Pd₇Ce phase (14). The order-disorder transformation was followed by measuring the resistance changes with temperature of palladium-12.5 per cent cerium up to 800°C and it was found that, at a temperature of 735±5°C, the alloy disordered producing a substantial rise in electrical resistance, as shown in Figure 4(a). When examined in the electron microscope, material "quenched" from above this order-disorder temperature showed diffraction patterns with split spots in the superlattice positions. This pointed to the fact that, even after fast cooling, the alloy exhibited extensive short range order.

Similar observations of the palladium-yttrium alloy system close to the solubility limit at palladium-12.5 per cent yttrium also revealed reflections corresponding to the formation of a Pd₇Y superlattice structure (15), which is isomorphous with Pd₇Ce, though in this case the extra spots were quite faint (15, 16). Electrical resistance measurements showed that the alloy disorders at a temperature of around 500°C (15, 16), as seen in Figure 4(b). The resistance plots (R/R₀) of Figures 4(a) and (b)

for palladium-12.5 per cent cerium and palladium-12.5 per cent yttrium alloys, respectively, show their strikingly different behaviours. The extrapolated resistance of the disordered palladium-12.5 per cent cerium alloy shows that, at room temperature, R disordered/R ordered is approximately equal to 5.5, while the experimental "quenched" value for disordered palladium-12.5 per cent yttrium shows that R disordered/R ordered = 1.06. The very large increase in the resistivity of palladium-12.5 per cent cerium on disordering cannot be attributed simply to the large strain energy associated with the cerium atoms because, as mentioned previously, the yttrium atoms are significantly larger than the cerium atoms, whereas the resistivity increase on disordering palladium-12.5 per cent yttrium is very small. One explanation might be a change in the effective valency of the cerium atoms on disordering, that is a change in the degree of 4f hybridisation.

The faint superlattice reflections observed on slow cooling Pd₇Y, as compared to Pd₇Ce, indicates less order in the former alloy. Work in this laboratory has shown that if the Pd₇Y material is aged at a temperature just below the order-disorder temperature, the superlattice

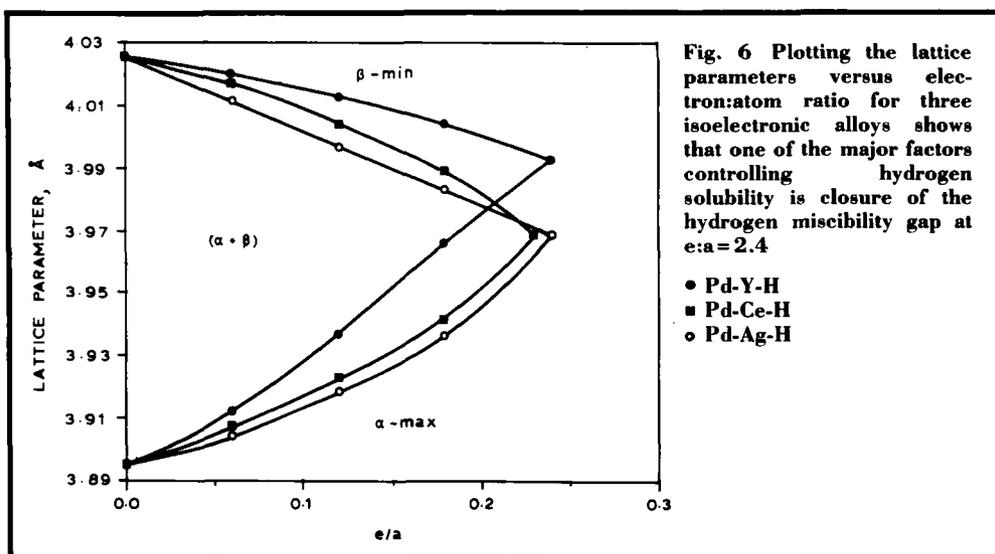


Fig. 6 Plotting the lattice parameters versus electron:atom ratio for three isoelectronic alloys shows that one of the major factors controlling hydrogen solubility is closure of the hydrogen miscibility gap at $e/a = 2.4$

- Pd-Y-H
- Pd-Ce-H
- Pd-Ag-H

reflections become more intense (16). This corresponds to a growth in the size of ordered domains, rendered visible by imaging with the superlattice spots. Figures 5(a) and (b) show the (001) diffraction pattern of a palladium-12.5 per cent yttrium alloy aged at 475°C for one week, and the antiphase domain structure of a similar sample aged at 475°C for four weeks. Longer ageing times were necessary to raise the diffracted intensities to the point where the ordered domains of Figure 5(b) could be successfully imaged. The light areas are the ordered domains and the dark contrast are the antiphase domain boundaries, which are areas of high strain involving Y-Y and Pd-Pd nearest neighbours.

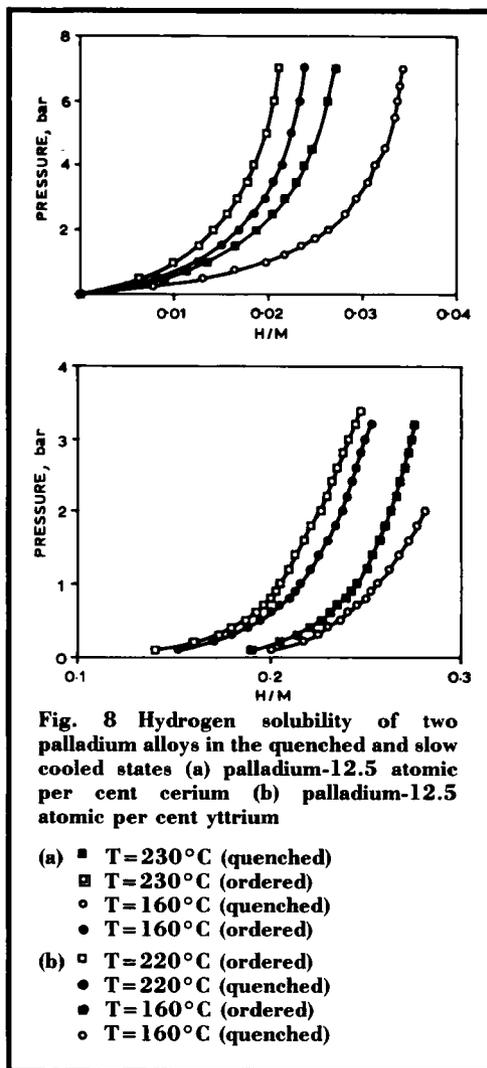
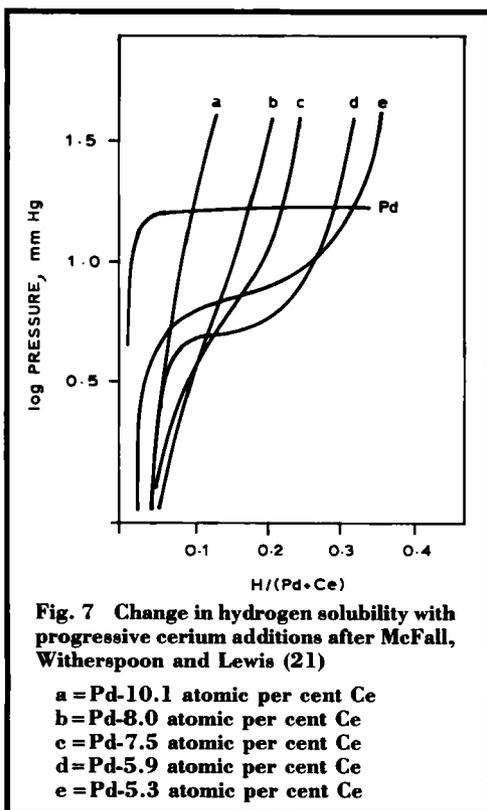
Hydrogen Absorption Behaviour

The first equilibrium studies of the absorption of hydrogen by palladium-rare earth alloys were carried out to ascertain the rare-earth concentrations necessary to suppress the formation of a discrete β -phase hydride from the α -phase in these alloys (6, 17). This work was later confirmed by Sakamoto and colleagues (18). These studies were a necessary precursor to research on the use of these alloys as hydrogen diffusion membranes, where the precipitation of a second phase hydride must be avoided at all costs. It

was found that, under operating conditions, a continuous metal-hydrogen phase could be guaranteed for palladium alloys containing 8 per cent yttrium, gadolinium or europium, 6 per cent cerium or 24 per cent silver. These alloys are isoelectronic with an electron to atom (e/a) ratio of 0.24, and the closure of the hydrogen miscibility gap at this value, see Figure 6, indicates one of the major factors controlling hydrogen solubility in these alloys. Indeed, it is widely acknowledged that changes in the hole populations of the Pd 4d-band, by both substitutional alloying elements and interstitial hydrogen, are a major factor in determining the hydrogen absorbing ability of these alloys. The saturated hydrogen contents of several palladium-cerium alloys have been plotted as a function of cerium content, and demonstrate a correlation between e/a and the extent of hydrogen solution, such that increasing cerium concentrations caused a decrease in the terminal hydrogen solubility (19). Thus Pd₇Ce has only a small hydrogen absorption capacity (20). Data by McFall, Witherspoon and Lewis (21) indicating the change in hydrogen solubility in palladium with progressive cerium additions are shown in Figure 7.

The hydrogen solubility in ordered and disordered forms of palladium-12.5 per cent

cerium has been explained in the pressure range 1.7 to 7.7 bar and temperature range 160 to 250°C (20). The results are plotted in Figure 8(a) and show that, at a given temperature and pressure, the disordered material absorbs significantly more hydrogen than does the ordered material, though in both cases the hydrogen solubility is small. Although the thermodynamic data were limited the results indicate very similar values of the relative partial molar enthalpy at infinite dilution $\Delta\bar{H}_H^0$ for both the quenched and the ordered forms of the material. The investigators also claimed that there was evidence to suggest a minimum in the variation of $\Delta\bar{H}_H^0$ with cerium concentration at around 8–9 per cent cerium. Both of these indications were later confirmed by others who examined the hydrogen solubility across the whole solid solution range of palladium-cerium (22). They found that $\Delta\bar{H}_H^0$ values for the disordered and ordered palladium-12.5 per cent



cerium alloy were very similar, at -17.4 and -16.8 kJ/mol, respectively. They also observed a minimum in $\Delta\bar{H}_H^0$ values for a cerium content around 10 per cent. However, despite the good general agreement between the trends observed by the two groups, their actual thermodynamic values show discrepancies which, at this juncture, cannot be explained.

Sakamoto, Flanagan and Kuji analysed their data for the whole range of palladium-cerium alloys in terms of a model which assumed the preferential occupation by hydrogen of sites surrounded only by palladium atoms (22).

They obtained good agreement with the experimental data and therefore postulated cerium atoms as being anti-trapping sites for hydrogen. They also plotted values for the relative chemical potential of hydrogen against the degree of order, calculated from resistance measurements, for Pd,Ce and found that the changes in the chemical potential were directly related to the state of order of the material.

Similar isothermal solubility studies were performed on ordered and disordered forms of Pd,Y in the pressure range 0 to 4 bar (16); these results are shown in Figure 8(b). As with Pd,Ce, the disordered palladium-12.5 per cent yttrium material absorbs more hydrogen than does the ordered material. However, in both the ordered and disordered forms, this alloy absorbs much more hydrogen than palladium-12.5 per cent cerium due to the trivalent nature of the yttrium atom (and thus more holes in the 4d band).

Values of the relative partial enthalpies and entropies of solution ($\Delta\bar{H}_H, \Delta\bar{S}_H$) of hydrogen in palladium-12.5 per cent yttrium were calculated for the ordered and disordered material, for the H/M range 0.19 to 0.26 (16). As with palladium-12.5 per cent cerium, the values of $\Delta\bar{H}_H$ and $\Delta\bar{S}_H$ are more negative for the quenched alloys, the $\Delta\bar{H}_H$ values being consistently 5 kJ/mol more negative than for the ordered alloy. A comparison of the solubility of hydrogen in palladium-8 per cent yttrium and palladium-12.5 per cent yttrium shows that, at any temperature below 450°C, palladium-8 per cent yttrium has a higher terminal hydrogen solubility than palladium-12.5 per cent yttrium. However, at low enough pressures palladium-12.5 per cent yttrium will dissolve more hydrogen than palladium-8 per cent yttrium. The fact that, at low pressures and high temperatures, palladium-12.5 per cent yttrium can absorb more hydrogen than palladium-8 per cent yttrium is unexpected. In the low pressure region the hydrogen content of the material is low (<0.1 H/M) and trapping of hydrogen by yttrium atoms may account for most of the hydrogen solubility. At higher hydrogen concentrations traps can no longer ac-

count for the greatest proportion of the hydrogen solubility and the palladium-12.5 per cent yttrium then shows a lower solubility for hydrogen than palladium-8 per cent yttrium. Modified Sieverts plots for palladium-12.5 per cent yttrium show that there is a strong hydrogen-metal interaction in this alloy at pressures below 0.25 bar.

In a paper on the thermodynamics of hydrogen in palladium-yttrium solid solution alloys Yoshihara and McLellan found very large decreases in the partial enthalpy of solution with increasing solute content which they attributed to the trapping of hydrogen by the yttrium atoms (23). They determined that the large contribution to the enthalpy term resulting from yttrium additions was due to the large lattice expansion it caused and not to any strong chemical affinity between yttrium and hydrogen. Hydrogen trapping by substitutional impurities in transition metals has been examined, based on a model of impurity atoms forming metal-hydrogen complexes (24). The perturbation of hydrogen atoms in transition metals, including palladium, was evaluated in terms of a volume and an electronic contribution, and good agreement with experimental data was found. This group of investigators predict that in solution with palladium, yttrium will have a trapping effect.

Kinetic Behaviour of the Hydrogen

It has been shown that the diffusion coefficients of the palladium-rare earth alloys: palladium-8 per cent yttrium, palladium-8 per cent gadolinium, palladium-5.75 per cent cerium and the palladium-noble metal alloy, palladium-25 per cent silver, were closely similar in the temperature range 100 to 500°C, despite their different lattice spacings (25, 26).

Recent studies of the diffusivities of a range of palladium-yttrium and palladium-cerium alloys have been made using an electrochemical technique, in the temperature range 10 to 50°C, and found that the activation energies of diffusion for both systems decreased as the rare-earth solute concentration increased (27).

The activation energies of palladium-cerium alloys were lower than those of the palladium-yttrium alloys and exhibited a shallow minimum at around 6 or 7 per cent cerium.

Ishikawa and McLellan also studied the diffusivities of hydrogen in a range of palladium-yttrium solution alloys in the same temperature range and using a similar technique (28).

Comparison of the two sets of data shows that, at yttrium concentrations below about 7 per cent, there is broad agreement as to the effect of increasing yttrium content on the diffusivities (D) of hydrogen at 298 K; Sakamoto detected a small increase in D while Ishikawa detected a small decrease, compared to pure palladium. However, at yttrium compositions of 8 and 10 per cent, the latter found a very large decrease in diffusivity which was attributed to large trapping contributions at the higher yttrium contents (28). The activation energies (E_a) and frequency factors (D_0) determined by Ishikawa were considerably greater than the corresponding values found by Sakamoto, across the whole range of yttrium concentrations studied.

A proposed explanation for the discrepancies between these two groups of workers is based on the work of Hughes (29), Wileman (30) and their colleagues on the diffusivity of hydrogen in a palladium-8 per cent yttrium alloy. Figure 9 shows the data for a palladium-8 per cent yttrium alloy which has been annealed at 600°C for two hours and slowly cooled to room temperature in a vacuum prior to any diffusion measurements taking place (30). Clearly the initial behaviour of the material on heating in hydrogen is quite different to the data collected on subsequent runs, after the material had been cooled in hydrogen. The activation energies and frequency factors for the material which had been cooled in hydrogen are far higher than those for the material cooled in a vacuum. The activation energies (E_a) are summarised in the Table.

The measurements given by Sakamoto were obtained for samples heated at 850°C for 2 hours and then vacuum cooled at a rate of 5–6°C/min (27). This material should be in the

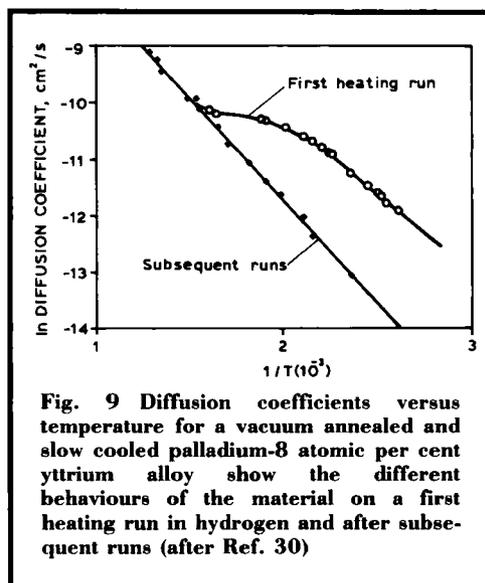


Fig. 9 Diffusion coefficients versus temperature for a vacuum annealed and slow cooled palladium-8 atomic per cent yttrium alloy show the different behaviours of the material on a first heating run in hydrogen and after subsequent runs (after Ref. 30)

low activation energy state determined by Wileman (30), and the activation energy value of 19.2 ± 1.0 kJ/mol of Sakamoto (27) is quite close to the value of 22.5 ± 0.4 kJ/mol obtained by Wileman.

On the other hand, the sample preparation procedure of Ishikawa and McLellan involved annealing at 627°C for 4 hours in hydrogen gas followed by cooling at 30°C/min again in hydrogen gas (28). This, in our experience, should result in samples being in the second, high, activation energy state described by Wileman (30). The value of the activation energy for this state as determined by Wileman is 30.5 kJ/mol (30), compared to the value of 42 kJ/mol determined by Ishikawa (28); although there is some difference between these values, they are both well in excess of the values for the initial heating state, determined by Sakamoto (27) and Wileman (30).

Wileman (30) and Hughes (29) attributed their observations of anomalous diffusion behaviour to the ordering of the palladium-8 per cent yttrium alloy on cooling in a vacuum, which produced a smaller activation energy for hydrogen diffusion when the material was first heated in hydrogen. The general shape of the curve supports this suggestion as it resembles

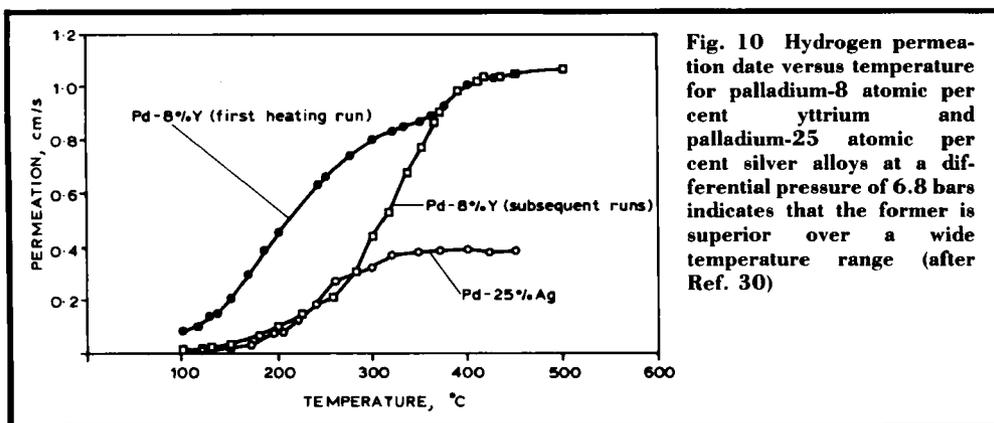


Fig. 10 Hydrogen permeation rate versus temperature for palladium-8 atomic per cent yttrium and palladium-25 atomic per cent silver alloys at a differential pressure of 6.8 bars indicates that the former is superior over a wide temperature range (after Ref. 30)

those of Goltsov and colleagues (31, 32) who studied hydrogen diffusion in ordered and disordered Cu₃Au and palladium-silver alloys. The fact that the lower activation energy state only persists up to 350°C, that is close to the proposed (12) order-disorder temperature in this material, also supported an explanation based on order-disorder.

Earlier magnetic susceptibility measurements indicated that subsequent cooling of the material in hydrogen did not allow re-ordering to occur and hence produced a higher activation energy and lower diffusivity for hydrogen (12). The fact that both Sakamoto (27) and Ishikawa (28) performed their measurements in the temperature range 0 to 50°C, well below the critical temperature of 350°C, means that both groups would find their data reproducible and consistent even after a large number of temperature cycles. Indeed, work in this laboratory has shown the initial ordered state is stable up to about 300°C for numerous temperature cycles in hydrogen gas. Sakamoto interpreted his resistivity measurements in terms of the material showing no sign of order (27), but work in this laboratory has shown that hydrogen diffusion and solubility are much more sensitive to order than is the electrical resistivity.

Whether or not this material actually undergoes an order-disorder transformation as described is very difficult to prove unequivocally, however, it is certain that these materials when cooled in vacuum or in hydro-

gen produce very different diffusion behaviours at up to 350°C. While the data of Wileman (30) do not extrapolate exactly to the data of Sakamoto (27) or of Ishikawa (28) (this may be due to the very small hydrogen concentrations used by Sakamoto and Ishikawa compared to those of Wileman), the observed increases in activation energy and frequency factor of Ishikawa over those of Sakamoto are clearly predicted. This shows that great care is necessary when selecting a particular bulk pretreatment for this material prior to making observations.

Diffusion Membrane Technology

The successful employment of an alloy as a hydrogen diffusion membrane requires that: (i) the alloy permeates a considerable amount of hydrogen at moderate temperatures and pressures, (ii) the material is mechanically stable and does not degrade appreciably with use, and (iii) the membrane is resistant to poisons which may "block" the membrane surface during its operation.

At present these criteria are best satisfied by the commercially used palladium-25 per cent silver membranes.

Work by Wise suggested that the palladium-rare earth alloy membranes containing 6 per cent cerium and 8 per cent yttrium (both approximately isoelectronic with palladium-25 per cent silver) showed permeabilities in excess of those displayed by palladium-25 per cent silver under the same conditions of temperature

Activation Energies of Palladium-Yttrium		
Material	Initial run, after cooling in vacuum	Runs, after cooling in hydrogen
Pd-8% Y (30)	22.5 ± 0.4 kJ/mol	30.3 ± 0.4 kJ/mol
Pd-8% Y (27) Pd-8.1% Y (28)	19.2 ± 1.0 kJ/mol	42.0 kJ/mol

and differential pressure (6). Further work by Fort, Farr and Harris confirmed that both a palladium-6.6 per cent yttrium and a palladium-10 per cent yttrium membrane were capable of allowing more hydrogen to permeate than was possible with palladium-25 per cent silver (33). In addition they noted that, after heavy surface oxidation, palladium-yttrium samples were more permeable than similarly treated palladium-25 per cent silver. This was due to the incomplete nature of the surface oxide formed on palladium-yttrium alloys (which exposes an active palladium-rich sub-layer) compared to the impervious tenacious oxide associated with the palladium-25 per cent silver alloy. They also commented on the appreciable solid solution hardening in the palladium-rare earth alloys, due to the large atom size differences, and the consequent possibility of maximising the permeabilities of these materials by the use of thinner membranes and/or larger gas differential pressures.

Hughes and colleagues established further the improvements in permeation afforded by the use of palladium-rare earth diffusion membranes, and also studied the effects of S.R.O. on the permeation characteristics of these materials (25, 26, 29). They found considerably enhanced permeabilities for palladium-8 per cent yttrium and palladium-5.75 per cent cerium membranes on initial heating in hydrogen, as compared to values obtained on subsequent heating and cooling runs. This enhancement of permeability was attributed to the alloy being "ordered" in its initial condition with the presence of hydrogen suppressing the ordering on subsequent runs. Electron microscope observations on the effect of hydro-

gen in a palladium-12.5 per cent yttrium alloy, which is the only system that can be easily studied in this way, indicate that in this alloy at least, ordering occurs normally in the presence of hydrogen (16), although at this composition we would expect the order to be more stable than in the non-stoichiometric palladium-8 per cent yttrium alloy. Nonetheless, recent measurements have confirmed both the very large enhancements of permeation which are available on initial heating of a palladium-8 per cent yttrium diffusion membrane up to 350°C (compared to subsequent heating and cooling) and its superiority over a wide range of temperatures and differential pressures when compared with palladium-25 per cent silver (30), see Figure 10. Wileman and Harris (34) have demonstrated the quite different rates of permeation of the hydrogen isotopes, protium and deuterium through a palladium-8 per cent yttrium membrane over a wide range of temperatures and pressures. The possibility of using this material in a cascade system for the large scale separation of hydrogen isotopes has been discussed (35).

Difficulties in working these materials have so far prohibited their use as diffusion membrane materials. The reported hydrogen softening of palladium-rare earths alloys may help overcome these problems (7). It is also worth noting that a number of researchers have acknowledged the superior mechanical stabilities, longer working lifetimes and resistance to carbon embrittlement of palladium-8 per cent yttrium compared to palladium-25 per cent silver membranes (30, 33, 36). Indeed the permeability behaviour of palladium-8 per cent yttrium has been compared with a wide range

of palladium-based membrane materials in a review published here previously (37).

Concluding Remarks

Solid solutions formed by the dissolution of rare-earth atoms in palladium are surprisingly extensive possibly due to a d-band filling contribution to the large lattice expansion observed in these alloys.

Palladium-rare earth solid solution alloys display order-disorder transformations.

Palladium-rare earth alloys are able to absorb hydrogen exothermically at moderate temperatures and pressures. The amount of hydrogen absorbed decreases with increasing rare-earth content.

The hydrogen solubilities in these materials are affected by the order-disorder transformations in such a way that the disordered alloys absorb more hydrogen than the ordered alloys under identical conditions of temperature and pressure.

The kinetic behaviour of hydrogen in these alloys is also influenced strongly by the state of order, and thus may only be described adequately by taking into account the differences between sample pretreatments.

Palladium-rare earth alloys are good candidates for use as hydrogen purification and isotope separation membranes and exhibit considerably improved permeability over conventional palladium-silver materials.

References

- 1 I. R. Harris and M. Norman, *J. Less-Common Met.*, 1968, **15**, 285
- 2 M. Norman and I. R. Harris, *J. Less-Common Met.*, 1969, **18**, 333
- 3 J. R. Thompson, *J. Less-Common Met.*, 1964, **6**, 94
- 4 J. D. Speight, *J. Less-Common Met.*, 1973, **30**, 159
- 5 I. R. Harris and M. Norman, *J. Less-Common Met.*, 1970, **22**, 127
- 6 M. L. H. Wise, J. P. G. Farr, I. R. Harris and J. R. Hirst, Congrès Int. L'Hydrogene dans les Metaux, Paris, 29 May-2 June, 1972, 72
- 7 J. R. Hirst, M. L. H. Wise, D. Fort, J. P. G. Farr and I. R. Harris, *J. Less-Common Met.*, 1976, **49**, 193
- 8 D. T. Hughes, Ph.D. Thesis, University of Birmingham, 1978
- 9 J. R. Thompson, *J. Less-Common Met.*, 1967, **13**, 307
- 10 O. Loebich and E. Raub, *J. Less-Common Met.*, 1973, **30**, 47
- 11 J. W. Brooks, M. H. Loretto and I. R. Harris, *Met. Sci.*, 1976, 397
- 12 D. T. Hughes, J. Evans and I. R. Harris, *J. Less-Common Met.*, 1980, **76**, 119
- 13 N. Kuwano, T. Shiwaku, Y. Tomokiyo and T. Eguchi, *Jpn. J. Appl. Phys.*, 1981, **20**, 1603
- 14 D. A. Smith, I. P. Jones and I. R. Harris, *J. Mater. Sci., Lett.*, 1982, **1**, 463
- 15 Y. Sakamoto, M. Yoshida and T. B. Flanagan, *J. Mater. Res.*, preprint
- 16 M. Doyle and I. R. Harris, to be published
- 17 M. L. H. Wise, J. P. G. Farr and I. R. Harris, *J. Less-Common Met.*, 1975, **41**, 115
- 18 Y. Sakamoto, K. Yuwasa and K. Hirayama, *J. Less-Common Met.*, 1982, **88**, 115
- 19 J. Evans, I. R. Harris and P. F. Martin, *J. Less-Common Met.*, 1980, **75**, 49
- 20 D. A. Smith, I. P. Jones and I. R. Harris, *J. Less-Common Met.*, 1984, **103**, 33
- 21 W. D. McFall, T. C. Witherspoon and F. A. Lewis, *J. Chem. Soc., Chem. Commun.*, 1973, (4), 102
- 22 Y. Sakamoto, T. B. Flanagan and T. Kuji, *Z. Phys. Chem.*, 1985, **143**, 61
- 23 M. Yoshihara and R. B. McLellan, *Acta Metall.*, 1988, **36**, (2), 385
- 24 P. Vargas, H. Kronmuller and M. C. Bohm, *Z. Phys. Chem.*, 1985, **143**, 229
- 25 D. T. Hughes and I. R. Harris, *J. Less-Common Met.*, 1978, **61**, 9-21
- 26 D. T. Hughes and I. R. Harris, *Z. Phys. Chem.*, 1979, **117**, S185
- 27 Y. Sakamoto, H. Kaneko, T. Tsukahara and S. Hirata, *Scr. Metall.*, 1987, **21**, 415
- 28 T. Ishikawa and R. B. McLellan, *Acta Metall.*, 1987, **353**, 781
- 29 D. T. Hughes, J. Evans and I. R. Harris, *J. Less-Common Met.*, 1980, **74**, 255
- 30 R. Wileman and I. R. Harris, *J. Less-Common Met.*, to be published
- 31 V. A. Goltsov and G. E. Kagan, Congrès Int. L'Hydrogene dans les Metaux, Paris, 29 May-2 June, 1972, 249
- 32 V. A. Goltsov, V. B. Vykhodets, P. V. Gel'd and T. A. Krylova, *Fiz. Met. Metalloved.*, 1970, **30**, (3), 657
- 33 D. Fort, J. P. G. Farr and I. R. Harris, *J. Less-Common Met.*, 1975, **39**, 293
- 34 R. Wileman and I. R. Harris, *J. Less-Common Met.*, 1985, **109**, 367
- 35 J. Evans, I. R. Harris and D. K. Ross, *J. Less-Common Met.*, 1983, **89**, 407
- 36 D. Fort and I. R. Harris, *J. Less-Common Met.*, 1975, **41**, 313
- 37 G. J. Grashoff, C. E. Pilkington and C. W. Corti, *Platinum Metals Rev.*, 1983, **27**, (4), 157