The Palladium-Hydrogen System

PART III: ALLOY SYSTEMS AND HYDROGEN PERMEATION

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Hydrogen absorption by series of palladium alloys with several other metals has now been quite extensively investigated with reference to systematic alterations of pressure-composition relationships, other related thermodynamic factors and various physical parameters. Hydrogen permeation has been an important area of both academic and technological interest with relation, for example, to effecting reductions of deformations associated with phase transitions, while retaining the high values of hydrogen solubilities and hydrogen diffusion coefficients in palladium at convenient temperatures.

Characteristic examples of three types of change of form of p–n relationships at 25°C, as the contents of elements alloying with palladium are gradually increased (4,37,70,74–83,95–98,104,108,153,154), are illustrated in Figure 9. As for the palladium-hydrogen system itself (4), such relationships have been determined from direct equilibrations with hydrogen gas, as well as being derived from measurements of electrode potential. Similarly as for palladium-hydrogen, temperature dependences of the p–n relationships have been used to supplement calorimetric data (110) in deriving heats and entropies of hydrogen absorption, both at initially low values (79–82,95,100,108) of hydrogen content (n → o) and over $\alpha \rightleftharpoons \beta$ transition regions (4,37,70,74–83,104,154,178).
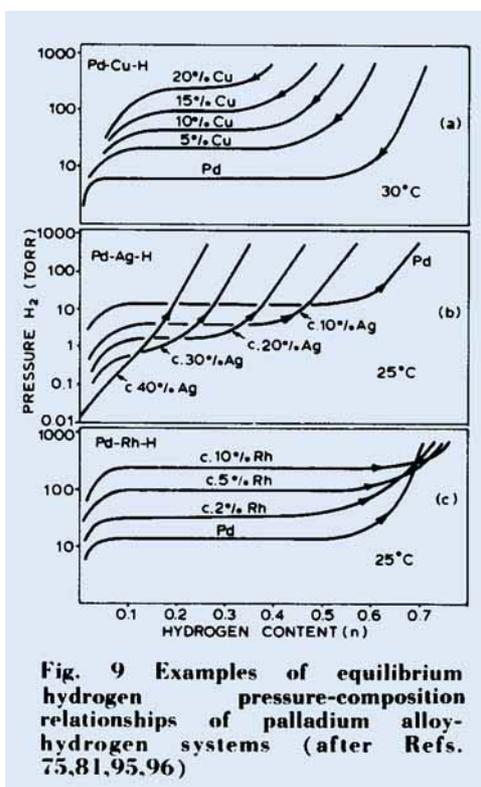
The sequence of relationships in Figure 9(c)

shows gradual increases with increasing rhodium content in the range of n over which α and β phases coexist. This sequence now seems unique to the palladium-rhodium-hydrogen system (45,75,153,154), since some suggestions of similarities of the palladium-manganese-hydrogen system (179) seem doubtful in view of possible incomplete equilibrations.

The remaining families of p–n isotherms for palladium alloy-hydrogen systems would thus seem to be divisible into two groups represented by those in Figures 9(a) and 9 (b). In both cases the ranges of n over $\alpha + \beta$ phase regions are successively shortened with increasing content of the alloying element, even in the cases of alloys with readily hydride-forming transition or inner transition elements such as vanadium (82) or cerium (76), but the corresponding values of equilibrium pressure are being successively increased (74,79,81,82), as in Figure 9(a), or decreased (37,70,75,80), Figure 9(b).

Decreases, in the range of n over $\alpha + \beta$ regions, with increasing amounts of alloying elements, have continued to be deduced from X-ray determinations of α and β phase lattice constants for additional palladium alloy-hydrogen systems (4,79–82,157,180–182).

Apart from the probable case of the palladium-nickel-hydrogen system (50), these general trends of decreasing extents of α, β coexistence with increasing contents of alloying element are similar to the effects of increasing temperature in the palladium-hydrogen system, being accompanied by decreases in the extents of hystereses of absorption and desorption relationships between hydrogen contents and other experimental parameters (4,69,96–98). This has been taken as complementary to decreases in the value of critical temperatures for two phase coexistence and, as discussed

1000
100
10
Pd-Cu-H
20°/. Cu
15°/. Cu
10°/. Cu
5°/. Cu
Pd
(a)
30°C

PRESSURE H₂ (TORR)
1000
100
10
1
0.1
0.01
Pd-Ag-H
Pd
c.10°/.Ag
c.20°/.Ag
c.30°/.Ag
c 40°/. Ag
(b)
25°C

1000
100
10
Pd-Rh-H
c.10°/. Rh
c.5°/. Rh
c.2°/. Rh
Pd
(c)
25°C

0.1 0.2 0.3 0.4 0.5 0.6 0.7
HYDROGEN CONTENT (n)

Fig. 9 Examples of equilibrium hydrogen pressure-composition relationships of palladium alloy-hydrogen systems (after Refs. 75,81,95,96)

later, has importance in choices of alloy compositions as hydrogen permeation membranes.

In addition to the arguments concerning the solubility of hydrogen in the palladium-silver alloys, the extents of decreases of hydrogen solubilities with increasing contents of other alloying metals have been used (95,104,108) in support of an essentially protonic nature of the hydrogen entities. However, in order to allow for proposed levels of electron donation it has seemed necessary to postulate adoptions of oxidation states by the alloying elements which can be difficult to reconcile with their relative positions in sequence of electronegativities.

Moreover as for the palladium-hydrogen system, latterly there has been increasing emphasis on the account to be taken of lattice expansions accompanying hydrogen absorption (26,37,166) in palladium alloys. There has also been attention to the localised as well as to the continuing effects of the alloying metals as exemplified by appearance, potential measure-

ments (183) and by Mössbauer Spectroscopy examinations (133,180,184,185). For example, evidence of preferential location of hydrogen around rhodium atoms (186) might be correlated with wider ranges of α and β phase coexistence with rhodium content in the palladium-rhodium-hydrogen system in Figure 9(c). A particular example of the significance of differences in the distribution of alloying atoms has been provided by measurements, made under high pressures of hydrogen, of changes of electrical resistivity of a palladium-iron alloy of approximate composition Pd_3Fe (187). Figure 10 illustrates the substantial differences between the ranges of pressures (hydrogen chemical potentials) over which evidence was found of significant hydrogen absorption in ordered and disordered structures of the alloy.

The two main families of p–n isotherms illustrated in Figures 9(a) and 9(b) also differ from one another in regard to the direction of changes of the heats of hydrogen absorption with alteration of alloying metal content (4,37,70,74–76,79–82,100,178), relative to heats of hydrogen absorption in pure palladium. Thus those alloys with the pattern of Figure 9(b) in general exhibit more exothermic heats of hydrogen absorption than palladium, both at infinite dilution (n → 0) and over regions of α and β coexistence, while the converse (less exothermic heats of absorption than palladium) appears generally true for alloy series associated with families of p–n isotherms as in Figure 9(a).

Attempts to provide underlying reasons have so far stressed two alternative ways by which the different series of alloys may themselves be divided. In one line of argument (100,178), emphasising differences in electronic structure, it has been pointed out that patterns similar to Figure 9(a) are followed by alloys formed by palladium with other transition elements, and those of Figure 9(b), accompanied by more exothermic heats of hydrogen absorption, tend to occur with alloys of non transition elements.

An alternative division (76, 82, 100) has been based on findings that the patterns of p–n relationships in Figure 9(b) are followed by alloys of palladium with elements which
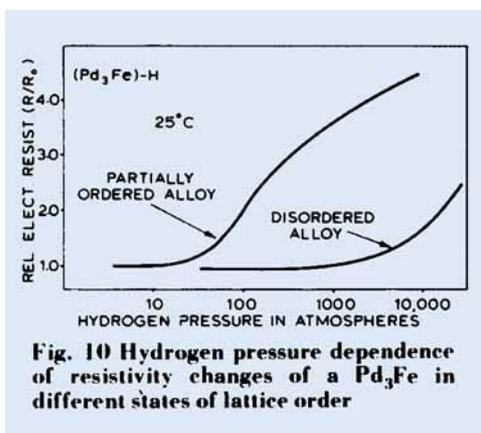
Fig. 10 Hydrogen pressure dependence of resistivity changes of a Pd₃Fe in different states of lattice order

reported has been ~17K with a $Pd_{55}Cu_{45}$ composition (46). With increasing content of alloying element in several alloy series the transition temperature passes through a maximum value and, as for $PdH_n(D_n)$, plots of transition temperature against hydrogen content also exhibit maxima (46). Recent studies with palladium-silicon alloys (191) have shown that superconducting transitions also can be found with amorphous materials.

For many of the investigated palladium alloy-hydrogen systems, the alloy element can only be considered to be in solid solution up to relatively low limits of concentration (37,75, 80,82,85,108,133,180,181,189,190,192,193), and only a few studies have so far been reported

produce overall average increases of f.c.c. lattice constants ("expanded alloys") and vice versa. Since additions of platinum to palladium produce very small increases of lattice constant (188), the palladium-platinum-hydrogen system constitutes a marginal exception to this latter division. However, it may be possible that differences of elastic constants provide a deciding feature in this case. In explanations based on size factors, it might be argued that atoms of alloying elements causing increases of lattice parameters in an elastic medium could produce overall expansions in the volumes of interstices which could result in lower energies being required to introduce hydrogen, as reflected by the high exothermic heats of hydrogen absorption. It is in any event interesting, as illustrated in Figure 11, that relative extents of increases of initial lattice parameter with contents of alloying element, quite closely parallel extents of decreases of isobaric (1 atm) hydrogen solubilities in such chemically diverse substitutionally alloying metals as cerium (76), silver (70–72,86,95–98,104,160), lead (80) and with interstitially incorporated boron (37,189).

Occurrences of superconducting transitions at very high contents of hydrogen have been studied with several series of palladium alloys. In some series higher transition temperatures have been recorded than with pure palladium (46,143,190), and again slightly higher values have been found for corresponding deuterides (46). The highest transition temperature so far
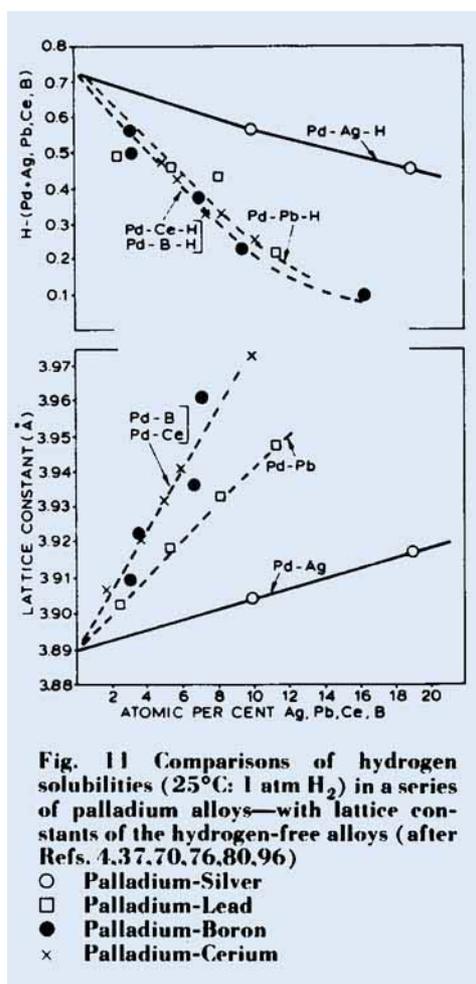

Fig. 11 Comparisons of hydrogen solubilities (25°C: 1 atm H₂) in a series of palladium alloys—with lattice constants of the hydrogen-free alloys (after Refs. 4,37,70,76,80,96)
O   **Palladium-Silver**
□   **Palladium-Lead**
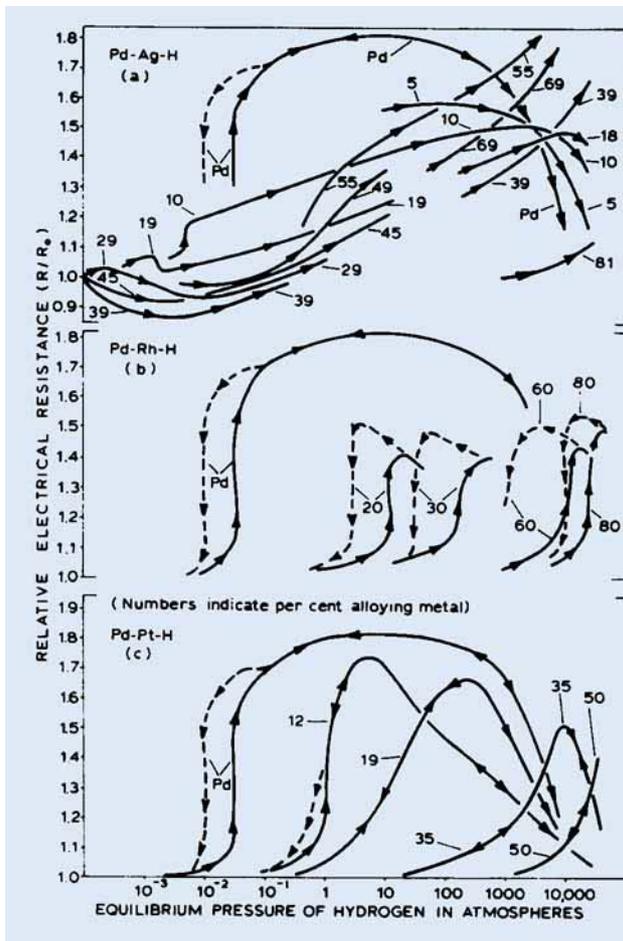●   **Palladium-Boron**
×   **Palladium-Cerium**

Fig. 12 Examples (at 25°C) of relationships for palladium alloy-hydrogen systems between relative electrical resistivity and equilibrium hydrogen pressures (after Refs. 4,45,50, 62, 68–70, 74, 116, 154, 196)

with higher alloy percentage intermetallic phases (194,195).

However, palladium can form binary alloys with certain neighbouring elements also crystallising in the f.c.c. structure, which approximate to solid solutions over the entire composition range.

In principle these systems have offered possibilities of studying gradual changes in alloying behaviour from pure palladium to that of the pure alloying element. In practice this has required extension of studies into the range of high hydrogen pressures, which at upper limits correspond to particularly high fugacities (45,196). Here, difficulties of making direct measurements of hydrogen contents have so far required that these are inferred from changes in

physical properties such as thermoelectric power (50,197) and electrical resistivity.

Examples of relationships derived between electrical resistivity and high hydrogen pressures obtained with three such series of alloys (45,50,68,69,154,196), combined with data previously derived over lower ranges of pressure (4,70,75), are illustrated in Figure 12.

The somewhat complex case of the palladium-silver-hydrogen system (70,196) in Figure 12(a) at 25°C illustrates, in keeping with the family of p-n isotherms in Figure 9(b), that initial increases of silver content are associated with pronounced changes of resistivity, complementary to regions of $\alpha \to \beta$ transitions or quasi transition, at increasingly lower pressures than for the $\alpha \to \beta$ transition for pure palladium.

This trend may be seen to continue for compositions of up to approximately $Pd_{50}Ag_{50}$, but for still higher silver contents significant changes of resistivity only become perceptible at increasingly higher pressures, as shown by the examples of $Pd_{31}Ag_{69}$ and $Pd_{19}Ag_{81}$. These provide an indication that substantial absorption of hydrogen by pure silver should only occur at 25°C at hydrogen pressures in excess of 30 kilobars.

Trends in the form of relationships for the palladium-rhodium-hydrogen and palladium-platinum-hydrogen systems (50,68,69,154) in Figures 12(b) and (c) are somewhat more simply continuous in appearance.

In the case of the palladium-rhodium-hydrogen system (154), measurements of approximate hydrogen contents attained under high hydrogen pressures have endorsed indications from the persistence of the hysteresis effects illustrated in Figure 12(b) that $\alpha \rightleftharpoons \beta$ phase hydride transitions continued to occur for alloying contents up to 80 per cent rhodium. These findings suggested the possibility of the formation of a β-phase hydride by pure rhodium at still higher pressures, and subsequent analogous studies of resistivity changes at 250°C have since indicated the formation of such a rhodium hydride at pressures in the region of 40 kilobars (155).

Figure 12(c) illustrates, for the palladium-platinum series of alloys, that continuously increasing hydrogen pressures again are needed to effect significant hydrogen absorption as platinum contents are increased (68,69). This is consistent with trends in p-n relationships (4,74) similar to those in Figure 9(a) which also would be consistent with universal decreases of hydrogen solubility with increasing hydrogen content at any given reference of hydrogen pressure at 25°C.

In contrast to the pattern in Figure 12(b) for the palladium-rhodium-hydrogen system, Figure 12(c) also illustrates a gradual reduction of hysteretic differences between "absorption" and "desorption" relationships with increasing platinum content. Again this is consistent with indications from p-n relationships and X-ray

studies (4,50,69,74) of complementary decreases of the critical temperature of α and β phase coexistence to around 25°C, for platinum contents of about 25 per cent. However the resistivity changes with hydrogen pressure in Figure 12(c) also provide evidence of a continuation of substantial hydrogen absorption by alloys with platinum contents much higher than 20 per cent, over what have been termed regions of quasi two phase coexistence (68). Even for an alloy containing 70 per cent platinum, the onset of what would seem likely to be a further such region of absorption has been detected at hydrogen pressures of around 30 kilobar (50,69). Extrapolations of available data have suggested that analogous absorptions of hydrogen by pure platinum could be expected to occur at hydrogen pressures of near 100 kilobar, at 25°C.

For the palladium-platinum alloys with ≥ 20 per cent platinum, the absence of hysteretic effects and accompanying lower levels of macroscopic deformation in cycles of absorption and desorption of hydrogen have been found to be of some practical advantage. Because of this, measurements of changes of the electrical resistivity of certain palladium-platinum and other suitable alloy compositions have been usefully employed for repetitive analytical determinations of the solubility of hydrogen in solutions (4,198), and for estimating high values of hydrogen chemical potentials in electrochemical studies (39,50,62).

Hydrogen Diffusion Coefficients and Hydrogen Permeation Studies

Determination of diffusion coefficients of hydrogen in palladium have now been extended over a wide range of temperatures by a variety of techniques. These include, in addition to derivatives from steady rates of hydrogen permeation across a known concentration gradient and from breakthrough times related to detection of hydrogen at the side of membranes remote from hydrogen introduction (4,71–73,86,89,104,169), phase boundary independent methods such as nuclear magnetic resonance (4,104,200), Mössbauer studies (184),
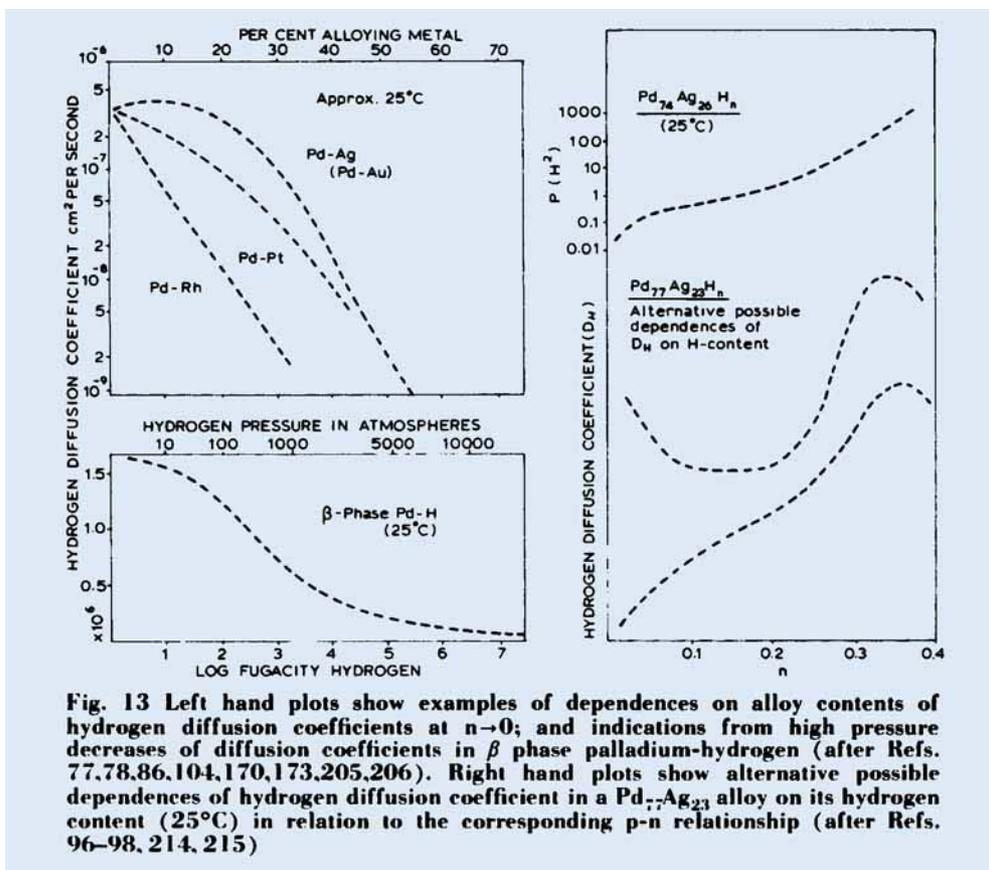
Fig. 13 Left hand plots show examples of dependences on alloy contents of hydrogen diffusion coefficients at n→0; and indications from high pressure decreases of diffusion coefficients in β phase palladium-hydrogen (after Refs. 77,78,86,104,170,173,205,206). Right hand plots show alternative possible dependences of hydrogen diffusion coefficient in a $Pd_{77}Ag_{23}$ alloy on its hydrogen content (25°C) in relation to the corresponding p-n relationship (after Refs. 96–98, 214, 215)

quasi elastic neutron scattering (29,118,136,163–165,201) and anelastic Gorsky Effect measurements (51,169–173). At very low α phase hydrogen contents, a large measure of agreement now exists between values derived by the various methods (104,202). At 25°C these are of the order of 10^{-7}/cm²/s representing an average value over the narrow α phase range of contents within which the only reported trend has been that of a slight decrease with increasing hydrogen content (86). Only a few studies have been reported of hydrogen diffusion coefficients in platinum but these (57,58,203,204) have suggested values of approximately two orders of magnitude lower (say 10^{-9}/cm²/s) than in palladium, near 25°C.

Values of about 10^{-6}/cm²/s have been derived for the Fick hydrogen diffusion coefficient in β phase palladium hydride for hydrogen contents of n∼0.7 (4,71,72,86). Such values are thus about an order of magnitude higher than the α phase values. However studies of break-through times (86) and of relaxation times associated with changes of electrical resistivity at high pressures (45,205) have indicated that at still higher hydrogen contents there are marked decreases of diffusion coefficient. These have been attributed to "blocking" of the diffusion process due to reductions in the numbers of vacant octahedral interstitial positions (206).

Academic interest has been sustained in correlations between Fick and Einstein diffusions coefficients (71,72,86,104,171), differences between values for the three hydrogen isotopes (including the finding over a wide temperature range of higher values for deuterium than protium (hydrogen)) (51,104,

171,204), and problems of interpretation at low temperatures (18,51,169–171,201,207,208), and near phase transitions and critical points (36,86,104,171).

Much interest also has continued in the method of hydrogen purification by its permeation through palladium alloys. As quite recently reviewed by Knapton (209), a wide variety of alloys already have been proposed for this purpose, and others continue to be examined (210). Factors which influence practical utilisation include those of resistance to poisoning of surface catalytic activity, suitable mechanical properties over desirable ranges of temperature, and also convenience of manufacture—including quality control.

Other basic considerations are that concentrations of the alloying element should be sufficient for critical temperatures, corresponding to α and β phase coexistence, to be decreased to ambient or below in order to reduce deformation in cycles of use (4,62,96–98, 104,158,176,181), and that diffusion coefficients and solubilities of hydrogen at convenient input pressures should both continue to have high values.

In regard to values of diffusion coefficients, characteristic examples in Figure 13 show that initial, small percentage, additions of most binary alloying elements (77,78,85,86,97,98, 104,170,173,181,206) produce only relatively small decreases from values (at 25°C) for pure palladium—when compared at low values of hydrogen content, that is as n → o.

Sustained or increased hydrogen solubilities at convenient input pressures and temperatures are features generally associated with palladium alloy-hydrogen systems exhibiting similar sequences of changes of form of p–n isotherms to those in Figure 9(b) and also for a specific case in Figure 13. As examples of this group of systems, compositions from the palladium-boron series (37,211,212) and from series of alloys of palladium with transition metals of Subgroup III and the closely allied lanthanide series have been suggested for practical utilisation, the palladium-yttrium system being a promising example (181,210). The palladium-

gold (207) and, as illustrated in Figure 9(b), the palladium-silver series (4,95,96) alloys also belong to this general class of systems. Compositions from the latter series such as $Pd_{77}Ag_{23}$ and $Pd_{77}Ag_{25}$ have continued to be widely employed as commercially suitable materials, although certain measures of deformation still have been observed after many cycles of use (98,160,211). Several studies of both hydrogen and deuterium diffusion coefficients in these compositions have been reported (71,72,85,86,170,214,215).

For the palladium-silver series of alloys measurements have been reported of gradual changes of diffusion coefficient with changes of hydrogen content, principally by the electrochemical breakthrough technique (86,104,214). For alloys with relatively high contents of silver, such as $Pd_{40}Ag_{60}$ and $Pd_{50}Ag_{50}$, results (86,104) show a continuous increase of diffusion coefficient with increasing hydrogen content from initially lower values than those of pure palladium at n → o; this is consistent with trends suggested by studies of the shifts with temperature of internal friction peaks associated with Zener relaxation effects (97,127,216). However, for compositions near to $Pd_{77}Ag_{23}$ two alternative trends of change of diffusion coefficient have been suggested from results so far available (97) as diagrammatically represented in Figure 13.

Some Concluding Comments

The last two decades have seen substantial expansions of experimental information concerning the palladium-hydrogen system over wider ranges of temperature and pressure, with generally increased precision of the measurement and control of hydrogen content. Several further physical parameters have been studied.

These advances have taken place against a background of much increased levels of activity in the research field of metallic hydrides formed by other transition elements and alloys, with which a need for correlation of ideas concerning chemical binding, including the gradual modification of bond type from those of the alkali, alkaline earth, lanthanon and actinon

hydrides, has now been increasingly appreciated.

In regard to structural considerations, there has been increasing attention to evaluation of the effects of introduction of individual hydrogen entities, in regard to their localised stress and spatial influences on neighbouring palladium atoms, with reference to such issues as mechanisms of diffusion, isotope effects, phase transitions and associated hysteresis and gross deformational phenomena.

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