# The Hydride Phase Miscibility Gap in Palladium-Rare Earth Alloys

## X-RAY AND EQUILIBRIUM HYDROGEN PRESSURE STUDIES

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*Recent years have witnessed a very substantial increase in the body of data concerning the effects of various alloying elements on the phase relationships of the palladium-hydrogen system.*

There seems some underlying technological interest in recent developments (1–9) in palladium alloy systems because of the possibilities of developing palladium alloys with improved characteristics for use as diffusion membranes for hydrogen purification and allied purposes (10). In addition to the important issues of surface kinetics and membrane thickness, other key factors for improved diffusion characteristics are those of a decreased susceptibility to deformation during the course of hydrogen absorption and desorption cycles, combined with a retention of satisfactorily high rates of hydrogen permeation under particular conditions of temperature and hydrogen pressure gradients across the membranes. The permeation rate is governed by internal hydrogen concentration gradients as reflected by the corresponding p-c(n)-T relationships between equilibrium hydrogen pressure, p, hydrogen content, c (expressed as the ratio H:M of hydrogen to metal atoms and generally represented by n), and temperature, T.

## F.C.C. Phase Miscibility Gap

In the palladium-hydrogen system two f.c.c. phases, designated $\alpha$ and $\beta$ (or $\alpha'$) with low and high concentrations of hydrogen, respectively (located in octahedral interstices in both cases), can co-exist at room temperature over a range of hydrogen contents which may be termed the $\alpha/\beta$ miscibility gap (1–5).
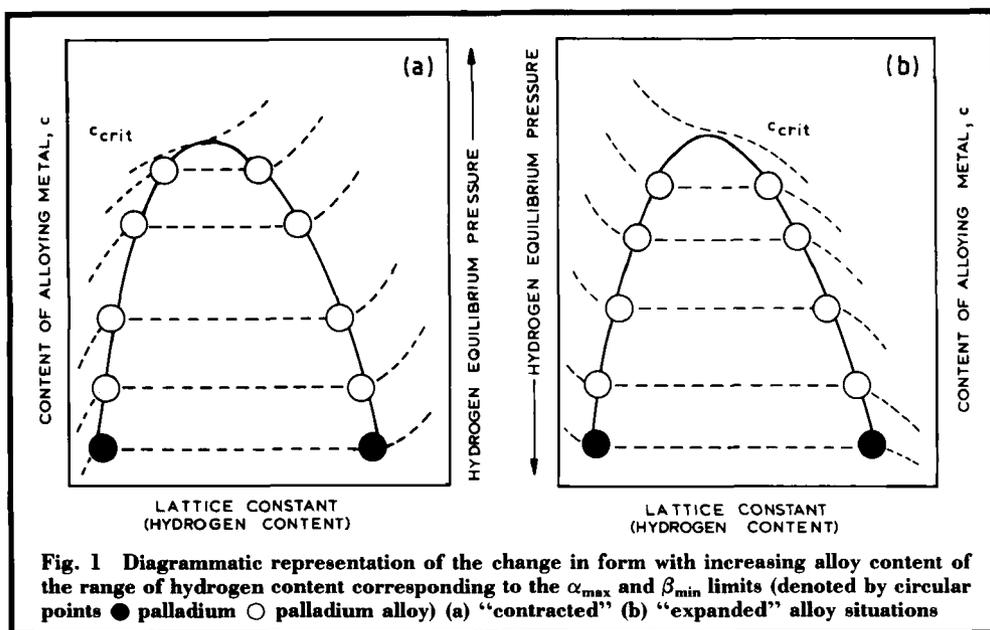
Semiquantitatively it has been convenient to symbolise the limits of the miscibility gap as $\alpha_{max}$ and $\beta_{min}$. In experimental practice

however, p-n relationships do not exhibit very sharp cusps, whether derived by direct gas phase equilibration studies or, often in more precise detail, from dynamic changes of electrode potential. This presents problems in defining points, on precisely located spinodal curves, which could be taken to correspond to the exact onset of the transitions. An additional physical complication is the possible existence of $\alpha$ and $\beta$ phases or domains within ranges of n adjacent to the main pressure invariant regions of p-n relationships; this has encouraged possibilities of correlations with catastrophe transition behaviour (9).

Nevertheless, making use of an approximately direct dependence of hydrogen content on the f.c.c. lattice constant (3, 11), useful estimates of the miscibility gap have been derived from X-ray measurements of the lattice constants of $\alpha$ and $\beta$ phases, identified in conjunction and referred to as $\alpha_{max}$ and $\beta_{min}$. A recent X-ray investigation has been concerned with several palladium-rare earth-hydrogen systems (2), and represents a substantial amplification of earlier analogous studies (3, 4, 5).

## Alterations of Gap Width

Figure 1 illustrates the generally observed similarities in the trends of change, with increasing alloy content, of the range of hydrogen contents corresponding to the miscibility gap, either from comparison of plots of p-n data (1, 6–9) or from plots of lattice parameter values regarded as corresponding to $\alpha_{max}$ and $\beta_{min}$ (2–5). The X-ray data have been obtained

**Fig. 1 Diagrammatic representation of the change in form with increasing alloy content of the range of hydrogen content corresponding to the $\alpha_{max}$ and $\beta_{min}$ limits (denoted by circular points ● palladium ○ palladium alloy) (a) "contracted" (b) "expanded" alloy situations**

using specimens electrolytically loaded with hydrogen to a mixed phase content; subsequent hydrogen loss during X-ray measurements being effectively prevented by an inhibitory surface coating.

One or other form of the plots in Figure 1 is common to most data available for binary palladium alloy systems, with the exception of the palladium-nickel and palladium-rhodium series (2, 8, 9). It seems that palladium-ruthenium is not an exceptional case provided that the ruthenium is homogeneously dispersed within its low limits of solid solubility in palladium (8).

Thus both Figures 1(a) and 1(b) show a similar trend of decreasing width of the $\alpha/\beta$ miscibility gap with increasing alloy concentration. Taken by themselves, however, the X-ray data do not reveal the important division of alloying metals into two main sub-Groups, consisting alternatively of those producing either increases or decreases of the invariant hydrogen pressure over the main region of $\alpha$ and $\beta$-phase co-existence. This distinction is a central consideration in theoretical analyses of the energetics of hydrogen absorption (1-9), and it also has an important bearing on the utility of

particular alloys as diffusion membranes (10).

Nevertheless apart from this limitation, in all cases extrapolations of the loci of X-ray parameters versus alloy content data provide useful estimates of the concentration, $c_{crit}$, of alloying metal sufficient to close the miscibility gap. For alloying additions above $c_{crit}$, hysteresis effects and accompanying macroscopic structural deformations produced during absorption and desorption cycles can be expected to be substantially decreased. Unfortunately in many systems $c_{crit}$ is also close to the limit of solid solubility of the alloying element in palladium (1-9).

## Alloys of Transition Elements

In the continuing debate on the most important factor governing differences between alloying elements in their overall effects on the p-n relationships and on related thermodynamic parameters, considerations of the influence of relative size have been specifically emphasised in recent studies. These have substantially expanded information on alloys of palladium with the more electropositive transition elements of Groups III, IV and V (1-9). By themselves elements from these Groups form metallic

hydrides with higher hydrogen contents at lower hydrogen chemical potentials (equilibrium hydrogen pressures) than palladium. When alloyed with palladium over the limited range of concentrations where solid solutions form, they exhibit decreases in the $\alpha/\beta$ miscibility gap (1–5, 8–10), generally similar to those in Figure 1. Comparison of the pattern of change of p-n relationships with increasing alloying content has provided useful opportunities for examining whether relative atomic size differences alone would be the decisive factor which accounts for increases or decreases of equilibrium hydrogen pressures over regions of the miscibility gap (9).

Thus in sub-Groups V and IV, niobium and zirconium, elements of the 4d long period, produce slightly expanded f.c.c. lattice constants, in contrast to their respective congener 3d period elements vanadium and titanium, which produce a contraction.

Studies of alloys of these four elements with palladium have shown that, in the cases of palladium-niobium-hydrogen and palladium-zirconium-hydrogen, there are significant shifts (9) towards correspondence with the pattern in Figure 1(b). Nevertheless both these systems still constitute marginal formal exceptions to a precise, simple correlation between expanded alloys and the trends in Figure 1(b), as does the palladium-platinum-hydrogen system.

## Expanded Palladium Alloys

In the case of palladium alloys containing Group III transition metals, all of the elements including the rare earths (lanthanides) and even scandium, with the smallest atomic volume, fall into the "expanded" category. Consistent with a size effect correlation, all the p-n relationships of palladium-Group III alloy systems reported so far (6–9), including the marginal case of the palladium-scandium-hydrogen system (12), exhibit a decrease in $p_{\alpha, \beta}$ with an increase in alloy content. Thus alloys from all of these systems present potential alternatives to palladium-silver compositions as hydrogen diffusion alloys.

In addition to such technological considera-

tions, the large number of rare earths with closely spaced gradual variations of properties present comparison possibilities which should encourage future attempts to resolve uncertainties concerning the role of fundamental underlying, and in some respects competing, factors. These would necessitate formidable and lengthy experimental programmes of work, however, particularly when possibilities of variations of degrees of lattice order are taken into account (2).

Nevertheless, some recent studies have made significant progress in considerably extending knowledge of the p-n relationships in the $\alpha$ phase ranges of n over a substantial range of temperatures for palladium alloys with samarium, gadolinium, dysprosium and erbium (6, 7).

An even larger number of palladium-rare earth alloys have been included in X-ray studies. With each of the seven elements, samarium, europium, gadolinium, dysprosium, holmium, erbium and ytterbium, five alloy compositions containing up to 8 atomic per cent of the alloying element have been examined (2). Ternary diagrams have also been prepared. For all of these alloys the recent studies have clearly indicated closure of the miscibility gap at values of $c_{crit}$ corresponding to approximately 9 atomic per cent of each of the alloying rare earth elements, but have also enabled interesting trends in the changes of lattice parameters of both the hydrogen-free and hydrogenated alloys to be obtained.

## Concluding Remarks

When in the future this X-ray information is supplemented by p-n data, the theoretical and practical implications could be significant. The overall graduated continuity of properties of the rare earths with increasing atomic number, part-modified at europium and ytterbium, would seem to present unique possibilities for formulating more precise judgements concerning the relative significances of dimensional, electronic and elastic parameter influences on p-n data, from comparisons of the respective palladium alloy-hydrogen systems.

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# Platinum-Enhanced Corrosion Resistance in Amorphous Metals

The attainment of amorphous ("glassy") structures in certain metallic alloys has aroused considerable industrial interest because of the pronounced enhancement of properties such as corrosion resistance, ductility, and magnetic properties that can be achieved, compared to alloys in their normal crystalline state.

The enhancement of the corrosion resistance of conventional crystalline base metal alloys by small additions of the platinum group metals is well documented; the addition of 0.1 per cent palladium to titanium is, perhaps, the best known example and is widely used in chemical engineering applications. None the less it is, perhaps, surprising to find that small additions of platinum can significantly enhance the corrosion resistance of amorphous alloys.

The results of studies made on amorphous chromium alloys have recently been reported by M. Tenhover, G. A. Shreve, R. S. Henderson and D. B. Lukco of the BP Research Center, Ohio, U.S.A., (*Appl. Phys. Lett.*, 1989, **55**, (17), 1724–1726). They prepared amorphous alloys of Cr-*M* and Cr-Pt-*M*, where *M* is phosphorus, boron, carbon or nitrogen, as sputtered thin films 0.5 to 1.0 $\mu$m thick on glass slides. Corrosion testing was conducted in hydrochloric acid over a temperature range of 25 to 250°C, in 50 weight per cent hydrofluoric acid at room temperature, in refluxing concentrated nitric acid at 121°C and in refluxing sulphuric acid at 100°C.

Amorphous $Cr_{85}P_{15}$ was observed to be stable in hydrofluoric, nitric and sulphuric acid solutions, whereas crystalline chromium dissolved rapidly in the reducing acids, hydrochloric and sulphuric. Both materials, however, corroded rapidly in hot concentrated hydrochloric acid, whereas amorphous chromium-platinum-phosphorus alloys were very stable in all four test solutions. More particularly, $Cr_{74.9}Pt_{0.1}C_{25}$ in the amorphous form was also stable in all four test solutions. In the crystalline state, however, it was only stable in hydrofluoric acid.

More detailed work on the effect of platinum concentration in amorphous $Cr_{(85-b)}$-$Pt_b$-$P_{15}$ alloys shows that there is a trade off between corrosion rates in oxidising and in reducing acids. In nitric acid, the corrosion rate increased substantially when the platinum content exceeded a critical value, while in the hydrochloric acid the corrosion rate decreased dramatically to a low rate at a similar amount of platinum addition. Thus there is an optimum platinum content of about $b=0.1$, that is $Cr_{84.9}Pt_{0.1}P_{15}$. High temperature tests in hydrochloric acid showed that the platinum-containing alloys had higher temperature stability in terms of the transition from passive to active behaviour.

Analysis of the surfaces of corroded specimens revealed an enrichment of platinum concentration in the top 20 to 30 Å of the surface, which was present in the metallic unoxidised state. Cathodic polarisation measurements showed the platinum-containing alloys to have a hydrogen exchange current three orders of magnitude higher. The authors conclude that the platinum additions accelerate the passivation reaction, changing both anodic and cathodic reaction kinetics.

In summary, the authors state that the use of trace additions of platinum to amorphous chromium alloys produced alloys that are among the most corrosion resistant known, thus offering a new freedom in the design of corrosion resistant materials.     C.W.C.