

Palladium Alloys for Hydrogen Diffusion Membranes

A REVIEW OF HIGH PERMEABILITY MATERIALS

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The unique properties of palladium enable it to be used, either alone or more generally alloyed with silver, for hydrogen diffusion membranes. Recently palladium alloys containing rare earth metals have been described and some of them show considerable promise for this purpose.

Palladium holds a unique position among the metallic elements in being able to take into solution large quantities of hydrogen while simultaneously retaining a high degree of ductility. These attributes coupled with the high mobility or rate of diffusion of hydrogen in the lattice have been exploited in the use of palladium and subsequently of palladium-based alloys as hydrogen diffusion membranes. Earlier articles in this Journal (1, 2) have described the application of this principle to commercial diffusion units for the production of high purity hydrogen, and more recently to a hydrogen generator for military requirements (3). In these applications the permeability of the palladium alloy to all other gases at the operating temperatures is so low as to be negligible in practice, and the alloy therefore functions as a highly specific filter for the production of ultra-pure hydrogen, or for removing hydrogen from mixed process gases.

A limitation to the use of pure palladium for hydrogen diffusion has its basis in the pressure-concentration isotherms for the palladium-hydrogen system shown in Figure 1 (4). At temperatures below 300°C and pressures below 20 atm, increasing the hydrogen concentration leads to the formation of the β phase which can coexist with the α phase. The β phase has a considerably expanded lattice compared with α , for

example a hydrogen/palladium ratio of 0.5 results in an expansion of about 10 per cent by volume. Nucleation and growth of the β in the α matrix therefore sets up severe strains in the material resulting in distortion, dislocation multiplication and hardening. After a few hydrogenation/dehydrogenation cycles splitting of the diffusion membrane may occur.

One method whereby the phase change can be avoided is to ensure that the palladium diffusion membrane is always operated in the single phase region of the Pressure-Composition-Temperature diagram (5). This may be achieved by maintaining the temperature above the critical value of 300°C as long as the membrane is in a hydrogen atmosphere, or by ensuring that cooling is allowed only when it is in a dehydrogenated condition with the hydrogen pumped from the system. Such expedients do not, of course, avoid the volume changes that inevitably occur, but in a single phase region the composition varies smoothly and the distortion phenomena associated with nucleation and growth are circumvented.

With these limitations in mind it is nevertheless possible to operate pure palladium membranes successfully for the large scale separation of hydrogen from mixed gases. Diffusion installations in the Union Carbide Corporation with individual outputs of 9 million cu ft/day have been described (6).

To overcome the drawbacks of pure metal as a membrane material, the alloying of palladium may be considered as having the following objectives. First it is desirable that the α - β phase transition should be suppressed in the alloy so that distortion is avoided. The permeability of the alloy should also be as high as possible, preferably above that of palladium, and the mechanical characteristics should be such that it can be worked to thin foil or tubing for use in diffusion units. The success of palladium as a membrane is closely connected with the catalytic activity of the surface, allowing the ready absorption and dissociation of the hydrogen molecule, and it is further desirable that the alloy should be tolerant to poisoning by impurities in the hydrogen. A large number of palladium systems have therefore been studied and described in the literature, claiming alloys with one or more of these desirable features. A selection of some of the more important of these will be considered in this brief review, and the pertinent data is summarised in the Table. For comparison purposes permeability figures are given in the table based on 350°C and 300 psi, these being typical operating conditions for commercial hydrogen diffusion cells. In this review all permeability values are given in $\text{cm}^3/\text{cm}^2/\text{s}$, referred to membranes 0.025 mm (0.001 in) thick at the pressures and temperatures specified.

Palladium-Silver Alloys

The breakthrough in hydrogen diffusion technology came with the discovery by Hunter (7) that when 20 per cent or more silver is added to palladium, the resulting alloy is dimensionally stable and does not distort on cycling in hydrogen (8). It is now well established that this is the result of the α - β miscibility gap being depressed to well below room temperature. Further and unexpectedly it was found that silver increased markedly the permeability of palladium to hydrogen. The variation of diffusion rate with silver content is indicated in the Table. The rate is found to reach a maximum at

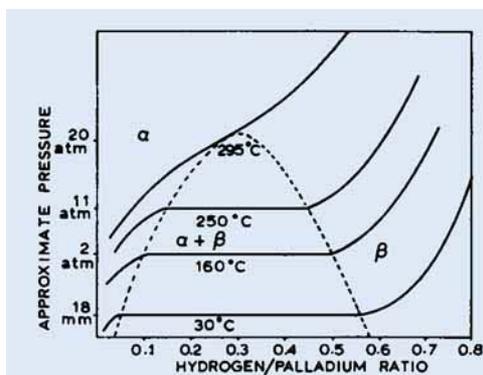


Fig. 1 Absorption relationships in the palladium-hydrogen system. Unalloyed palladium undergoes an α - β transition on low temperature hydrogenation leading to gross distortions

around 23 to 25 per cent silver and alloys of this composition are normally used in diffusion units. The permeability of these alloys is nearly double that of pure palladium, but falls with increasing silver content to about 10 per cent of the latter at 50 per cent silver.

It may be of interest to consider the particular features of palladium-silver alloys which give rise to the high observed permeabilities. The flow of gas by diffusion through a membrane is governed by Fick's law and the rate may be expressed in the form:

$$V = K \left(\frac{a}{t} \right) DX$$

where V is volume of hydrogen diffusion per unit time
 K is constant
 a = membrane area
 t = membrane thickness
 D = diffusion coefficient
 X = concentration gradient (dc/dx in Fick's equation)

The product DX is therefore related to the permeability of the membrane. Almost without exception the value of D for palladium is decreased on alloying, and this holds for palladium-silver alloys (9). Consequently high permeabilities will only result if a high concentration gradient can be established in the alloy. The solubilities of hydrogen were measured in early work by Sieverts and others

Permeability of Miscellaneous Palladium Alloys to Hydrogen at 350°C, 300 psig			
Material weight per cent	Permeability cm ³ /cm ² /s	Remarks	Ref.
Palladium	1.43	—	—
80Pd-20Ag 77Pd-23Ag 70Pd-30Ag 48Pd-52Ag	2.46 2.48 1.46 0.13	Hydrogen output maximum at 20 to 25 per cent Ag.	
95Pd-5Au 80Pd-20Au 60Pd-40Au 45Pd-55Au	1.52 1.37 0.60 0.13	Small increase in permeability at low Au contents. Alloys more resistant to sulphur poisoning.	12
90Pd-10Cu 70Pd-30Cu 60Pd-40Cu 55Pd-45Cu 45Pd-55Cu	0.69 0.12 1.52 0.25 0.01	Sharp maximum in output at 40 per cent Cu, corresponding with ordered β -phase in Pd-Cu system.	13
99.5Pd-0.5B	1.35	Interstitial boron tends to block lattice sites.	12
90Pd-10Ni 95Pd-5Ru	0.27 0.47	Low permeabilities for Fe, Ni, Ru, Pd and Rh additions.	12
65Pd-30Ag-5Pt 68Pd-30Au-2Ru	— —	Examples of wide range of complex alloys claimed in literature.	20
85Pd-13Ag-2Ni 70Pd-20Ag-10Rh	— —		21
73Pd-24Ag-3Au Pd-20Ag-5Au-1.26Ru	— —		22
68Pd-25Ag-5Au-2Ru Pd-10Ag-1Au+0.1 each of Ru, Al, Pt.	— —		23
92.3Pd-7.7Ce 87.3Pd-12.7Ce	2.24 1.27	The higher Ce alloy is prone to poisoning by oxidation.	
93.4Pd-6.6Y 90Pd-10Y	4.99 5.38	Estimated from 200 psi results by the \sqrt{P} (Sieverts Law) relationship.	25

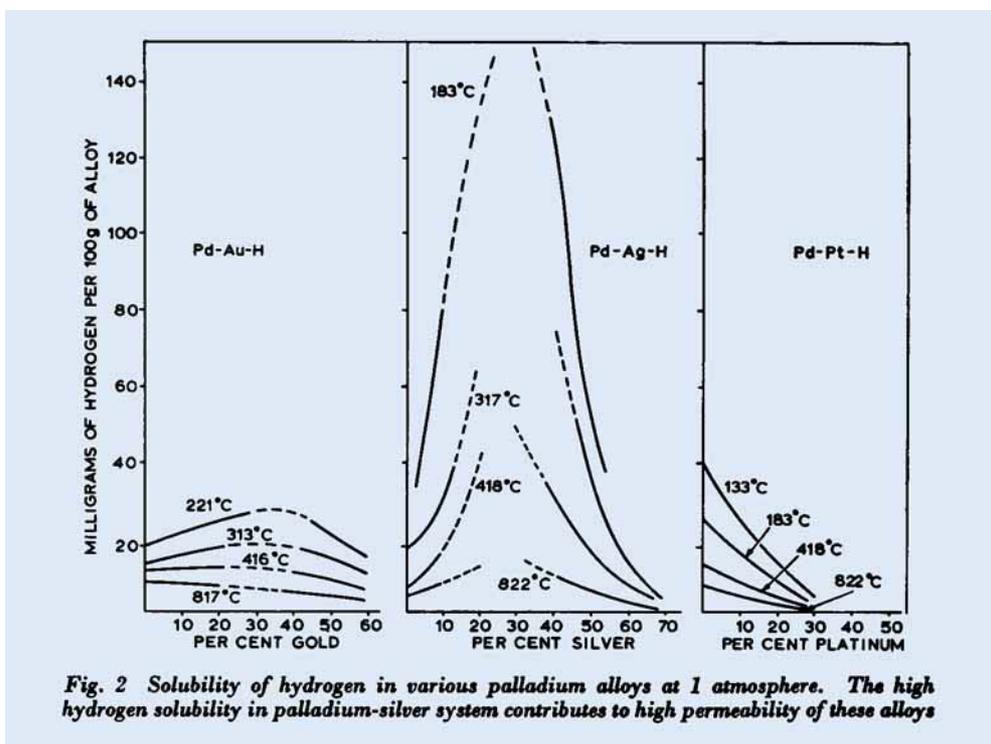


Fig. 2 Solubility of hydrogen in various palladium alloys at 1 atmosphere. The high hydrogen solubility in palladium-silver system contributes to high permeability of these alloys

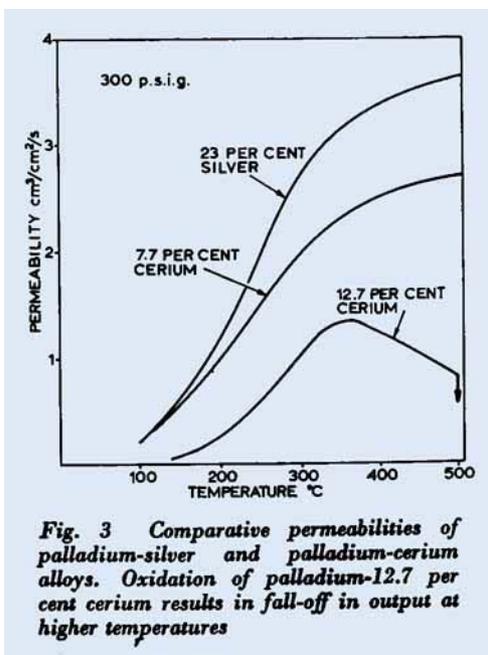
(10, 11) and the results obtained are illustrated in Figure 2. The exceptionally high peak occurring in the palladium-silver system contrasts markedly with the more usual behaviour exemplified in the palladium-gold and palladium-platinum alloys. As a result the DX product for palladium-silver is high and accounts adequately for the large hydrogen throughputs for alloys in the 20 to 25 per cent silver range.

Gold and copper are, like silver, elements from Group 1B of the Periodic Table, and have therefore received a good deal of attention as alloying elements in palladium. Some slight enhancement of permeability has been reported for small gold additions by McKinley (12) but above 20 per cent the permeability is reduced. However, the gold-containing alloys were shown to be more resistant to poisoning by sulphur in the ingoing gas than palladium-silver. Consequently although these alloys do not appear to have been widely used they could be advantageous if sulphur is present in

the feed gas to the diffusion unit.

Initial additions of copper cause a similar reduction in permeability, but at copper contents near 40 per cent, a sharp maximum occurs (13). This maximum is associated with the ordered body centred cubic β -phase which forms in the palladium-copper system. In earlier work by Piper (14) the diffusion coefficients for hydrogen in these alloys were measured. The ordered β -CuPd phase was found to have the highest room temperature diffusivity of any metal-hydrogen system, that is $D_{25^\circ\text{C}} = 2 \times 10^{-5} \text{ cm}^2/\text{s}$ compared with a value of $2 \times 10^{-7} \text{ cm}^2/\text{s}$ for pure palladium. Unfortunately although the diffusion coefficient is extremely high, the hydrogen solubility is reduced to a low value on alloying with copper (15). As a consequence the permeability which is proportional to the DX product passes through a peak but without attaining values much in excess of unalloyed palladium.

Boron additions as a means of increasing



the permeability have been suggested on several occasions (16, 17, 18) but in general the results obtained are not significantly better than with pure palladium. Boron is a relatively small atom and enters the palladium lattice in octahedral interstitial sites. The boron atoms therefore cause a net expansion of the lattice and it has been argued that this expansion will result in a more open network of palladium atoms for the diffusion of hydrogen. Against this, boron occupies and thereby blocks a number of interstitial sites which are no longer available for hydrogen transport. Diffusion coefficients measured by Allard and co-workers (17) were shown to fall off much more rapidly with increasing boron content than for substitutional alloys, indicating that the blocking of lattice sites is the dominating effect.

Many isolated observations have been reported on the effect of a wide range of other elements when added to palladium, including iron, nickel, ruthenium, platinum (8) and chromium (19), together with various ternary and more complex alloys, for example (20, 21, 22 and 23), but no material significantly

better than palladium-silver had emerged until the recent Birmingham University work on rare earth metals in palladium.

Palladium-Rare Earth Alloys

This work indicates that high permeabilities and dimensional stability are shown by alloys of palladium with certain of the rare earth metals. In spite of large atomic diameter differences in the systems, the solid solubility of these metals in palladium is anomalously high, and the behaviour of some of these solid solution alloys has been assessed for diffusion membranes. For example, the size difference for the palladium-yttrium system is 29 per cent, but nevertheless the solubility limit is 12 atomic per cent.

The palladium-cerium alloys (24) were among the first to be studied, but at low pressure differentials across the membranes. The initial claims of high permeabilities for these alloys, well in excess of those for palladium-silver, were not substantiated by subsequent measurements made in the laboratories of Johnson Matthey. For the latter the palladium-cerium alloys were made by arc melting, and worked to sheet 0.25 mm thick. Two compositions were studied, 7.7 and 12.7 per cent cerium (6 and 10 atomic per cent respectively) and permeability results compared directly with similar membranes of palladium-23 per cent silver alloy. The materials were tested over a wide range of conditions of practical interest, up to 500°C and 600 psig.

An example of the results obtained is shown in Figure 3. The plots for the 7.7 per cent cerium alloy and the silver-palladium alloys were obtained after the membranes were fully conditioned by heating and cooling over several cycles, and were therefore reproducible. The hydrogen throughput of the 7.7 per cent alloy is seen to be about 25 per cent lower than silver-palladium over the range studied. The 12.7 per cent cerium alloy showed quite different behaviour. For this material the membrane could not be conditioned satisfactorily and the curve given in

Figure 3 is for the initial heating cycle of this alloy. The diffusion rate increased as expected up to 350°C but started to fall off to a low value on heating to higher temperatures. After cooling and repeating the heating there were no indications that recovery of the permeability to hydrogen occurred. When removed from the cell it was found that this membrane had discoloured on the hydrogen inlet side, and it appeared likely that the fall-off in performance was due to oxidation of the alloy with the formation of an impervious layer of cerium oxide, caused by hydrogen impurities.

The poisoning of this alloy by oxidation was overcome by coating the membrane with 500Å of palladium applied by vacuum evaporation. Subsequent to this treatment reproducible results were obtained for this material also, as shown in Figure 4, but the permeability proved to be lower than the 7.7 per cent alloy.

A subsequent and more promising development has recently been reported in which palladium-yttrium alloys have been shown by the Birmingham workers to be considerably more permeable than palladium-silver (25). Measurements were made over a wide range of temperatures and pressures, with results typified by the comparative permeability plots

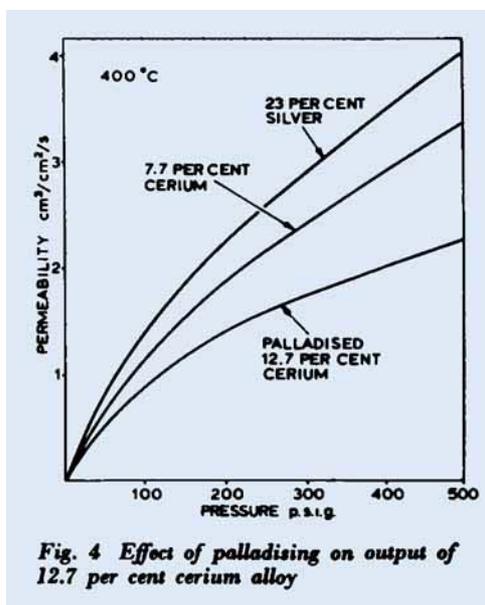


Fig. 4 Effect of palladising on output of 12.7 per cent cerium alloy

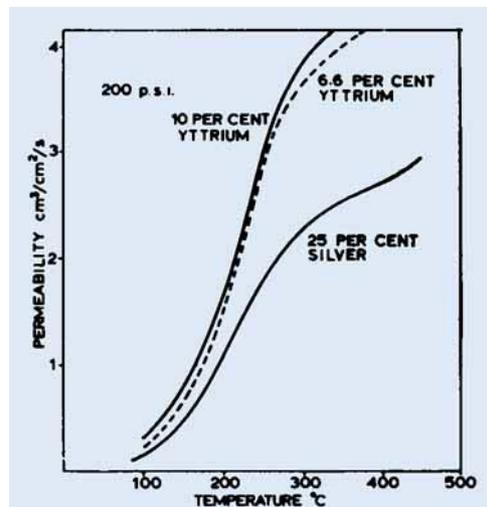


Fig. 5 Palladium-yttrium alloys show high permeabilities to hydrogen

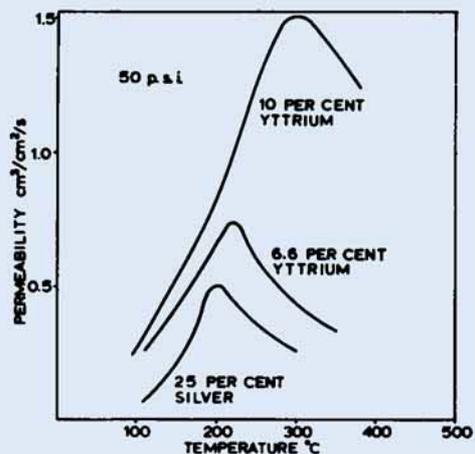


Fig. 6 Anomalous low-pressure behaviour of palladium-silver and palladium-yttrium

shown in Figure 5. Hydrogen throughput for the alloys of 6 to 10 per cent yttrium are seen to be about 50 per cent higher than for palladium-25 per cent silver tested under the same conditions.

A further advantage claimed for the yttrium alloys is that they are less susceptible to poisoning by oxidation than the cerium alloy of the earlier work. Evidence from scanning electron micrographs indicates that Y_2O_3 formation results in a flaky surface layer of

oxide over a substantially pure palladium layer on the alloy surface. The non-coherent form of this oxide hence does not act as a barrier for hydrogen diffusion.

In these investigations a curious behaviour was reported in the results obtained at pressures below 100 psi for both the yttrium and silver alloys. As shown in Figure 6, a pronounced maximum permeability was present at some intermediate temperature, rather than the steady increase which normally occurs. Behaviour of this type had not previously been reported for palladium-silver alloys and is not observed in commercial diffusion units, but may occur, as for example in the palladium-cerium alloys, under conditions where some poisoning effect is present. In the work reported it is most likely that inadequate flow of gas through the inlet side of the test cell was responsible for this anomaly. Even though high purity cylinder hydrogen was used it would appear that some blanketing of the membrane has occurred, due to the accumulation of impurities. This behaviour is obviously absent in the measurements at higher pressures, where good agreement is obtained at all temperatures with earlier results such as those of Darling (26). A comprehensive review of contaminants in the hydrogen and their effect on permeability determinations has recently been published by Musket (27) these should be fully recognised if consistent results are to be obtained.

Consequently the palladium-yttrium alloys represent a considerable advance in the technology of hydrogen diffusion alloys and could lead to more effective utilisation of palladium in diffusion units. The rare earth alloys are also considerably harder and stronger than palladium-silver, which may be advantageous in the practical applications of these alloys. It remains to be seen, however, whether this extra strength will lead to problems in processing the material. The palladium-silver alloy used as thin walled tubes in the current range of Johnson Matthey diffusion units is a reliable and well-proven material, and by normal metallurgical standards is relatively

easy to fabricate. Nevertheless, in the production of the thin walled tubes careful and critical working procedures are required to yield a consistent high quality product. The extra hardness of the palladium-yttrium alloys may make comparable fabrication difficult, and further work is obviously necessary on this aspect, together with the studies of the long-term stability and oxidation resistance of these materials.

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