The Purification of Hydrogen

A REVIEW OF THE TECHNOLOGY EMPHASISING THE CURRENT STATUS OF PALLADIUM MEMBRANE DIFFUSION

By G. J. Grashoff, C. E. Pilkington and C. W. Corti

Johnson Matthey Group Research Centre

The purification or separation of hydrogen has traditionally been based on solid-state diffusion technology utilising noble metal membranes. The development of this technology, which has been centred around improved diffusion membrane materials based on the silver-palladium alloy system, is reviewed in this paper. It is shown that, despite the emergence of alternative techniques, diffusion technology based on silver-palladium membranes remains the most suitable technique for the production of high purity hydrogen, a product which is required increasingly in many high technology applications.

Although the ability of metals and particularly palladium to selectively permeate hydrogen has been known for over a century, the commercial utilisation of this property for the purification of hydrogen is relatively recent. The development of silver-palladium alloys as diffusion membrane materials in the late 1950s overcame the principal technical difficulties associated with the technique and enabled the successful development of commercial equipment, a technology with which Johnson Matthey has been closely associated from the beginning.

Since that time several other techniques for hydrogen purification have been developed and are at various stages of commercial exploitation. As hydrogen is becoming increasingly important in many major areas, including the electronics manufacturing industry, it is an appropriate time to review the status of membrane diffusion for hydrogen purification and to highlight the current developments in membrane materials, especially palladium alloys, in the context of their potential influence on hydrogen purification technology and its industrial applications.

Hydrogen Purification Techniques

Since the introduction of the technique for hydrogen purification by selective diffusion through palladium alloy membranes several other purification techniques have been developed. These fall broadly into three categories:

Chemical—Catalytic Purification

Physical —Metal Hydride Separation
Pressure Swing Adsorption
Cryogenic Separation.

Selective Diffusion—
Noble Metal Membrane Diffusion
Polymer Membrane Diffusion
Solid Polymer Electrolyte Cells.

Each technique has limitations as well as advantages, which are summarised in the Table, and it is appropriate to consider these in a comparative way, prior to discussing the development and status of noble metal membrane diffusion in more detail.

Feed Gas Capability and Flexibility

In terms of the scale of operation most, if not all, of the available techniques are capable of being operated over a wide range from small laboratory requirements through to large scale industrial production. However, practical and economic considerations impose restraints so that only two techniques are actually utilised over this whole range, namely Catalytic Purification and Polymer Membrane Diffusion. The two physical techniques, Cryogenic Separation and Pressure Swing Adsorption are best suited to large scale applications and the remaining techniques, including Palladium Alloy Membrane Diffusion, are utilised for small to medium outputs.

There are two other aspects of importance to be considered in selecting a purification technique besides the scale of operation. The first is its ability to cope with a range of gas feedstocks in terms of hydrogen content (that is whether rich or lean) and the second concerns the limitations imposed by the technique in terms of the chemical composition of the feedstock. These include both the selectivity of the technique against gases other than hydrogen and its resistance to "poisoning" by constituents present as impurities in the feed gas.

All techniques can operate well with hydrogen-rich gas feedstocks. Catalytic Purification removes oxygen by reaction with hydrogen to form water, and carbon monoxide by oxidation or methanation; this technique is used to upgrade relatively pure hydrogen produced, for example, by electrolysis. Pressure Swing Adsorption also requires hydrogen-rich gas streams since it functions by selective adsorption of impurities. Cryogenic Separation can tolerate a wider range of hydrogen content in the feed gas, typically 30 to 80 per cent, but is limited in gas composition to those constituents that will selectively condense at cryogenic temperatures. Metal Hydride Separation and the two diffusion techniques, Palladium Membrane and Polymer Membrane, have the ability to deal with feed gases lean in hydrogen. The Hydride Separation and Palladium Diffusion techniques are based on the very selective adsorption and diffusion of hydrogen, respectively, and the purity of the output hydrogen is not affected by the leanness of the feed gas. However, Polymer Membrane Diffusion is based on a differential diffusion rate principle and purity of the output hydrogen will be affected by the hydrogen concentration as well as by the nature of the other constituents that are present in the input gas stream.

Many of the techniques are sensitive to "poisoning" by certain impurities in the gas feedstock, particularly those which rely on selective reactions (adsorption, diffusion); sulphur compounds and, in some cases, carbon dioxide are the chief poisons. The major poisons for each technique are listed in the Table.

Hydrogen Recovery

The level of recovery of hydrogen from feed gases varies considerably from one technique to another. Metal Hydride Separation, Pressure Swing Adsorption and Polymer Membrane Diffusion have relatively poor recovery levels, typically in the range 70 to approximately 85 per cent, while Cryogenic Separation and Solid Polymer Electrolyte techniques can attain recovery levels of about 95 per cent. Only Palladium Membrane Diffusion and Catalytic Purification techniques can achieve high recovery levels of up to 99 per cent from hydrogen-rich gases. Where impure or lean hydrogen feed gases are used the recovery levels are somewhat lower.

Hydrogen Purity

As can be seen from the Table, many techniques have limitations with regard to the purity of hydrogen produced. At the lowest levels, typically low to mid 90s per cent, are the Cryogenic Separation and Polymer Membrane Diffusion methods. Metal Hydride Separation can achieve a 99 per cent purity level with the Solid Polymer Electrolyte technique attaining almost a factor of 10 better purity. Two methods are capable of producing moderately high purity levels of 99.999, namely Pressure Swing Adsorption and Catalytic Purification, but where very high purities of 99.9999 or better are required, only Palladium Membrane Diffusion comes into consideration.

Membrane Diffusion

In France in 1863 Henri Sainte-Claire Deville and L. Troost (6, 7) observed the diffusion of hydrogen through homogeneous plates of iron and platinum. Three years later, in

1866, Thomas Graham (8), the then Master of the Royal Mint, London, demonstrated that hydrogen diffused through heated palladium. Following experiments with foil, Graham began working with palladium tubes manufactured by Johnson Matthey. After this early work numerous other people investigated the metallurgy of palladium-hydrogen, but

Thomas Graham's Discovery

His duties at the Royal Mint absorbed all Graham's energies for some years, but in 1866 he was able to return to the work that had been his continuing interest, the diffusion of gases. Using a closed palladium tube, made for him by George Matthey, he found that the metal would absorb more than 600 times its own volume of hydrogen, while if coal gas were substituted only the hydrogen penetrated the palladium. No similar effect could be obtained with iridium or osmium. A year later he showed that hydrogen could be occluded by palladium electrolytically when immersed in dilute sulphuric acid and in contact with a piece of zinc.

His last major contribution, published only a few months before his death, was on the relation of hydrogen to palladium, his opinion being that they formed an alloy or compound and that hydrogen was "the vapour of a highly volatile metal" to which he gave the name hydrogenium. He also investigated a number of alloys containing varying percentages of silver, again prepared for him by George Matthey, and showed that these also occluded hydrogen provided that the alloying element did not exceed 50 per cent.

Using his influence at the Royal Mint, Graham had a number of medallions made in his "alloy" of palladium and hydrogenium that he distributed to his many friends to demonstrate the nature of this unusual combination of a gas and a metal. In sending one to the then Chancellor of the Exchequer, Robert Lowe, he wrote:

> *"The little medallion is composed of about 9 parts of palladium (a rare metal) and 1 part of hydrogenium by bulk. If the latter took the form of a gas, it would measure 8 or 9 cubic inches, or 3 port wine glasses full, to be very plain."*

From this early work there stems the modern design and operation of equipment to generate high purity hydrogen from a range of intake gases for many industrial applications. L.B.H.

Comparison of Hydrogen Purification Techniques

Technique (Ref.)	Principle	Typical feed gas	Hydrogen output per cent		Scale of use	Comments
			Purity	Recovery		
Cryogenic Separation (1)	Partial condensation of gas mixtures at low temperatures	Petrochemical and refinery off-gases	90–98	95	Large scale	Prepurification step necessary to remove CO_2, H_2S and water
Polymer Membrane Diffusion (2)	Differential rate of diffusion of gases through a permeable membrane	Refinery off-gases and ammonia purge gas	92–98	>85	Small to large	He, CO_2 and H_2O may also permeate the membrane
Metal Hydride Separation (3)	Reversible reaction of hydrogen with metals to form hydrides	Ammonia purge gas	99	75–95	Small to medium	Hydrogen absorption poisoned by O_2, N_2, CO and S
Solid Polymer Electrolyte Cell (4)	Electrolytic passage of hydrogen ions across a solid polymer membrane	Purification of hydrogen produced by thermochemical cycles	99.8	95	Small	Sulphur-containing compounds poison the electro-catalysts
Pressure Swing Adsorption (5)	Selective adsorption of impurities from gas stream	Any hydrogen rich gas	99.999	70–85	Large	The recovery is relatively low as hydrogen is lost in the purging step
Catalytic Purification	Removal of oxygen by catalytic reaction with hydrogen	Hydrogen streams with oxygen impurity	99.999	Up to 99	Small to large	Usually used to upgrade electrolytic hydrogen. Organics, Pb-, Hg-, Cd- and S-compounds poison the catalyst. H_2O produced
Palladium Membrane Diffusion	Selective diffusion of hydrogen through a palladium alloy membrane	Any hydrogen containing gas stream	⩾99.9999	Up to 99	Small to medium	Sulphur-containing compounds and unsaturated hydrocarbon impair permeability

attempts to utilise the selective permeability of palladium to hydrogen for industrial purposes were not pursued until much later, mainly because of the severe distortion suffered by palladium when in contact with hydrogen.

In the 1950s the Atlantic Refining Company of Philadelphia, working co-operatively with J. Bishop and Company of Malvern, Pennsylvania (later to become Johnson Matthey Inc.) laid the ground work for the first practical palladium alloy hydrogen diffusion process (9). They had two particular objectives, the first and major one being to reduce the amount of distortion suffered by pure palladium when in contact with hydrogen and the second to increase the permeability of hydrogen through the membrane. To fulfil these objectives the diffusion characteristics of a wide range of palladium alloys were investigated, and it became apparent that silver was the only element to increase the diffusion rate of hydrogen, as shown in Figure 1. In addition, it substantially decreased the amount of distortion experienced by unalloyed palladium in contact with hydrogen (10, 11). Thus, on the basis of this work J. Bishop in the U.S.A. and Johnson Matthey in Europe further developed the technology to successful commercialisation in the early 1960s (11, 12).

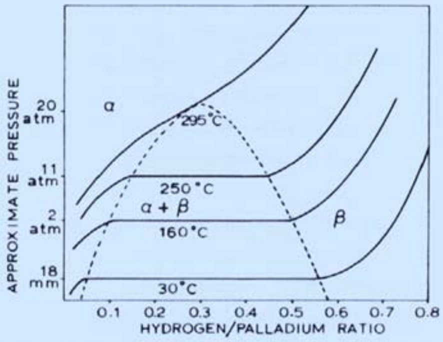


Fig. 2 Typical absorption relationships in the palladium-hydrogen system. With pure palladium an $\alpha \rightarrow \beta$ transformation occurs on low temperature hydrogenation, and results in hardening and gross distortion of the metal

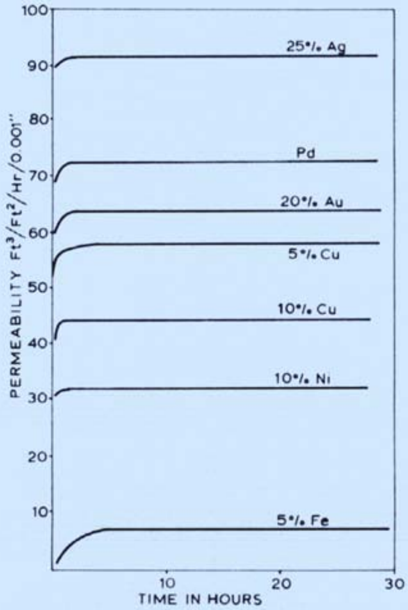


Fig 1 Hydrogen output for palladium and a number of palladium binary alloys, hydrogen pressure = 50 psi; temperature = 540°C

Metallurgical Properties of Membrane Diffusion Materials

Despite the early work on platinum and especially palladium it was not until well into this century that work was done that explained the metallurgy of the noble metal/alloy-hydrogen systems and enabled significant advances in hydrogen diffusion technology to be made. Work to determine isotherms in the palladium-hydrogen system was conducted by Bruning and Sieverts in 1933 (13), Gillespie and Downs in 1939 (14) and Gillespie and Sieverts in 1948 (15). Some time later these data were extended to higher pressures (16) while others reported data for higher and lower temperatures (17, 18). A typical example of a pressure-temperature composition diagram for the palladium-hydrogen system is shown in Figure 2, after Bruning and Sieverts.

At temperatures below 300°C and pressures below 20 atmospheres, increasing the hydrogen concentration leads to the formation of the β-palladium hydride phase which can co-exist with the α-phase. The β-phase has a considerably expanded lattice compared with the α-phase, 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. This can result in premature fracture of the diffusion membrane after undergoing only a few hydrogenation/dehydrogenation cycles.

One method of avoiding the phase change in pure palladium is to ensure that the diffusion membrane is always operated in the single phase region of the pressure-composition-temperature diagram. This may be achieved in pure palladium 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 takes place only when it is in a dehydrogenated condition with the hydrogen completely removed from the system.

To overcome the restrictions of pure palladium as a membrane material, it is necessary to suppress the $\alpha \rightarrow \beta$ transition and so avoid distortion. As Hunter reported in 1956 (19), a number of elemental additions to palladium can suppress the transition sufficiently to eliminate or significantly reduce distortion. Silver-palladium alloys are dimensionally stable at silver levels above 20 per cent and in addition have higher hydrogen diffusion rates than pure palladium while their good mechanical properties make fabrication into thin sheet and tube relatively easy.

The success of palladium and palladium

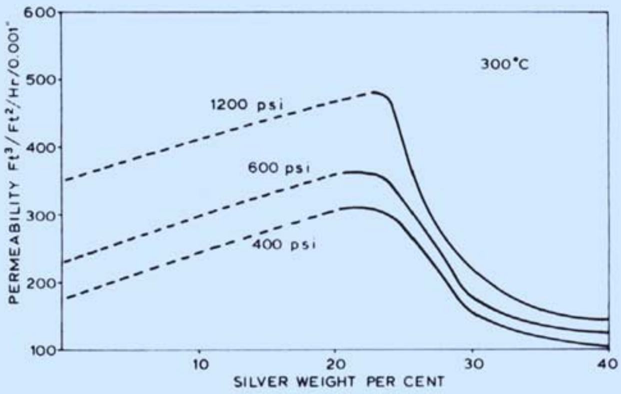


Fig. 3 Diffusion data for a series of silver-palladium alloys, measured at the three specified pressures and at a temperature of 300°C

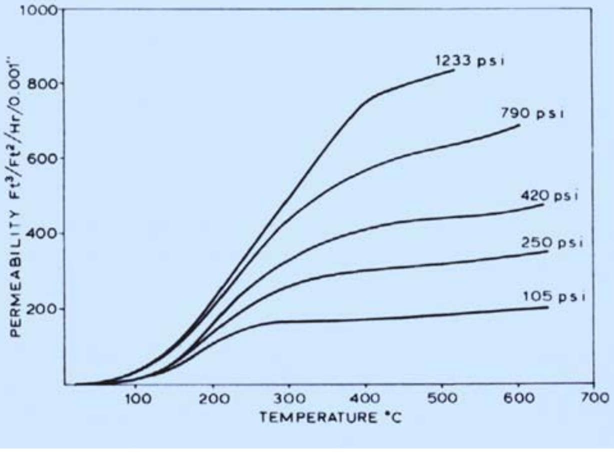


Fig. 4 The effect of temperature on the rate of diffusion of hydrogen through 23 per cent silver-palladium, at the five specified pressures

alloys as diffusion membranes depends on the catalytic activity of the surface, a factor that is absent from some other metals which will also diffuse hydrogen such as tantalum, vanadium and niobium. These Group V metals are exothermic hydride formers and show pressure/concentration isotherms very similar to those of palladium; in addition they exhibit high diffusion coefficients for hydrogen. On account of their lower intrinsic cost these base metals have attracted a certain amount of interest, but they are generally considered to be unsuitable for use as diffusion membranes due to the well-documented embrittlement that occurs on absorption of hydrogen.

In spite of these drawbacks, the use of vanadium, niobium and tantalum for the diffusion of hydrogen was claimed by Makrides in a patent published in 1964 (20). An essential feature of the patent is the coating of the Group V metal with a thin layer of palladium. This layer facilitates entry and exit of hydrogen into and out of the Group V metal, which is otherwise difficult owing to the poor catalytic activity of the surface for dissociation and recombination of hydrogen. Another disadvantage of the Group V elements is the ready poisoning of the membrane caused by the formation of stable oxides.

The significant step forward in hydrogen diffusion technology resulted from work in the late 1950s and early 1960s by Hunter in the U.S.A. (10,19) and by Darling in the U.K. (21,22). They established substantial data on hydrogen diffusion through a wide range of silver-palladium alloys, thus allowing the selection of the optimum, high performance hydrogen diffusion alloy.

Darling collected diffusion data across a wide range of both temperatures and pressure. Some data typical of that determined by Darling for a series of palladium alloys containing between 0 and 40 per cent silver are shown in Figures 3 and 4 (23). Figure 3 shows the diffusion characteristics at 300°C of a range of alloys at three pressures. This curve is typical of the diffusion characteristics at other temperatures, and the significant feature to note is the rapid drop in hydrogen permeability for silver contents higher than 23 per cent. Clearly silver in excess of 23 per cent should not be used if optimum diffusion is required, and, as noted earlier, alloys of about this composition possess suitable mechanical properties.

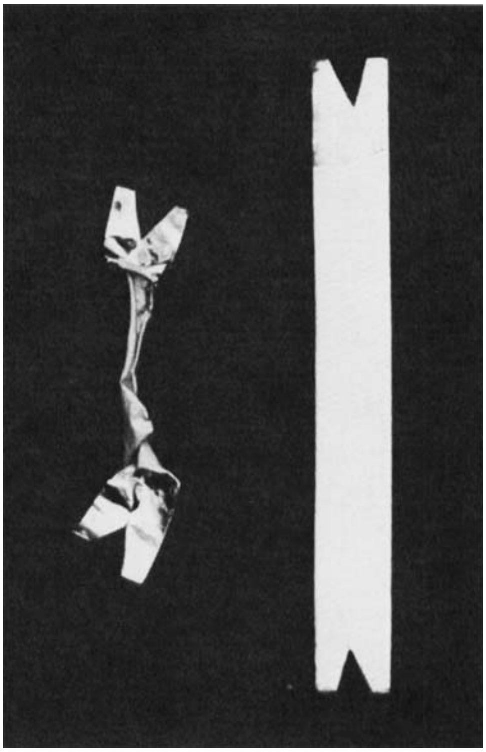


Fig. 5 Identical specimens of palladium (left) and silver-palladium (right) after thirty thermal cycles in hydrogen

The mechanical stability of each of the silver-palladium alloys varies because of the varying amount of β-palladium hydride phase that can form at different compositions. Below 20 per cent silver the amount of distortion increases and is a maximum at pure palladium, see Figure 5. Alloys containing 20 per cent or more silver show none of the damaging effects of β-formation when cycled in hydrogen at temperatures above ambient. As the $\alpha \rightarrow \beta$ phase transformation is suppressed, β- cannot form and distortion does not occur.

Another factor that is important when considering the hydrogen diffusion performance of

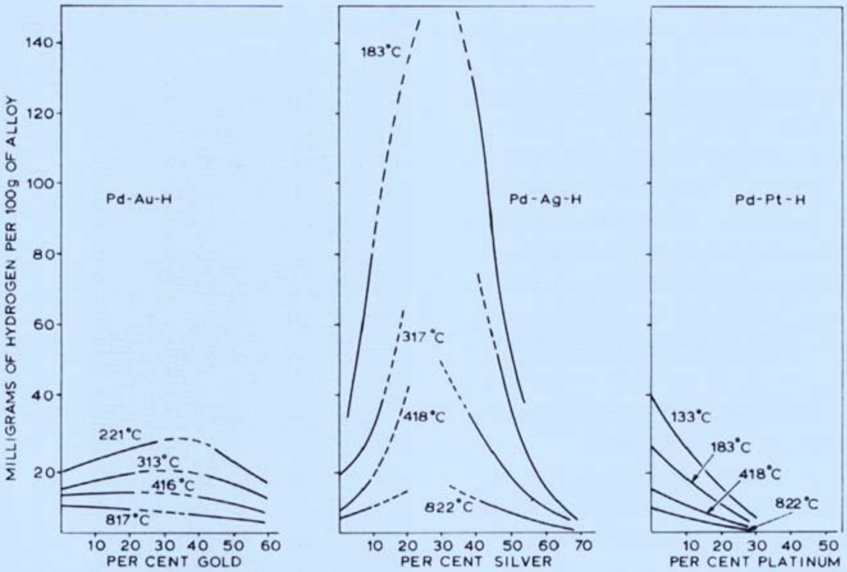


Fig. 6 The solubility of hydrogen, at a pressure of 1 atmosphere, in three palladium alloy systems. The high solubility in silver-palladium alloys contributes to their high hydrogen permeability

different materials is the solubility of hydrogen within the metal/alloy lattice. The solubilities of hydrogen in a number of palladium alloy systems were measured by Sieverts and his co-workers in 1915 (24) and 1935 (25), and the results obtained are illustrated in Figure 6.

The high peak in solubility occurring in the silver-palladium system contrasts markedly with the more usual behaviour shown by the gold-palladium and platinum-palladium alloys. The diffusion coefficients of many palladium alloys are similar and generally decreased by alloying (26). The permeability of a material is defined, through Fick's law of diffusion, as the product of the diffusion coefficient and the concentration gradient which in turn is related to the solubility (27). Thus, it is the high solubility that accounts for the superiority of the silver-palladium alloys, particularly with compositions around 23 per cent silver.

From the foregoing information, particularly that relating to diffusion, solubility and mechanical stability, the suitability of a palladium alloy in the 20 to 25 per cent silver range as a commercial diffusion membrane material is clear. The diffusion data of Darling (21,23) shows that in this range of silver content the optimum alloy contains 23 per cent of silver.

For use in industrial equipment it is important to maximise the performance of the membrane in terms of hydrogen output while ensuring consistent performance and durability. There are three important factors to consider in this respect:

(a) membrane thickness
(b) temperature of operation
(c) pressure of operation.

The effect of membrane thickness on the diffusion of hydrogen through palladium and silver-palladium alloys is well established and conforms closely to a relationship where the rate of diffusion is inversely proportional to membrane thickness. Thus membranes should be as thin as possible, compatible with maintaining both mechanical integrity and durability.

The effect of temperature at different pressures on the diffusion rate is shown schematically for a 23 per cent silver-palladium alloy in Figure 4. This is typical of the behaviour of other silver-palladium alloys containing up to 40 per cent silver. As can be seen in Figure 4, the graphs show a change of curvature between 200 and 400°C, and the curves at higher temperatures run virtually parallel to the temperature axis. Thus, generally there is a temperature above which significant temperature increases do not result in significant increases in diffusion rate.

From the shape and disposition of the curves shown in Figure 4 it can be seen that at any specific temperature there is an increase in diffusion rate with an increase in pressure. Pressure and diffusion rate are linked by the expression $D = Kp^n$ where D is the diffusion rate, K is a constant, p is the pressure and n is the pressure exponent. Experimental derivation of the value of the pressure exponent has shown that it decreases as the pressure rises for palladium or any particular silver-palladium alloy at constant temperature. The rate of decrease with palladium alloys containing silver in the range 20 to 25 per cent is less pronounced than with pure palladium or higher silver containing alloys, and some curves typical of the behaviour of alloys in the range 20 to 25 per cent silver are shown in Figure 7.

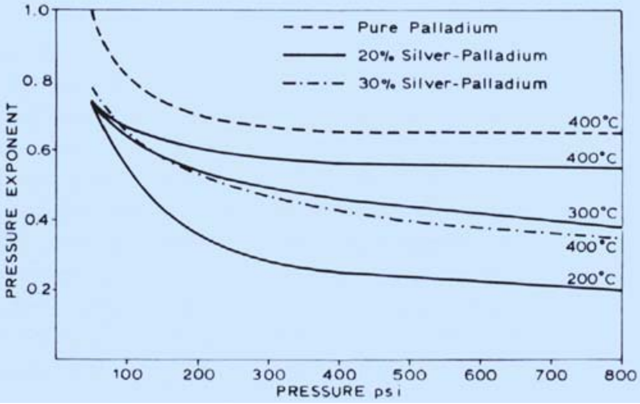
These materials start with a direct proportionally between diffusion rate and pressure but at about 400 psi a much less favourable dependence asserts itself, especially for higher silver alloys at low temperatures. While the pressure exponents for the alloys are high at low pressures, the values can drop to as low as 0.20 (that is the rate of diffusion varies as the fifth root of the pressure) at higher pressures. The pressure exponent increases at constant pressure if the temperature is raised, as shown in Figure 7, and examination of the complete range of conditions shows that few advantages are to be gained by operating any of the membrane materials above 400 psi unless the temperature is kept above 500°C. Equally, when operating at low pressure—100 psi for example—Figure 4, little is to be gained by increasing the temperature beyond 300°C.

It can be seen that temperature and pressure are interrelated and, because of the nature of the processes occurring during the hydrogen diffusion process, a set of optimum operating conditions can be selected. For the 23 per cent silver-palladium alloy, for example, a temperature of 350°C and a pressure of 300 psi maximises the hydrogen output while ensuring high durability and allowing a simple and safe design of diffusion unit to be constructed.

The Potential for Improvements in Diffusion Technology

For the future it is reasonable to assume that improvements in diffusion technology will result from the development of new materials and/or of design concepts which increase the quantity of hydrogen diffused per unit time per unit volume of material. As stated earlier the

Fig. 7 The relationship between pressure, pressure exponent and temperature for palladium and two silver-palladium alloys



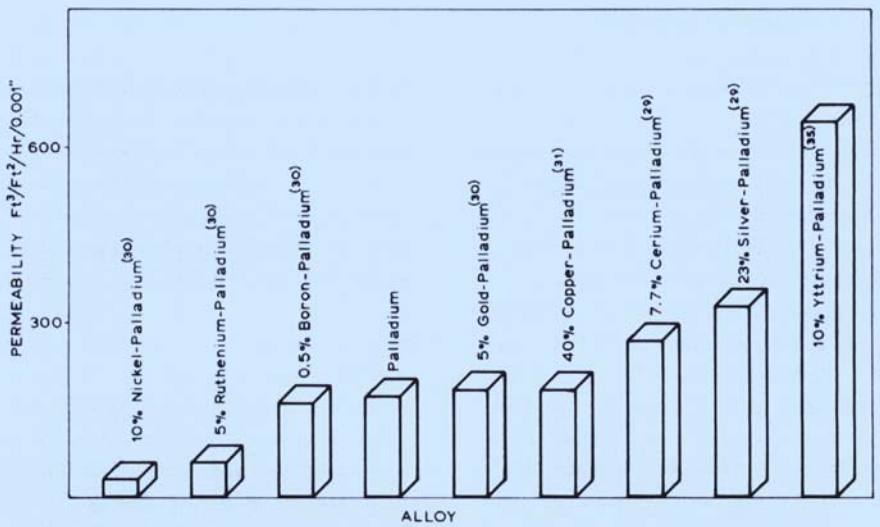


Fig. 8 The maximum hydrogen permeability of palladium and a number of palladium binary alloy systems at a temperature of 350°C and 300 psi pressure

flow of gas through a membrane is governed by Fick's Law which may be expressed in the form:

$$V = K(a/t)\,DX$$

where

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

A simple and obvious way of improving the value of V would be to decrease the thickness of the membrane. This is attractive in theory but has obvious practical difficulties associated with it; but improvements in the mechanical properties and processing of diffusion materials may yet overcome these difficulties and allow the use of thinner membranes.

When considering the properties of a material and how these must be altered to improve the volume of hydrogen diffused it is clear that improvements in both the diffusion coefficient D and the concentration gradient X would result in an increase in V, (the volume of hydrogen diffused per unit time). From much of the work undertaken on palladium and a range of palladium-based alloys, reviewed recently (27), it is clear that the DX product, which is related to the permeability of the membrane, remains relatively constant or decreases.

In nearly all cases (26), the value of D is decreased by alloying and it is only in the case of silver-palladium alloys that DX is increased, the decrease in D being outweighed by the increase in solubility X.

Figure 8 shows schematically the relative hydrogen permeability of some palladium alloys. Some elements, gold and copper for example, which replace substitutional silver, have been reported to show slight improvements in permeability over pure palladium (28,29). The addition of boron, which enters the palladium lattice at interstitial sites, is also claimed to be a beneficial addition (22,29,30,31) but the alloy shows a lower permeability than pure palladium.

Rare-earth-palladium alloys, with hydrogen permeabilities significantly better than silver-palladium alloys have been reported (32,33). Farr and Harris (32) first reported work on a range of cerium-palladium alloys; a maximum in hydrogen permeability was recorded for the 7.7 per cent cerium-palladium alloy. Knapton (27) was unable to reproduce the improved permeabilities reported for these alloys and attributed the lower-than-expected permeation rates to the formation of tenacious surface oxide.

A little later in 1975 Fort, Farr and Harris (33) reported the results of their work on 6 to 10 per cent yttrium-palladium alloys which showed significant increases in hydrogen permeability over 25 per cent silver-palladium alloys, see Figure 8.

The yttrium-palladium alloys do not suffer from the various problems associated with the formation of impervious, tenacious oxides and can benefit from a greater solid solution hardening (34). The latter will permit improved hydrogen permeability, by enabling higher differential pressures or thinner diffusion membranes to be used.

The work of Hughes and Harris (35) confirmed the enhanced permeability performance of yttrium-palladium over both silver-palladium and cerium-palladium alloys. It further established that the hydrogen diffusion coefficients in each of the three alloys were similar and that the improved performance of the yttrium-palladium alloy was due to a substantially greater hydrogen solubility gradient in the diffusion membrane.

Work has continued to investigate the properties of rare-earth-palladium alloys (36, 37) and some preliminary observations on the physical and mechanical properties of the materials have shown, among other things, extensive short range order. Further work (38) has determined that the permeabilities to hydrogen, but not solubilities, are influenced by the state of order in cerium-palladium and yttrium-palladium. This is of significance because it implies higher hydrogen diffusion coefficients to achieve the higher permeabilities observed in the ordered state compared with the disordered condition.

It is apparent that the permeability and mechanical properties of the rare-earth-palladium alloys, in particular yttrium-palladium alloys, offer opportunities for significant advances to be made in hydrogen diffusion technology. These improvements will result from the optimisation of alloy compositions, as increased data on properties become available, and from the development of material processing techniques that satisfy diffusion equipment design requirements.

Applications of Hydrogen Purification Technology

The selection of the optimum purification technique for specific industrial applications must be based on both technical and economic considerations. As the Table shows, the degree of purification of hydrogen obtained from the different methods varies from around 90 per cent for the Cryogenic and Polymer Membrane techniques to 99.9999 per cent for Palladium Alloy Membrane diffusion. The amount of hydrogen recovered also varies considerably and can have a major impact on process economics, particularly for large scale applications.

The use of diffusion technology using palladium alloy membranes can be related to either the need for high purity gas or, where high purity is relatively unimportant, to the convenience of local and portable sources of hydrogen supply.

Traditionally, analytical and metallurgical processing requirements utilise palladium alloy diffusion technology coupled to an impure hydrogen feed from electrolytic plants or commercial bottled gas. Here diffusion technology is used profitably to upgrade the hydrogen, removing impurities and moisture down to 0.5 vpm. A major and growing application is in semiconductor manufacture, particularly in the epitaxial growth stage. Recent experience in Europe, for example, suggests that the use of high purity hydrogen, produced by the application of palladium alloy diffusion technology, leads to significantly improved yields in manufacture and hence decreased production costs.

The use of self-contained and portable generators (39, 40), which produce hydrogen from methanol-water mixtures by catalytic decomposition followed by diffusion through silver-palladium membranes, is now increasing worldwide, particularly for those applications where the convenience and reliability of local on-site production is an important criterion. Such applications include the cooling of power station alternators where security of supply is considered important, and a range of metallurgical furnace operations. In these cases, the dryness and low impurity level of the hydrogen are also of importance for electrical and metallurgical integrity considerations. The ready availability and nature of the fuel and the ability to produce from it low cost hydrogen of over one thousand times its own volume combine to produce a useful portable supply of hydrogen (41).

A newer and potentially important application of palladium diffusion technology is in the recovery of hydrogen from industrial waste gas streams, particularly where it can be used to offset the cost of purchasing hydrogen as a feed gas. A recent report (42) describes how the use of such technology at a U.K. petrochemical plant has resulted in a reduction in hydrogen consumption by 40 per cent.

In the modern commercial diffusion unit many features are combined which contribute to its wide popularity and use. These include compactness and robustness of construction which leads to a high reliability in service that has been proven over decades; high output efficiency as well as purity of hydrogen which is produced at ambient temperature, and the simplicity of operation with minimum operator attention and low running costs (43). The modular nature of such commercial units enables a wide range of outputs to be obtained compatible with individual requirements.

Conclusions

The techniques currently available for the purification or separation of hydrogen have been described in terms of their flexibility with respect to feed gas and the quality of hydrogen produced. The advantage of diffusion technology based on palladium alloy membranes in producing high purity dry hydrogen at high output efficiencies from feed gases of a wide range of hydrogen contents emphasises the merits of this well-established technology for many important industrial applications.

The current technology of membrane materials centres around the use of 23 per cent silver-palladium which not only leads to optimum permeability, but also overcomes the problems of distortion associated with pure palladium, while it is relatively easy to fabricate to the thin sheet and tube required. Possible opportunities for improvements in diffusion technology have been discussed, and include alloy development and design considerations.

References

1 C. L. Newton, "Cryogenics" in: Kirk-Othmer Encyclopaedia of Chemical Technology, 7, 3rd Edn., 1978

2 W. A. Bollinger, D. L. MacLean and R. S. Narayan, *Chem. Eng. Prog.*, 1982, **78**, (10), 27

3 L. J. Kaplan, *Chem. Eng.(N.Y.)*, 1982, **89**, (16), 34

4 J. M. Sedlak, J. F. Austin and A. B. LaConti, *Int. J. Hydrogen Energy*, 1981, **6**, (1), 45

5 *Chem. Eng.(N.Y.)*, 1979, **86**, (26), 90

6 H. St.-C. Deville and L. Troost, *Comptes rendus*, 1863, **57**, 965

7 H. St.-C. Deville, *Comptes rendus*, 1864, **59**, 102

8 T. Graham, *Phil. Trans. Roy. Soc.*, 1866, **156**, 399

9 J. B. Hunter, *U.S. Patent* 2,773,561; 1956

10 J. B. Hunter, Symposium on the Production of Hydrogen, American Chemical Society, New York, 1963

11 J. B. Hunter, *Platinum Metals Rev.*, 1960, **4** (4), 130

12 H. Connor, *Platinum Metals Rev.*, 1962, **6** (4), 130

13 H. Bruning and A. Sieverts, *Z. Physik. Chem. (Leipzig)*, 1933, **A-163**, 432

14 L. J. Gillespie and W. Z. Downs, *J. Am. Chem. Soc.*, 1939, **62**, 2501

15 L. J. Gillespie and A. Sieverts, from "Hydrogen in Metals" ed. D. P. Smith, Chicago University Press, 1948

16 P. S. Perminov, A. A. Orlov and A. N. Frumkin, *Dokl. Akad. Nauk SSSR*, 1952, **84**, 749

17 P. L. Levine and K. E. Weale, *Trans. Faraday Soc.*, 1960, **56**, 357

18 R. Suhrmann, G. Wedler and R. Schumicki, *Naturwiss.*, 1959, **46**, 600

19 J. B. Hunter, *U.S. Patent* 2,773,561; 1956

20 A. C. Makrides, M. A. Newton, H. Wright and D. N. Jewett, *U.S. Patent*, 3,350,846; 1964
21 A. S. Darling, *British Patent* 827,681; 1958
22 A. S. Darling, *British Patent* 956,176; 1964
23 A. S. Darling, Johnson Matthey, unpublished work
24 A. Sieverts, E. Jurisch and A. Metz, *Z. Allgem. Chem.*, 1915, **92**, (4), 329
25 A. Sieverts and H. Hagen, *Z. Phys. Chem.*, 1935, **174A**, (3–4), 247
26 G. L. Holleck, *J. Phys. Chem.*, 1970, **74**, (3), 503
27 A. G. Knapton, *Platinum Metals Rev.*, 1977, **21**, (2), 44
28 D. L. McKinley, *U.S. Patent* 3,350,845; 1967
29 D. L. McKinley, *U.S. Patent* 3,439,474; 1969
30 K. D. Allard, T. B. Flanagan and E. Wicke, *J. Phys. Chem.*, 1970, **74**, (2), 298
31 H. F. A. Topsoe, *Dutch Patent* 7018485; 1971
32 J. P. G. Farr and I. R. Harris, *British Patent* 1,346,422; 1974
33 D. Fort, J. P. G. Farr and I. R. Harris, *J. Less-Common Met.*, 1975, **39**, 293
34 D. Fort and I. R. Harris, *J. Less-Common Met.*, 1975, **41**, 313
35 D. T. Hughes and I. R. Harris, *J. Less-Common Met.*, 1978, **61**, 9
36 J. W. Brooks, M. H. Loretto and I. R. Harris, *Met-Sci.*, 1976, **10**, 397
37 J. R. Hirst, M. L. H. Wise, D. Fort, J. P. G. Farr and I. R. Harris, *J. Less-Common Met.*, 1976, **49**, 193
38 D. T. Hughes, J. Evans and I. R. Harris, *J. Less-Common Met.*, 1980, **76**, 119
39 J. E. Philpott, *Platinum Metals Rev.*, 1976, **20**, (4), 110
40 *Platinum Metals Rev.*, 1981, **25**, (1), 12
41 *Processing*, Oct., 1982
42 C. Rapoport, *Financial Times*, Nov. 29th 1982
43 Johnson Matthey Equipment Brochure, "Diffusion Units", JMM 7730/5M/879/CBA

Alloys of Titanium with the Platinum Metals

Phase diagram information is crucial to the understanding and the application of alloys, and over the years many attempts have been made to survey the literature on alloy phase diagrams and to compile the known data in a useful and readily available form. Some four years ago the *Bulletin of Alloy Phase Diagrams* was launched as one part of a joint programme by the American Society for Metals and the U.S. National Bureau of Standards to provide evaluated phase diagrams and associated structural, lattice parameter and thermodynamic data.

Two recently available issues have included contributions by Dr. Joanne L. Murray of the Center for Materials Research at the National Bureau of Standards who, having surveyed the literature up to and including 1981, has evaluated the binary systems of titanium with iridium, osmium and ruthenium (*Bull. Alloy Phase Diagrams*, 1982, **3**, (2), 205–212, 212–216 and 216–221, respectively) and more recently with palladium, platinum and rhodium (*ibid.*, 1982, **3**, (3), 321–329, 329–335 and 335–342, respectively).

The phase diagrams presented are labelled "provisional" which is not meant to indicate quality, but only to record that they have been published as soon as possible, to stimulate comment and criticism before they are made available in a more permanent form. Efforts are now being made to calculate phase diagrams from thermodynamic models, and hence to extrapolate data to temperatures and compositions for which there are no measurements. In some instances Murray has used thermodynamic calculations to test uncertain phase boundaries and both thermodynamic calculated and assessed diagrams are presented, so increasing the value of these most useful surveys.

Cancer Chemotheraphy

The fourth international symposium on platinum co-ordination complexes in cancer chemotheraphy was held at the University of Vermont, Burlington, U.S.A., during June. The purpose of the meeting was to consider new developments in the biology, chemistry, clinical aspects, pharmacodynamics and toxicology of platinum complexes as they relate to cancer therapy. Twenty-one invited papers were read, and the programme provided time for observation and discussion of over eighty poster presentations.

The search for new drugs having less toxicity and at least comparable activity to the established drug cisplatin is continuing, and a number of alternative platinum complexes are presently undergoing clinical trials.

A review of this important and highly successful meeting, which was attended by over 180 delegates from 12 countries, will be given in the January 1984 issue of this journal, while the full proceedings will be published by Martinus Nijhoff in early 1984.