A New Hydrogen Purification Process

COMMERCIAL DEVELOPMENT OF PALLADIUM ALLOY DIFFUSION CELLS

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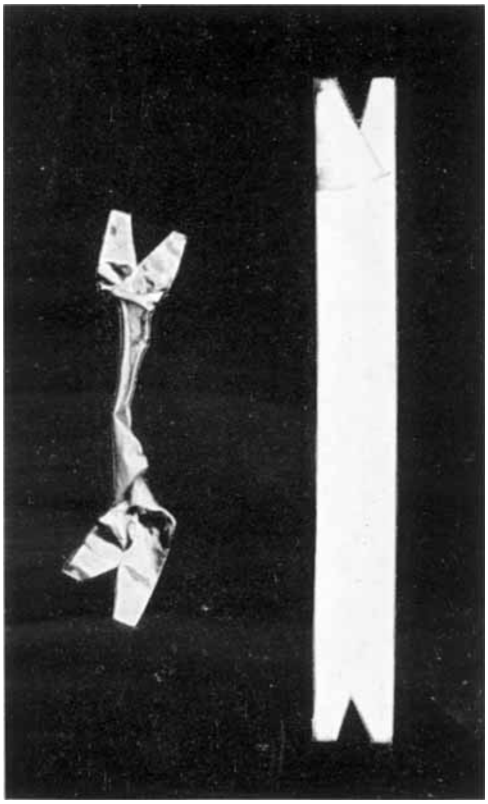
The discovery of a palladium alloy having remarkable stability as well as a hydrogen transfer rate more than twice that of pure palladium underlies the development of a new industrial process for the separation or purification of hydrogen.

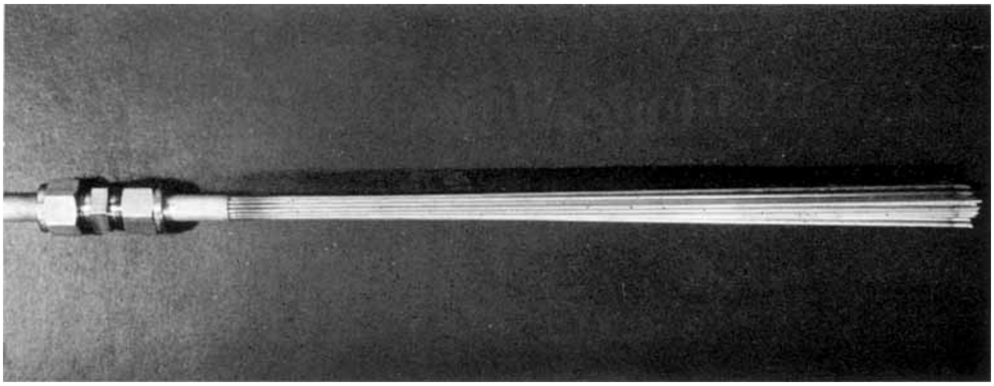
The selective diffusion of hydrogen through a palladium membrane has been well known since it was first demonstrated by Thomas Graham in 1866; equally well known has been the dimensional change that occurs when palladium is alternately heated and cooled in hydrogen. This deformation, which is generally understood to be the result of an α-β phase change in the metal as the hydrogen is occluded and released, has severely limited the development of diffusion equipment for the commercial separation and purification of hydrogen.

Effect of Alloying Additions on Palladium

It had also been generally believed that the alloying of another metal with palladium would serve only to reduce its ability to transfer hydrogen, and investigations with additions of copper, gold, nickel, iron, platinum and ruthenium have in fact proved this to be the case. If, however, silver is alloyed with palladium some unexpected results are obtained. Some compositions show a reduced permeability, others give essentially the same permeability as the parent metal, but in a very narrow critical range the rate of hydrogen transfer is found to increase remarkably. With the alloy finally established as the most effective, the hydrogen permeability at 500°C is about 25 per cent greater than for palladium, while at 300°C the difference in performance has increased to some 150 per cent. Although this remarkable increase in permeability of



Specimens of pure palladium (left) and of the silver-palladium alloy (right), initially the same size, after thirty cycles of heating and cooling in hydrogen



A typical Bishop design of diffusion cell, comprising a cluster of small diameter silver-palladium alloy tubes manifolded together. A range of units has been made available for laboratory, pilot plant and full-scale commercial operation

the new alloy is of real value, it would be insufficient in itself to justify the consideration of large-scale commercial applications. But fortunately it was found that this alloy also possessed a remarkable stability on heating and cooling in hydrogen. The difference in behaviour is clearly shown in the illustration.

Both specimens, originally the same size —pure palladium on the left and the silver-palladium alloy on the right—have been alternately heated (to the same temperature) and cooled through thirty cycles in an atmosphere of hydrogen. Similar tests extended over long periods have shown the alloy to remain unaffected.

When pure palladium is used for hydrogen separation or purification, protective measures must be taken to avoid this type of damage occurring to the diffusion element, either by the complete removal of hydrogen from both sides of the palladium membrane before heating or cooling, or by maintaining the unit above the critical temperature at which the unstable beta phase begins to form. The silver alloy requires no such special handling since no deterioration can occur during starting up or shutting down.

Based upon this new alloy, a range of diffusion cells has been designed by J. Bishop & Co for laboratory, pilot plant and full size commercial units. In designing such diffusion cells three basic considerations are involved. The cell must, of course, contain a maximum of surface area in a minimum of space; the transfer surface should be as thin as possible and yet be capable of withstanding a high differential pressure; and cell construction must be such that it can be manufactured by conventional techniques at a reasonable cost.

Design of Diffusion Cells

In the design finally established for the Bishop units, and illustrated above, high surface area in a small volume is achieved by the use of a cluster of small-diameter silver-palladium tubes manifolded together. The small tubing provides also a thin wall with adequate mechanical strength. This design also combines rugged construction with adaptability to many types of application.

Palladium alloy hydrogen diffusion cells thus make possible both cheaper hydrogen and ultra-pure hydrogen. Both are of great interest, but not necessarily to the same user. Cheaper hydrogen not of extreme purity is an advantage to all users, while the ultra-pure product is rapidly finding specialised applications in the metal working, electronics, nuclear and chemical fields. The development described here shows great promise both for the separation and purification of hydrogen and offers an inexpensive solution to an otherwise difficult problem.