

The Large Scale Production of Hydrogen from Gas Mixtures

A USE FOR ULTRA THIN PALLADIUM ALLOY MEMBRANES

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A method of pure hydrogen production using palladium alloy membranes to separate hydrogen from hydrogen-rich gas mixtures has been employed for many years in laboratory and industrial practices. Generally, palladium-silver membranes have been employed. Over the years a number of papers describing this method have been published in this journal (1-4). There are many publications by British, Japanese, Russian, etc., producers describing such units with productive capacities of up to 100 Nm³/h. These units are intended for the purification of technical grade hydrogen and operate in areas such as rare element metallurgy, the electronic industry and general laboratory practice. Recently it has been reported by Johnson Matthey (3, 4) that units capable of separating up to 50 Nm³/h of hydrogen from methanol-water cracking gas have been used as constituents of self-contained hydrogen generators.

One may ask the obvious question: why not use palladium alloy membranes for large-scale hydrogen production? It is easy for anyone to obtain the answer that this method does not provide a sufficient return on capital investment, due to the high cost of the noble metals involved. It is less evident that both the durability and the hydrogen recovery level of the usually employed membranes are also somewhat deficient. Indeed, the existing membrane units are generally used only for relatively small-scale purification of technical grade hydrogen, and not for its separation from mixtures containing less than 95 per cent hydrogen.

Nonetheless, in principal, membrane technology promises significant advantages in

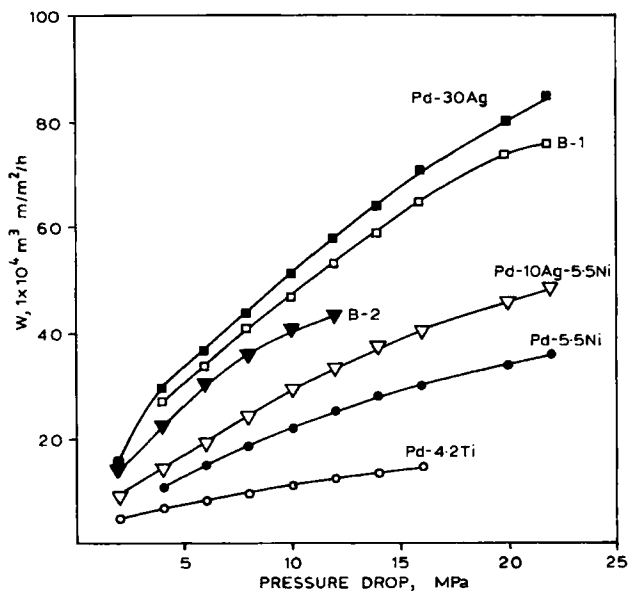
comparison with conventional technologies. Palladium alloy membrane units combine the compactness of polymer membrane units, the high product purity of the pressure swing adsorption technique, the recovery level of cryogenic separation and furthermore the ability to utilise great pressure drops as the directives for rapid permeation. There are, however, a number of reasons which prevent the attainment of either the investment return or the durability and recovery levels demanded in the case of large-scale hydrogen-rich mixture separation technologies.

In this respect, five key problems may be emphasised, namely, choice of membrane materials, minimisation of membrane thickness, design of the membrane holder, design of the membrane apparatus and start-up/shut-down technology. All the listed advantages can be realised and the disadvantages overcome by solving the key problems.

Key Problems of Palladium Alloy Membrane Technology

The choice of membrane material is the first highly significant problem. The palladium alloy has to possess excellent hydrogen permeability and be resistant to specific start-up/shut-down cyclic stresses. It is well known that hydrogen-palladium alloy interactions can induce the α - β phase transformation, which consequently alter atom spacings in the metal lattice, causing dimensional changes which are large enough to distort the membrane (5, 6). Thus conditions which favour the existence of β - and β -like hydride phases are dangerous in regard to the possibilities of membrane destruction. The task is therefore

Fig. 1 The variation of hydrogen permeability, W , with pressure drop for six different palladium alloys: $T=50^{\circ}\text{C}$, output pressure=0.1 MPa



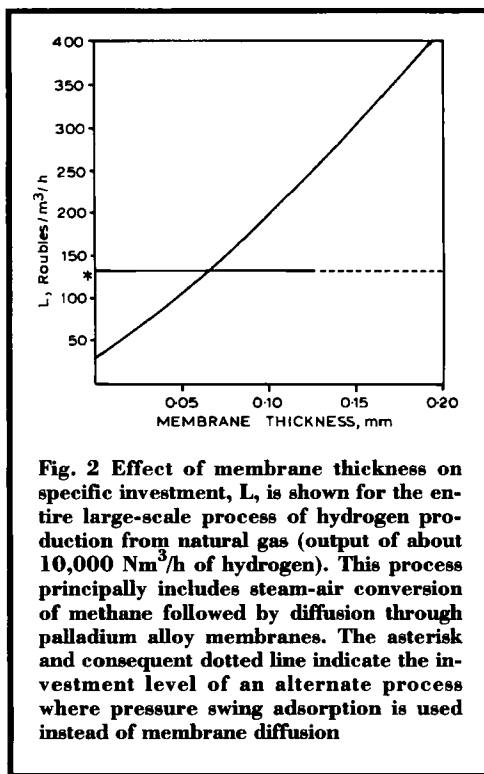
to develop an alloy which forms hydride phases only at temperatures substantially different from the operating conditions. Palladium membranes have usually been operated in the temperature range 400 to 600°C, within which there is good permeability and satisfactory durability.

The start-up/shut-down procedure has to be able to avoid hydride phase formation during its operation. Additionally, it should be emphasised that internal stresses and the consequent cracking of membranes are often induced by reasons other than β -phase formation. Certain palladium alloys seem unsuitable for use as membrane material for large-scale technology as they have insufficient resistance to specific start-up/shut-down stresses. For example, the widely employed 25 palladium-75 per cent silver alloy has low cyclic resistance and often cracks even if apparently suitable start-up/shut-down procedures are employed.

Different alloys also vary in hydrogen permeability, and this is illustrated by Figure 1. It may be noted that the permeability of the best alloy is about five times as high as that of the worst. In recent years a number of alloys with

large permeability and high cyclic resistance, such as the Soviet B-X group of alloys, have been developed (7). Such alloys may contain (10–30)Ag-(0.05–5)Au-(0–2)Y-(0.05–2)Ru-(0–1)Pt-(0.01–0.5)Al-(balance)Pd.

Minimisation of membrane thickness is the second key problem. Clearly, a decrease in membrane thickness while maintaining a constant membrane surface area, results in a proportional reduction in the cost of equipment. Furthermore, permeability through thin membranes is proportionally greater than through thick membranes. When calculating the dependence of the overall investment (namely, capital cost per unit of productive capacity) on membrane thickness, the decisive significance of the membrane thickness can be demonstrated convincingly. Such dependence is shown in Figure 2 for the investment level of the entire process of hydrogen production from natural gas where the cost of the 0.1 mm thick membranes constitutes about half of the total capital cost. It can be seen that 0.05 mm thick membranes provide an investment level near that of conventional technologies, while the use of 0.01 mm thick membranes would result in the most inexpensive technology for



the large-scale production of hydrogen from gas mixtures.

Such thin membranes could be destroyed, however, if there were substantial increases of the operating pressure drop across the membrane, and at present membranes for the separation of mixtures are required to work at pressure drops of between 1 and 20 MPa. Nevertheless, an increase of pressure drop would result in a greater productive capacity and recovery level. To summarise, there could be a difficult situation in trying to balance the problem of minimisation of membrane thickness; on the one hand, a decrease in the thickness can critically improve the entire technology, while on the other hand very thin membranes may not be strong enough to work at the conditions demanded.

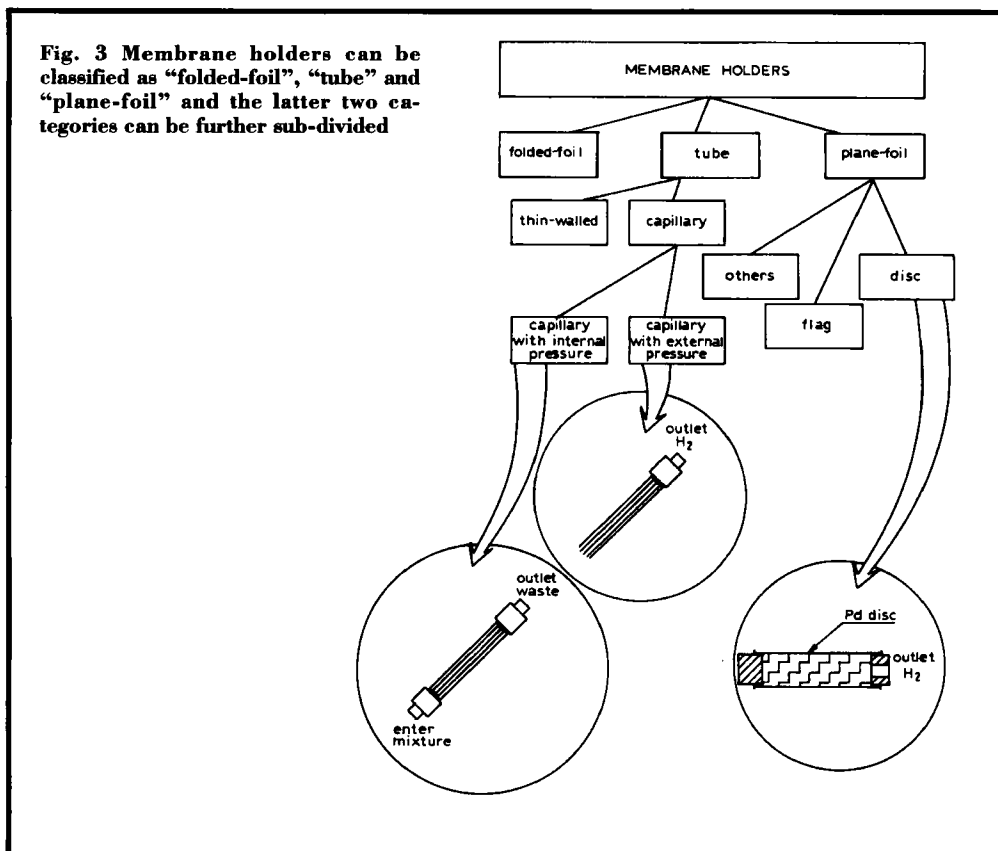
This problematic situation can be partly resolved by the use of a suitably designed membrane holder, which constitutes the third key problem area. A simple classification of

membrane holders is presented in Figure 3, the holders being divided into "tube", "plane-foil" and "folded-foil". Three examples of holder design are also shown in Figure 3, namely "disc", "capillary with external pressure" and "capillary with internal pressure".

Each type of membrane holder may be further characterised by the type of connection between the palladium alloy and the adjoining material. Welding or soldering has been used, but it is difficult to weld thin membranes and hence soldering often seems to be the more attractive method. On the other hand strong erosion can occur during the course of the soldering operation due to dissolution of palladium alloy in the liquid solder; and even if this dissolution is not complete, the boundary alloy formed can be easily damaged by hydrogen and by the mutual diffusion of components at high operating temperatures. The use of hard silver or gold solder can be advantageous, although the operational life of capillary holders with silver solder is usually not more than one or two months. Different kinds of welding may be used, such as arc welding, pressure welding, electron beam and laser welding. Pressure tight welds can be produced by each of these methods, although mutual diffusion of palladium alloy and steel components at the operating temperatures can still constitute a significant problem which may result in the destruction of either the membrane or the weld. Residual after-weld defects and stresses also have to be taken into account, although multilayer welding techniques can usually avoid these difficulties.

There can be a large variety of alternative membrane holders, many of them having the same defects, such as low ranges of practical pressure drop and short operational life. It seems that the first of these limitations can be removed in the case of "plane-foil" holders with membrane support, and also by the use of "capillary" holders. In the present paper "tube" holders with tube diameters of less than 1 mm and wall thicknesses of less than 0.1 mm are designated as "capillary" holders. "Plane-foil" holders have an evident advantage of

Fig. 3 Membrane holders can be classified as “folded-foil”, “tube” and “plane-foil” and the latter two categories can be further sub-divided



lower cost, due to the lower cost of foil in comparison with that of tubes. On the other hand, “tube” holders also have certain particular advantages especially in the case of “capillary” holders, which allow thin membranes to be operated under large pressure drop conditions without any membrane support. Experience has shown, however, that the membrane support can provoke corrosion of the palladium alloy, and in addition the support can create difficulties for optimum gas flow and can reduce the purity of the output hydrogen. The design of compact gas collectors is more successful in the case of “tube” holders, but this last consideration is close to another key problem, which is discussed below.

The fourth key problem is the overall design of the membrane assembly. As mentioned above, one aim is to create compact equipment

and this is easy in the case of “tube” membrane holders but “plane-foil” and “folded-foil” holders demand more complex collectors for the purified hydrogen. Designs must also provide optimum rates of gas flow near the membrane surface in order to attain maximum levels of productive capacity and recovery.

Necessary temperature conditions near the membranes can be achieved either by external heating of the apparatus or by preliminary heating of the gas mixture. The later seems preferable for large scale hydrogen production, and it should be noted that if preliminary heaters are used without heat exchangers then the expenditure on energy can constitute up to half the cost price of the hydrogen produced. The membrane apparatus adopted needs to be equipped with internal heaters for the gas mixture and internal heat

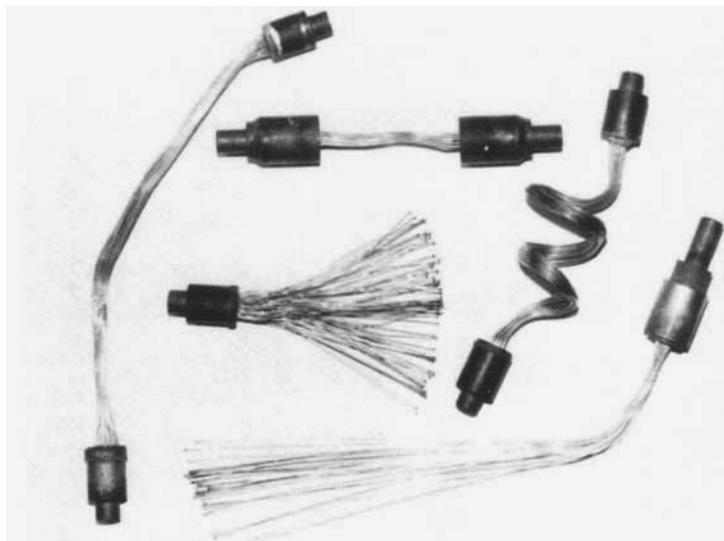


Fig. 4 A variety of capillary membrane holders designed by GIAP are displayed

exchangers in order to conserve the heat, while the outlet gas temperature should not be more than 200°C.

The development of optimum start-up/shut-down technology, which is the fifth key problem, has been partially discussed above. It should again be noted that this technology requires specific control of temperature and pressure, and the use of certain alternative blow gases has also to be considered. For example, heating to the operating temperature and cooling during the course of shut-down can be usefully carried out in a nitrogen atmosphere in order to obtain a long operational life for the membranes.

GIAP Style Development

The problems reviewed above are common key problems for any organisation which is going to attempt to improve palladium alloy membrane technology. The solutions to these problems and the relative significance of each depend, however, on which branch of industry the proposed technology is principally intended for.

The State Institute of Nitrogen Industry

(GIAP) began to investigate palladium alloy membrane technology for the nitrogen industry more than twenty years ago. The conditions and the needs of the nitrogen industry may be characterised as:

(a) high pressures of technological and waste hydrogen-rich gas, from 3 to 32 MPa

(b) a wide range of hydrogen content in the mixtures, typically 40 to 75 volume per cent

(c) the presence of nitrogen, methane, ammonia, water, carbon dioxide, and carbon monoxide as possible components of the mixture and also the probable occurrence of small amounts of oil

(d) rapid growth in the demand for relatively low cost hydrogen. With regard to the last item it should be emphasised that the hydrogen-rich mixtures occurring in the nitrogen industry can provide a cheap source of pure hydrogen if appropriate technology can be developed for its recovery.

Accordingly, certain directions of research were decided upon and resulted in the development of an original GIAP style in regard to metal membrane technology.

The use of the B-X series of alloys has been

one of the most important directions of improvement. These alloys possess good hydrogen permeability and the membranes can provide operational lives of more than two years. The B-X alloys are resistant to "poisoning" by constituents present as impurities in the gases from the nitrogen industry. These conclusions were formed in the course of long term testing carried out by GIAP.

Different types of membrane holders were also designed and tested in GIAP, the most advanced being "capillary with internal pressure" and "capillary with external pressure". These are shown in Figure 4. B-X capillary tubes with wall thicknesses of from 0.05 to 0.1 mm are used and the free end of the tubes are sealed. The hydrogen-rich mixture flows along the external surface of the tubes and pure hydrogen is ejected from the internal tube space due to the pressure difference between the open and the sealed ends of the tube. The "capillary with internal pressure" holders have two heads, and both ends of the tubes are open. The mixture flows into and around the internal space of the tubes and pure hydrogen is removed from their external surfaces. Due to the successful design of the holder head and the development of steel to B-X powder welding technology (8, 9), the GIAP membrane holders in both "internal" and "external" variants can operate at pressure drops of up to 30 MPa and are characterised by operational lives of more than two years.

Three categories of membrane apparatus have been designed, namely: small-scale constructions, constructions for portable hydrogen generators and large-scale constructions. In the first case the units are capable of producing up to 2 Nm³/h of hydrogen, and external electrical heaters have been used. Portable hydrogen generators possess a closed heat recovery system and hence the feed gas is delivered to the membrane at a suitable temperature, and the hot waste gas mixture is passed to the heat recovery system. The large-scale constructions consist of a pressure-tight columnar vessel containing membrane cells, with each cell having a number of contain-

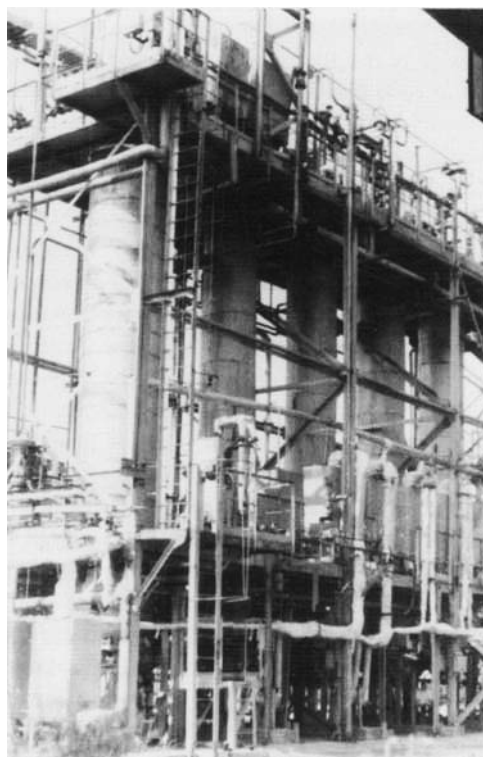


Fig. 5 This diffusion membrane installation is in operation at a fertiliser production plant in Rovno, Ukraine. Ammonia purge gas under a pressure of 20 MPa is used as feed mixture. The installation is capable of producing up to 2000 Nm³/h of hydrogen at a pressure of 3 MPa. Regular output is 1300 Nm³/h. There are four 10 m high columnar membrane units, the fifth column being an ammonia separator

erised membrane holders, internal electric heaters for primary heating of the feed gas, and internal heat exchangers for heat recovery. An installation containing four such column units is shown in Figure 5; each column is about 10 m high and has a diameter of 0.8 m. The design has ensured suitable compactness, hydrogen recovery level and low energy requirement.

Over the years a number of membrane units have been installed in the U.S.S.R. utilising technology developed by GIAP (10). The largest installation, which is operating in Rovno, Ukraine, at a fertiliser production plant is shown in Figure 5. Ammonia purge gas under

a pressure of 20 MPa is used as the feed mixture. The installation is capable of producing up to 2000 Nm³/h of hydrogen under a pressure of 3 MPa. This output pressure is the same as the operating pressure of an organic synthesis plant which utilises pure hydrogen. The installation has operated successfully since 1988 and the level of recovery of hydrogen has reached about 96 per cent. After two years of operation the membrane cells were partially changed to modified ones. A number of similar installations are either under construction or are planned. The market for such units is defined by the number of users of pure hydrogen in industries such as metallurgy, organic synthesis and electronics, which are located near to nitrogen industry plants and/or close to petrochemical plants, as well as to the cost price of the output hydrogen, which in this case is markedly lower than pure hydrogen from alternate sources, for example the electrolysis of water.

It is evident that the techniques developed for the nitrogen industry may be utilised for other applications. For example, a number of self-contained and portable generators have been designed which produce hydrogen from organic materials by catalytic steam or steam-air conversion, followed by diffusion through membranes. Designs range from GV-1 (1 Nm³/h) to GV-500 (500 Nm³/h) and GV-3, GV-5, GV-25 and GV-500 have already been installed and tested. Different raw materials such as methanol, ethanol, methane, petrol and natural gas have been used as the source of hydrogen, as has cracked ammonia. The type of raw material may be changed from one to another, necessitating only a simple alteration of the catalyst. The cost price of hydrogen produced by these generators is markedly lower than that from electrolysis plants of similar capacity, which are usually used in the former U.S.S.R.

In concluding this section it should be noted that the economic level of membrane technology already achieved has allowed the development of installations capable of producing up to 5000 Nm³/h of hydrogen.

Alternate techniques, principally pressure swing adsorption, are preferable for larger outputs due to the fact that specific investments in palladium alloy membrane installations depend to some extent on the installation size, whereas for many of the alternative types of installations an increase in size generally results in economies of scale.

Forecast of Future Developments and Possible Applications

For the future it is reasonable to assume, as proposed by V. A. Goltsov (6), that further improvements in membrane technology will perhaps result from the development of new permeable gold-free and silver-free palladium alloys.

As stated in the previous sections, the main purpose will be to reduce specific investment requirements and hence, among other factors, the membrane thickness. Although further progress in this direction is possible by improvements in the methods described above, the most significant improvements could be related to the development of new multilayer membranes. Such membranes, consisting of at least two layers, for example an ultra-thin palladium alloy layer combined with a microporous nickel layer, would make the competitive position of membrane units unassailable, even if a reduction to an acceptable membrane thickness of 0.02 mm could be achieved, see Figure 2. Multilayer membrane development demands investigations into both the connection of ultra-thin foils and into problems of film coatings. Interaction between the various layers at the operating temperatures of the membranes will probably prove to be the most important problem to be overcome.

The employment of existing foil and tube membranes should increase with the growing market for hydrogen generators in order to supply users in the fields of metallurgy, organic synthesis, electronics industry, etc., with pure hydrogen when they are located near to nitrogen or petrochemical plants. Furthermore, certain specialised plants, such as

those manufacturing particular organic amines and production catalysts, could improve their product quality by changing their existing gas feed stock from a nitrogen hydrogen mixture, containing 90 per cent hydrogen, to moderately priced pure hydrogen obtained from modern membrane installations.

New membranes with ultra-thin noble metal layers could be used for new applications, such as in ammonia synthesis gas production, coal gasification and ferrous metallurgy.

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Platinum in High-Temperature Superconductors

High temperature superconductors have been known about since 1987 when YBaCuO superconductors with critical temperatures above 77 K, the temperature at which nitrogen liquefies, were first synthesised. If such superconductors are to become widely used, however, they will have to be able to achieve high current densities without the superconductivity of the material being destroyed. Thus flux pinning is essential in order to prevent magnetic flux interactions between superconducting regions, otherwise the critical magnetic flux density could be exceeded, destroying the superconductivity and causing Joule heating.

Platinum already finds a variety of applications in high temperature superconductor technology; now researchers at the International Superconductivity Technology Center, Nagoya, Japan have found that additions of platinum or rhodium in certain YBaCuO superconductors can produce a much increased critical current density ("Effects of the Platinum Group Element Addition on Preparation of YBCO Superconductor by Melt Growth Method", M. Yoshida, N. Ogawa, I. Hirabayashi and S. Tanaka, *Physica C*, 1991, 185–189, (IV), 2409–2410).

It has been reported previously that high critical current densities can be attained in large (123) crystals of YBa₂Cu₃O₇, which have fine (211) Y₂BaCuO₅ particles uniformly dispersed throughout them. This dispersion of (211) particles is reported to suppress crack formation, allow the oxygen diffusion rate to increase and also serve as flux pinning centres.

In the current work the microstructure of superconductors containing 0.5 weight per cent platinum group metals, and prepared by a partial melting and slow cooling process, were studied by optical microscopy, while the high critical current density was estimated from magnetisation hysteresis curves. It was found that the addition of platinum or rhodium facilitates the heterogeneous nucleation of the (211) phase; the mechanism for this is discussed. Other platinum group metals had no significant effect, however. For typical platinum-doped melt grown samples, at 77 K and 1 T, critical current densities exceed 18,000 A/cm²; corresponding values for other samples are less than 10,000 A/cm².

Ruthenium Oxide Contacts

If high temperature superconductors, such as YBCO, are to be used in electronic or electrical devices it will be necessary to form low resistance contacts with them. This must be achieved without degradation of the superconducting properties and a recent communication from the New York Institute of Superconductivity reports on the successful use of conducting metallic ruthenium oxide, RuO₂, as a low resistance contact electrode for YBCO thin films (Q.-X. Jia and W. A. Anderson, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1992, 15, (1), 121–125).

Double-layer contact electrodes of metallic ruthenium oxide overlain with either gold or silver overcame wire bonding problems, and reduced further the contact resistance.