Tanaka's Super-Thin Metal Foil Fosters Use of Hydrogen as Energy

Tanaka Kikinzoku Kogyo K.K. has developed an ultra-thin palladium (Pd)-based foil using advanced rolling process, supporting the promotion of hydrogen as an alternative energy source.

Amid the attention hydrogen has been getting recently as a clean source of energy, hydrogen purifier becomes necessary for efficient use to achieve ultra-high purity, especially for fuel cell application. Among the methods for purifying hydrogen, the membrane separation method is the most expected technology for miniaturization of hydrogen purifier. In the past, however, it was pointed out that membrane separation technology will assume high initial cost with the use of Pd-based alloy. To overcome this barrier, TANAKA Kikinzoku Kogyo succeeded in developing an ultra-thin Pd-based alloy foil fabrication process, which is applied for hydrogen permeation membrane, using an advanced rolling method. With this development, a remarkable dimension of Pd-based alloy foil can be fabricated, with thickness down to 5µm and width up to 200mm. It can reduce usage of palladium down to 1/9, thus significantly reducing cost.

Accompanying its oxidization, hydrogen emits only energy and water. In addition, it can be stored and transported in various forms. For these reasons, hydrogen attracts a great deal of attention as an environment-friendly, next-generation clean energy source that can replace conventional fossil fuels. In order to use hydrogen efficiently as an energy source, it is necessary to create high-purity hydrogen by refining it. In particular, in the case of polymer electrolyte fuel cells (PEFCs), removing impurity gases, such as carbon monoxide (CO), is a major factor that affects the life of electrodes. Meanwhile, in the manufacture of compound semiconductors, such as light-emitting diodes (LEDs) as energy-saving technology, ultra-high-purity hydrogen (9N: 99.9999999%) is required as process gas in the manufacturing process.

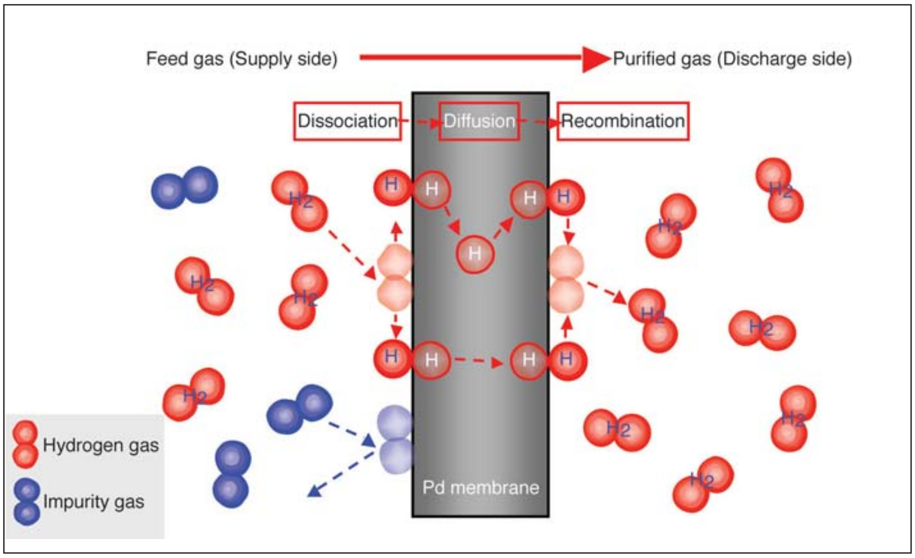

Fig. 1: Schematic diagram of hydrogen permeation mechanism for Pd-based alloy membrane

Hydrogen Purification Technology

There are several methods for purifying hydrogen. The main methods that have been considered as purifying methods for next-generation energy (mainly fuel cells) are the Pressure Swing Adsorption (PSA) method, Preferential Oxidation (PROX) catalyst method, and membrane separation method. In the PSA method, hydrogen is purified by repeating adsorption of impurity gas components to the absorbent and cleaning of the absorbent by desorption of the impurity gas components. As this method enables large-scale refining, it has been used for the refining of commercially available hydrogen gas, and the technology has already been established. However, this method has some drawbacks. Even high-performance equipment can produce hydrogen with a purity of about 5N (99.999%). Furthermore, the control of equipment is complex and the reduction of equipment size has been difficult, and hence energy efficiency is low. The PROX method has been used for household fuel cells, whose sales have begun in Japan. In this method, CO contained in the feed gas, which is harmful to electrode catalyst, is selectively oxidized using a catalyst and changed to carbon dioxide (CO_2). Hence, strictly speaking, this method is not a hydrogen purification method. In addition, this method requires a room for the reaction, and hence, there is a limit in the reduction of equipment size. Also, temperature control is important in order to efficiently drive the catalytic reaction. Some impurity gas components in the feed gas can cause the deterioration of the catalytic performance due to poisoning.

Meanwhile, the membrane separation method is a hydrogen purification method, which uses a metal membrane as filter. Pd-based alloy membranes have been generally used as metal membrane for hydrogen purification. Although non-Pd-based alloy membranes have also been developed, they have yet to reach practical application. This technology using Pd-based alloy membranes is a very old technology. The property of Pd membrane to permeate hydrogen was discovered by

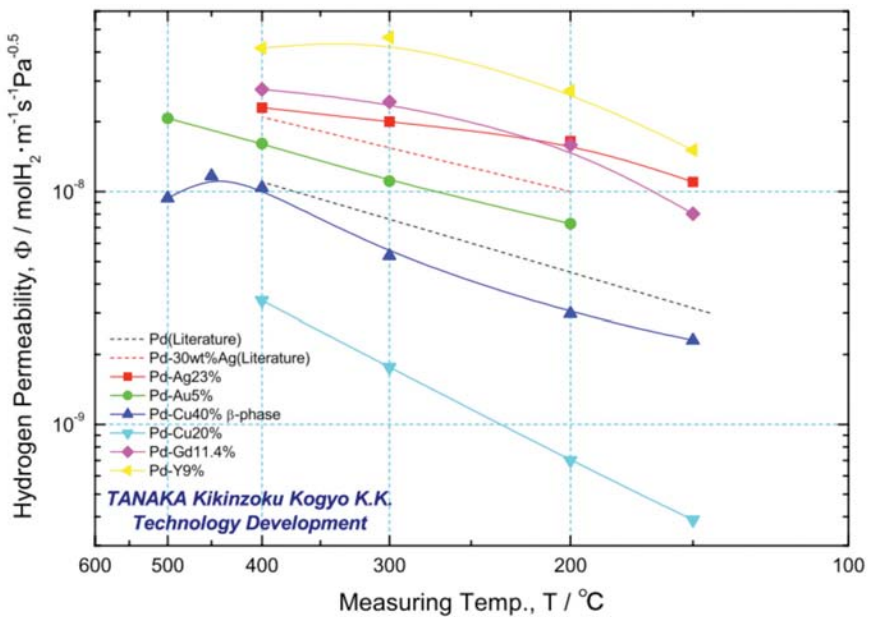

Fig. 2: Hydrogen permeability of various Pd-based alloys

T. Graham in 1866. This principle has been utilized in hydrogen purification equipment sold for use in experimental laboratories and semiconductor manufacturing since more than 50 years ago. Pd-based alloy membranes utilize the property of Pd-based alloys to selectively permeate hydrogen only, and their biggest advantage is the purity of permeated hydrogen. It is the only method able to easily achieve a purity of 9N. Furthermore, equipment only requires the installation of a membrane with a sufficient area to obtain targeted flow rate. Therefore, the reduction of equipment size is easy, and it is also possible to enhance energy efficiency through the use of a membrane reactor, which is combined with reforming reaction. This method, however, also has a disadvantage such that the initial cost is high as it requires pressure for the separation and refinement process, and uses Pd, which is a precious metal. Nonetheless, precious metals have unchanging property values and industrial recovery methods have been established, and therefore, it is possible to reuse the precious metal and recover the cost of the precious metal by establishing a circulation system for recovering Pd at the time of the disposal of equipment.

Hydrogen Purification by Pd-based Alloy Membrane

Figure 1 shows a schematic diagram of hydrogen permeation mechanism for Pd-based alloy membrane. Hydrogen molecules in the feed gas adsorbed on the Pd-based alloy membrane dissociate into hydrogen atoms through the catalytic action of Pd and dissolve into the Pd-based alloy. Dissolved hydrogen atoms diffuse between crystal lattice of the Pd-based alloy and reunite on the opposite side of the membrane surface and become hydrogen molecules. By maintaining the hydrogen partial pressure on the feed gas side higher than that of the purified gas side, concentration gradient develops in the Pd-based alloy membrane by the degree of solubility due to hydrogen partial pressure, making continuous purification of hydrogen gas possible. As components other than hydrogen molecules in the feed gas do not exhibit such reaction, the purified gas includes hydrogen molecules only, thus enabling the obtainment of ultra-high purity hydrogen gas. Through this mechanism, ultra-high purity hydrogen can be easily obtained if the Pd-based alloy membrane and the hydrogen purifier are free from defects, such as pinholes.

The flux of permeated (purified) gas obtained by the membrane separation method using a metal membrane is expressed by the following equation under the condition that hydrogen solubility in the metal membrane follows the Sieverts' law.

$$J = \frac{\phi}{l}\left(\sqrt{P_f} - \sqrt{P_p}\right) \quad ...(1).$$

Here, J denotes flux, and ϕ is hydrogen permeability, which is unique to material and depends on temperature, l is the membrane thickness, and P_f and P_p are hydrogen partial pressure at the feed side and the purified side, respectively.

As is evident from equation (1), in order to increase the flux of permeated gas, it is necessary to increase permeability, reduce the membrane thickness, and increase the difference in pressure (differential pressure). In order to increase permeability, it is necessary to increase the temperature to be used, or develop a new alloy with higher permeability. Hence, it is not easy to increase the flux by increasing permeability. As regards the membrane thickness, as pressure capacity reduces, and defects, such as pinholes, tend to be formed with thinner membrane thickness, there is a limit to reduce membrane thickness. Nonetheless, it is relatively easy to increase the flux through the reduction of membrane thickness. Meanwhile, limits on differential pressure are caused by either the design of equipment or laws. In addition, as its square root is used in the equation, it has little effects. From these understandings, establishing a technology to create a thin membrane without defects becomes a promising approach for easily obtaining a high flux of permeated gas.

Presently Pd-23wt%Ag or Pd-40wt%Cu is used as alloy composition of commercially available main Pd-based alloy membranes. Rolled Pd-based alloy foils with minimum thickness of 15µm are commercially available, and Pd-based alloy membranes with membrane thickness of 15 to 100µm are practically used as hydrogen separation membranes. Both alloys have a hydrogen permeability of about 1 to 3×10^{-8} $molH^2 \bullet m^{-1} \bullet s^{-1} \bullet Pa^{-0.5}$ (Fig. 2), although it depends on the temperature used.

Ultra-Thin Pd-Based Alloy Membrane

As described above, reducing the thickness of Pd-based alloy membrane is effective to increase the flux of purified gas. As technologies for

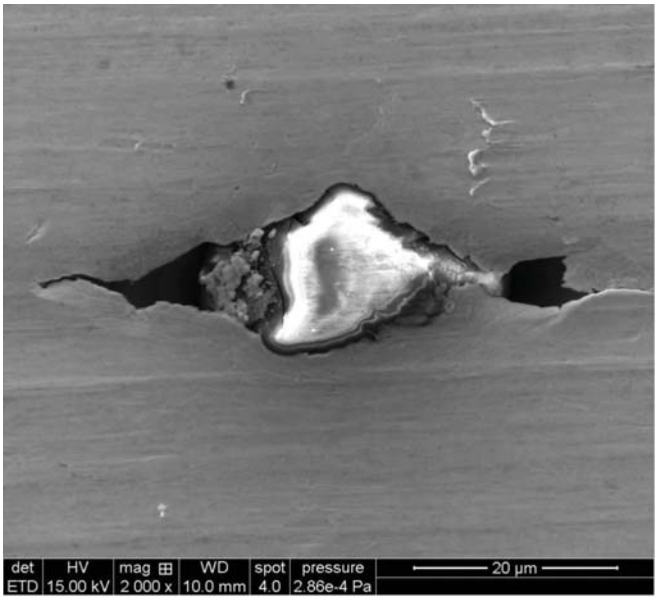

Fig. 3: Main cause of pinholes in Pd-based alloy foils (oxide inclusion)

Fig. 4: Ultra-thin Pd-based alloy foil (5µm × 200mm)

forming thin membranes, film formation processes, such as the sputtering method and plating method, are very effective means, and the development of thin membranes using these approaches have been conducted at various organizations. However, film formation processes require a substrate, and new technological development is necessary in order to form self-supported films with uniform film thicknesses. When using a membrane with a substrate as one, the reaction between the substrate and membrane, and the gas permeability of the substrate need to be considered. In addition, films produced by film formation processes tend to become non-dense film with relatively low densities, and it is difficult to suppress defects, such as pinholes. As a result, these processes can only produce films with a thickness of about 10µm. Furthermore, alloy composition control and texture control are not easy.

The development concept of TANAKA Kikinzoku Kogyo's Pd-based alloy membrane is defect-free ultra-thin rolled foils, and Tanaka has achieved a thickness of 5µm, and a width of 200mm. Rolled foils are produced using a classic technology called the rolling process. Rolled foils are manufactured using the melting and rolling processes that are classic metal processing methods only, and hence dense membranes can be formed easily. It is also possible to control alloy composition by melting and texture by thermochemical processing, and therefore rolled foils accommodate volume production. These are the advantages of rolled foils.

It is not an easy task to evolve the processing technology, whose limit was 15µm × 100mm (cross-sectional aspect ratio of 30/200,000) to 5µm × 200mm (cross-sectional aspect ratio of 5/200,000). It requires the development of handling and other peripheral technologies, as well as the rolling process technology. Furthermore, the number of pinholes increases extremely when foil thickness is reduced to 10µm or thinner. The main cause of the pinholes is insoluble inclusions, such as oxides (Fig. 3). These inclusions come from the work environment, raw materials, and alloy formation process, and therefore, it is of utmost importance to address these problems. Tanaka has a wide range of technologies and know-how involving precious metals. By fusing these technologies, Tanaka has newly created Ultra Clean Process and completed an ultra-thin Pd-based alloy foil measuring 5µm × 200mm (Fig. 4).

Conclusions

Tanaka Kikinzoku Kogyo has successfully developed an ultra-thin film technology for Pd-based hydrogen permeable membranes using the rolling process, and made it possible to produce a highly reliable Pd-based alloy foil measuring 5µm × 200mm with very few defects. It is one-third in thickness that of conventional Pd-based alloy foils for hydrogen permeable membranes, and hence, the developed Pd-based alloy foil provides three times the purified gas flux under the same temperature and pressure conditions. In other words, the amount of Pd used per flux has been reduced to one-ninth, making it possible to significantly reduce the initial cost, which was a disadvantage of the membrane separation method using Pd-based alloy. For example, in order to obtain a fuel cell output of 1kW, about 10-liter hydrogen gas per minute is necessary (*although it depends on operation conditions). While a conventional Pd-based alloy foil for hydrogen permeable membranes requires an area of 220sq.cm (4.0g in terms of the weight of Pd), an area of 73sq.cm (0.4g in terms of the weight of Pd), which is one-third that of the conventional foils, is suffice for the developed Pd-based alloy foil. More improvements, including further reduction of equipment size, accommodation to large-capacity hydrogen purifiers, simplification of components through the reduction of differential pressure, are also considered. The use of hydrogen separation by Pd-based alloy membranes will become possible in a wide range of fields. ❑

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