INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 18659–18667

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Repair of palladium membrane modules by metallic diffusion bonding

Ningning Lu [a], Donglai Xie [b,*], Fang Wang [b]

[a] The Key Laboratory of Fuel Cell Technology of Guangdong Province, South China University of Technology, Guangzhou 510640, China

[b] MOE Key Laboratory of Enhanced Heat Transfer and Energy Conservation, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:
Received 17 October 2013
Received in revised form
20 January 2014
Accepted 5 February 2014
Available online 28 February 2014

Keywords:
Hydrogen
Palladium membrane
Repair
Performance

ABSTRACT

Thin palladium membranes are easy to form defects during the preparation and application processes. The inter-metallic diffusion offers a method to repair large membrane defects such as wrinkles and cracks by pasting a membrane patch on the defect area. A repair procedure based on the inter-metallic diffusion bonding is developed. A repair permeation factor is introduced to denote the influence of the repair on membrane module performance. The repair factor is not only a function of the membrane repair patch size, but also the flow hydrodynamics of the membrane module and the position of the repair patch on the membrane module. Repair of the defects on two membrane modules has been successfully demonstrated. The integrity of the modules after repair is confirmed. The measured repair permeation factors are very close to those predicted ones.

Introduction

Palladium and its alloy membranes have attracted growing interests for their capability to separate ultra-pure hydrogen from gaseous mixtures and chemical compatibility with hydrocarbon containing gas streams [1–3]. They can be used as membrane separators, and can also be integrated with chemical reactors where chemical reaction and hydrogen separation occur simultaneously to simplify the hydrogen production process [4]. When being used, the membranes are usually in tubular or planar forms. Pd–Ag membrane tubes have been employed in a fixed bed membrane reactor by Itoh et al. [5] and in fluidized bed membrane reactors by Adris et al. [6] and Gallucci et al. [7]. Planar membrane modules consisting of membrane layer and porous substrate have been employed in many fluidized bed membrane reactors for hydrogen production [8–10]. Supporting the membrane layer on a porous substrate can significantly increase its mechanical strength and thermal stability, enabling the preparation of ultra-thin Pd and Pd-alloy membranes. Porous refractory ceramic, glass and stainless steel were successfully used as support for palladium membranes [11,12].

High investment cost is a major obstacle for commercialization of membrane purification on a large scale [13]. Considering the material cost and hydrogen permeability, thin Pd membranes are preferred in industrial applications. However, thin membranes are easy to form defects such as

* *Corresponding author*. Tel./fax: +86 20 22236985.
E-mail addresses: dlxie@scut.edu.cn, donglaixie@163.com (D. Xie).

http://dx.doi.org/10.1016/j.ijhydene.2014.02.027

wrinkles, cracks and pin-holes during the preparation and application of these membranes, which will reduce the purification selectivity, cause unpredictable performance and poor reproducibility of membrane modules. Without proper membrane repair technologies, a tiny pinhole will ruin a whole membrane module. Zeng et al. [13] demonstrated that pin-holes and cracks in thin Pd and Pd alloy membranes can be sealed by selective deposition of Pd within them, while practically maintaining the original metal layer thickness and the permeability. Recently Ryi et al. [14] reported a polishing treatment method after the palladium sputtering during the membrane preparation. It was confirmed that this method can successfully remove the pin-holes. While these methods are employed to repair those tiny defects in the dimension of microns, they may not be applicable to large defects in the dimension of millimeters such as cracks and wrinkles in the membrane surface. To reduce the operation cost of membrane separation, feasible methods need to be developed to repair large defected membranes, such as wrinkles and cracks.

The repair principle and procedure

Evidences have shown that for Pd and its alloy membranes supported on metal substrates, inter–metallic diffusion between the Pd membrane and the metal substrate can take place. Although the inter–metallic diffusion is a very slow process, it could be speeded up in the hydrogen environment [15]. Some researchers actually used the diffusion bonding to fabricate membrane modules [1,16]. This gives an implication that this characteristic can offer a method to repair large membrane defects such as wrinkles and cracks by pasting a membrane patch on the defect area.

Diffusion bonding techniques have been used in the aerospace industry to join similar or different metals. It is often used in combination with superplastic forming for the fabrication of aircraft and aerospace components. For different metallic parts, there are different diffusion bonding techniques. Li et al. [16] invented a method of bonding a metallic membrane with metallic module that involves pressing a smooth surface of the metallic membrane against a smooth surface of metallic parts, then heating the metallic membrane and metallic parts to a temperature above the half melting point of the metallic membrane, while subjecting the metallic membrane to a controlled environment of pressurized gas. The diffusion bonding technique offers a method of bonding a membrane patch to the defect area of a membrane surface.

The principle of inter-metallic diffusion is applied to repair the membrane defects, and the repair procedure includes:

1) Clean the membrane surface, especially the area around the defects. Keep the defect area flat and clean.
2) Cover the defect with a membrane patch. Place a small piece of membrane foil on the defect. The size of the membrane foil patch should be wide enough to cover the defect.
3) Press the membrane patch on membrane module surface with flanges, tightly. To prevent inter-metallic diffusion between the flange and the membrane foil, a piece of graphite gasket should be inserted between the membrane foil and the flange.
4) Heat the membrane module under hydrogen environment for at least 12 h. After the flanges are fastened, the membrane module is installed in a pressure vessel. Hydrogen and argon are directed to the vessel. Sweep gas nitrogen is delivered to the permeate side of the membrane module. The heating process is as follows:

A) Displace air in the vessel. Pure argon gas is directed to the vessel until its pressure reaches 0.2 MPa, and then released. This procedure is repeated 8 times. The vessel pressure is then kept at 0.2 MPa with argon inside.
B) Displace air in the permeate side of the membrane module. When the vessel is pressurized, nitrogen is directed to the permeate side of the membrane module to purge the air out. A small flow of nitrogen (about 1 ml min^{-1}) is maintained during the heating process, until hydrogen is confirmed to have been permeated from the vessel to the permeate side of the membrane.
C) Heat the module in argon environment. The vessel is heated by the electrical heater to 523 K with the vessel temperature ramping rate to be below 1 °C/min. The vessel pressure is maintained at 0.2 MPa during the heating process.
D) Heat in hydrogen and argon environment. When the vessel temperature reaches 523 K, both hydrogen and argon with molar flow rates controlled at 1:1 are charged to the vessel and the vessel pressure is maintained at 0.2 MPa. Heating the module in such environment until the temperature reaches 873 K and maintained at such temperature for at least 12 h.
E) Vessel cooling down and pressure release. Cool down the pressure vessel to a temperature of 573 K while maintaining the hydrogen and argon flow and reactor pressure. Then shut down the hydrogen flow while maintaining the argon flow. When the vessel is cooled down to ambient temperature, release the vessel pressure and take out the membrane module from the vessel.

Repair permeation factor

Hydrogen permeates through palladium or palladium alloy membranes via the "solution–diffusion" mechanism. It can be described by Sieverts' Law [17,18], i.e.,

$$M_s = Kle^{-\frac{E_p}{RT}}\left(P_H^n - P_L^n\right) \quad (1)$$

where M_S is the hydrogen permeation rate, K is the pre-exponential factor, E_p is the activation energy for permeation, R is the gas constant, T is the temperature, P_H is the hydrogen partial pressure in vessel side, P_L is the average hydrogen partial pressures in the membrane permeate side, and n is the parameter whose value depends on the limiting transport mechanism of hydrogen permeation through palladium or its alloy membrane. l is the membrane