Thin robust Pd membranes for low-temperature application

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It is known that hydrogen embrittlement could result in warping and destruction of pure Pd membranes, which limits the working temperatures to be above 293 °C. This study attempted to investigate the relationship between hydrogen embrittlement resistance and membrane geometry of ultrathin pure Pd membranes of 2.7–6.3 μm thickness. Thin tubular Pd membranes with an o.d. of 4 mm, 6 mm and 12 mm immediately suffered from structural destruction when exposed to H2 at room temperature. In contrast, thin hollow fiber membranes (outer diameter, 2 mm, thickness < 4 μm) exhibit strong resistance against hydrogen embrittlement at temperatures below 100 °C during repeated heating/cooling cycles at a rate up to 10 °C min⁻¹ under H2 atmosphere. This is ascribed to reduced lattice strain gradients during α–β phase transition in cylindrical structures and lower residual stresses according to in situ XRD analysis, which shows a great prospect in low temperature applications.

1. Introduction

Hydrogen embrittlement remains a vital challenge for industrial applications. For example, the high-strength steels looking to use as pressurized hydrogen containers and pipes suffer from hydrogen embrittlement due to hydrogen absorbing at dislocations, grain boundaries or precipitates.† Pd, V, Nb, Ta alloy membranes have attracted extensive attention in hydrogen and its isotopes separation, purification and production in membrane reactors, owing to their extraordinary hydrogen permeability and selectivity.†,‡ The thermal and chemical stability of Pd membranes represent a great challenge for their wide applications, e.g. α to β phase transition at temperatures below 573 K and at pressures below 20 bar, leading to large difference in lattice parameters and significant structural deterioration to the membranes,§–⊥ and the presence of sulfur-containing species leading to the formation of palladium sulfide species as in the case of zeolite catalysts.‡⁰–‡³ Several strategies have been developed to improve the stability, e.g., Pd nanoparticles packed inside the porous support to suppress the α to β phase transition,‡⁴± and the formation of Pd–Ag, Pd–Cu or Pd/Y alloys.‡⁵,‡⁶

The application of pure Pd membranes often limits its operating temperature above 300 °C.‡⁷–‡⁹ There are two phases in the Pd–H system, the one with lower hydrogen content is called α-phase, and the hydrogen-rich phase is usually termed β-phase. When below the critical temperature about 293 °C and at hydrogen pressure < 20 bar, the β-phase nucleates and grows in α-phase and this system is possible for the two phases to coexist.‡²–‡⁵ The α- and β-phase have the same lattice symmetry but very different volumes, for example, at 25 °C the H/Pd ratio of α-phase is about 0.015, whereas β-phase has nH/nPd ≈ 0.7 at 1 bar.‡⁶,‡⁷ When phase transition occurs, the expansion of volume for the phase transition is over 10%, which is accompanied by considerable mechanical stress and leading to the fracture of membrane.‡⁸,‡⁹,‡¹⁰

It is reported that the shear stress generated during the hydrogen absorption process significantly decreases when reducing the radius of the tubular structure.‡⁹ On the other hand, residual stresses, which are defined as stresses remaining in material or body after processing, in the absence of external forces or thermal gradients, can exist after many manufacturing processes involving heat treatment, machining or processing operations. They influence the properties of the component and its lifetime.‡⁰ Moreover, residual stresses play an important role in the crack formation, and they can translate into stress intensity factors acting on cracks that nucleate and propagate around the imperfections.‡¹ Because of these considerations, this study attempted to fabricate thin Pd membranes on capillary tubular support, which is expected to reduce the internal stress and correlated lattice strain gradients and thus suppress hydrogen embrittlement due to α–β phase transition.

2. Experimental

2.1 Fabrication of the membranes

Porous tubular supports with an outer diameter of 2 mm (porous alumina tubes with an average pore size of 100 nm,
Table 1  Performance data of the membranes investigated in this study

| Diameter (mm) | Porous support | Thickness (µm) | N₂ flux<sup>a</sup> (mol s<sup>-1</sup> m<sup>-2</sup>) | N₂ flux<sup>b</sup> (mol s<sup>-1</sup> m<sup>-2</sup>) | Multiple |
|---------------|----------------|---------------|---------------------------------|---------------------------------|----------|
| 2.00          | Alumina        | 4.00          | 2.12 × 10<sup>-10</sup>          | 3.72 × 10<sup>-11</sup>        | 0.18     |
| 2.00          | Alumina        | 2.70          | 2.70 × 10<sup>-10</sup>          | 3.12 × 10<sup>-10</sup>        | 1.16     |
| 4.00          | Alumina        | 3.50          | 7.69 × 10<sup>-9</sup>           | 1.66 × 10<sup>-8</sup>         | 2.16     |
| 6.00          | Alumina        | 3.90          | 4.43 × 10<sup>-10</sup>          | 1.10 × 10<sup>-8</sup>         | 24.86    |
| 12.00         | Alumina        | 6.30          | 1.25 × 10<sup>-9</sup>           | 2.02 × 10<sup>-8</sup>         | 16.15    |

<sup>a</sup> Before feeding hydrogen.  <sup>b</sup> After feeding hydrogen.
3. Results and discussion

3.1 Investigation of hydrogen embrittlement resistance at low temperatures

As mentioned above, P-2, P-4, P-6 and P-12, were exposed to H₂ at room temperature to evaluate the hydrogen resistance with pressure differential alternating between 1 bar and 4 bar (Table 1). It can be seen from Table 1 that the N₂ leak rate of P-6 and P-12 increased about 16–24 times immediately after exposure to H₂, indicating fracture of membranes. On the contrary, the N₂ flux of the P-4 only increased slightly and the P-2 remained almost unchanged, implying a strong resistance to hydrogen embrittlement. Fig. 2 shows surface and cross-sectional images of P-2, which exhibits a dense membrane surface and homogeneous thickness. No pinholes or micro pores can be observed from the images. There appear Pd grains on the membrane surface which represents the typical morphology of Pd membranes fabricated via electroless-plating approach.

To further investigate the hydrogen embrittlement resistance of P-4 and P-2, it was tested under repeated heating/cooling cycles between room temperature and 100 °C under a hydrogen atmosphere at a feed/permeate pressure differential up to 10 bar. The N₂ leak rate was measured at a 4.5 bar pressure differential between the temperature cycles as shown in Fig. 3 to evaluate the integrity of the membrane. It can be seen that both H₂ and N₂ flux of P-2 remained stable after 8 repeated cycles, after exposure to hydrogen atmosphere below 100 °C for about 157 h in total, while N₂ flux of P-4 increased steadily and tripled after 6 cycles. Note that the H₂ flux obtained was at an appreciable level of 10⁻⁷ mol s⁻¹ m⁻² Pa⁻¹ under the operating temperature of 100 °C and 10 bar pressure differential, which exhibits great prospects for low-temperature applications.

Meanwhile, as shown in Fig. 4, the surface morphology of P-2 before and after heating/cooling cycles is basically unchanged, and there is no major change in the surface grain size (Fig. 4a and b).

Subsequently, in situ XRD analysis was carried out to clarify the different behavior of these tubular membranes in the coexistence of α and β phase at room temperatures. The scanning procedure is as below: the scan was first conducted under N₂ atmosphere, and then switched to H₂ atmosphere, with each scan lasting for 1.5 min. Fig. 5 shows the in situ XRD patterns of Pd membranes with a diameter of 2 mm, 6 mm, and 12 mm, respectively. Peaks appearing on the right correspond to (111) of...
Fig. 4  SEM images of P-2 surface (a) and (c) before heating/cooling cycles, (b) and (d) after heating/cooling cycles.

Fig. 5  In situ XRD patterns of (a) P-2, (b) P-6 and (c) P-12 at room temperature when exposed to N$_2$ and H$_2$ atmosphere. (d) Comparison of the intensity of the $\alpha$-phase and $\beta$-phase peaks of P-2, P-6 and P-12 at the third minute.
Pd and a-phase, and the peaks on the left can be indexed to b-phase. Interestingly, it is found that the peaks of a-phase of P-2 and P-6 completely disappeared after 4.5 min of feeding hydrogen whereas that of P-12 disappeared after 6 min of feeding hydrogen. Fig. 5d shows the comparison of the peak intensities of P-2, P-6 and P-12 at 3rd min, which can be seen that the a-phase of P-2 is only 14.4% of the b-phase, the a-phase of P-6 is 44.7% of the b-phase, and the b-phase of P-12 is only 27.3% of the a-phase, implying that it takes a longer time to complete phase transition as to P-6 and P-12 than P-2.

It is known that the coexistence of two unequal phases with different specific volume causes internal stress.2 Since P-2 completes the α–β phase transition at the highest rate, the risk of lattice distortion due to internal stresses is diminished. This provides an explanation for the strong resistance of thin hollow fiber Pd membranes, as compared to conventional tubular membranes, is attributed to tubular structure effects originating from the suppressed internal stress, which coincides with modeling studies.29

Fig. 6a–c shows that the phase transition of pure Pd membranes occur in the temperature range of 150 °C to 200 °C at a feed pressure of 2 bar which has no relation to varying diameters, i.e. 2 mm, 6 mm and 12 mm. Fig. 6d indicates that the β–α phase transition is completed at temperatures above 170 °C for these membranes. Further detailed analysis (Fig. 7) shows that the peak change is completed at 150 °C for P-2 while there is certain α phase remaining as to P-6 at 150 °C, corroborating the faster phase transition process and shorter-term coexistence of two phases in P-2 with a lower diameter.

3.2 The phase transition investigation of P-6 at varying temperatures and pressures

It is known from above that the phase transition for P-2, P-6 and P-12 occurs at temperatures below 200 °C at a feed pressure of 2 bar, implying that these membranes can avoid destruction in H2 atmosphere at temperatures above 200 °C. Fig. 8 indicates that both H2 and N2 permeation of P-6 remained at a steady level during 8 repeated cycles between 200 and 400 °C under H2 atmosphere, except the slight increase after the first cycle. This observation confirmed the above results.

To further investigate the phase transition of P-6 at higher pressures, the feed pressure was increased from 2 bar to 10 bar while the permeate pressure remained as 1 bar. Fig. 9 shows the activation energy of H2 permeation between 200 °C and 400 °C at a feed/permeate pressure of 10/1 bar, which exhibits two stages in the temperature range of 200–250 °C and 250–400 °C. Note that the N2 permeation of P-6 tripled during the following 10 repeated cycles between 200 °C and 400 °C, while an obvious increase in N2 permeation was observed after only 4 repeated cycles between RT and 400 °C (Fig. 10). This implies the hydrogen embrittlement resistance at temperatures above 200 °C for P-6 even at a high feed pressure of 10 bar.
### 3.3 Residual stress measurement

To determine the diffraction crystal plane, a wide-angle scan of the sample was performed, as shown in Fig. 11. Considering the peak intensity and face spacing errors, the (311) face was selected as the diffraction crystal face and the scan range is 80.5°–84° in this study.

According to the equation for stress measurement by XRD method (eqn (2)), the stress $\sigma$ can be obtained from the slope of the line by measuring the diffraction line displacement at multiple $\theta$ angles and using $2\theta$ as the vertical coordinate and sin as the horizontal coordinate to calculate and plot the line closest to each experimental value using the least squares. $\theta$ angles are taken as 0°, 17°, 25°, 30°, 35°, 40°, 45° respectively, Young’s modulus $E$ takes 117 GPa and Poisson’s ratio $\nu$ takes 0.39 (from MatWeb). The results of P-2 and P-4 are plotted in Fig. 12, and the residual stress of P-2 is 248.91 MPa with an uncertainty of ±23.86, and that of P-4 is 701.66 MPa with an...
uncertainty of ±57.47. It is observed from Fig. 12 that P-2 and P-4 show tensile stress and the value of P-4 is greater than P-2, which means that P-2 is more resistant to fatigue than P-4. Given that the other fabrication conditions of P-2 and P-4 are the same, the greater tensile stress in P-4 than in P-2 is attributed to the difference in diameter. This may offer a new route for the development of metal materials against hydrogen embrittlement from the structural design point of view.

4. Conclusions

Thin hollow fiber Pd membranes (o.d. 2 mm, thickness < 4 μm) show strong resistance against α-β phase transition at temperatures between room temperature and 100 °C, and Pd membrane with a diameter of 4 mm also exhibits some degree of resistance to hydrogen embrittlement in this temperature range, whereas tubular membranes with an increased diameter of 6 mm and 12 mm immediately suffered from hydrogen embrittlement upon hydrogen exposure at room temperature.

In situ XRD analysis indicates a faster phase transition process and shorter-term coexistence of two phases in Pd membranes with a lower diameter. On the other hand, the stress measurement by XRD method presents a higher tensile stress for Pd membranes with a higher diameter. This is ascribed to reduced internal stress and lattice strain gradients with the decrease of the radius in cylindrical structures and lower residual stress, which may provide a route for the suppression of hydrogen embrittlement of other metal materials.

Conflicts of interest

There are no conflicts to declare.

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