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Effects of thickness and thinning methods on hydrogen permeation of Pd-plated V-15Ni membranes

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1. INTRODUCTION

Inexpensive methods for producing large amounts of highly pure hydrogen are required for the deployment of fuel cells since platinum, which is used as the electrode catalyst of polymer electrolyte fuel cells (PEFC), loses its electrode activity in the presence of trace amounts of CO of only 10 ppms. Metallic membranes for hydrogen separation can produce highly pure hydrogen of 7N (99.99999%) in one single step, but are not widely used since the only practical membrane available today, which is palladium-silver alloy, is expensive. Therefore, some attempts have been increasingly reported to use non-palladium based metal or alloys for hydrogen purification. [1-7]

The National Institute for Materials Sciences has investigated hydrogen separation membranes made of vanadium-15 nickel (V-15Ni) alloy, which has a higher hydrogen permeability and is much cheaper than palladium alloy. [8-10] Separation membranes should be made as thin as possible to increase hydrogen permeation flux. However, thinner membranes are increasingly affected by processes other than the hydrogen diffusion within the membranes, and so the flux does not increase in proportion to the inverse of the membrane thickness.

In this study, hydrogen permeation tests were conducted on specimens whose thickness was adjusted by polishing and cold rolling to obtain basic data for increasing hydrogen permeation flux.

2. EXPERIMENTALS

V-15Ni alloy was arc melted in an argon atmosphere, hot rolled, and prepared into plates of about 7 mm thickness. The plates were cut using an electric discharge machine, and the resultant pieces were cold rolled to a thickness of about 0.5 to 0.1 mm. Disks of a diameter of 12 mm were cut from the rolled plates, heated in vacuum at 1300℃ for 1 hour, and quenched to produce a bcc solid solution. Membrane specimens of 0.4 to 0.1 mm thickness were used. Specimens were prepared in two different ways. One set of samples was thinned by mechanical polishing, and the other set was cold rolled to the nearly desired thickness and then slightly polished for finishing. All the disk specimens were then chemically polished, subjected to fast atom bombardment in a DC sputtering machine for 45 minutes to clean the surface, covered by a layer of Pd-25Ag to a thickness of about 100 nm on both surfaces, and used as specimens for permeation tests. Hydrogen permeation tests were conducted using hydrogen of 7N purity (99.99999%) in a temperature range of 200℃ to 400℃. Hydrogen pressure of 100 kPa was applied on the primary side, and the secondary side was vacuum pumped. Diffusion coefficients were determined by the time-lag method from the initial section of the pressure build-up curve, and hydrogen permeability was determined using a mass flowmeter after the flow became steady.

3. RESULTS AND DISCUSSION

The diffusion coefficients of V-15Ni specimens that were polished to adjust the thickness are shown in

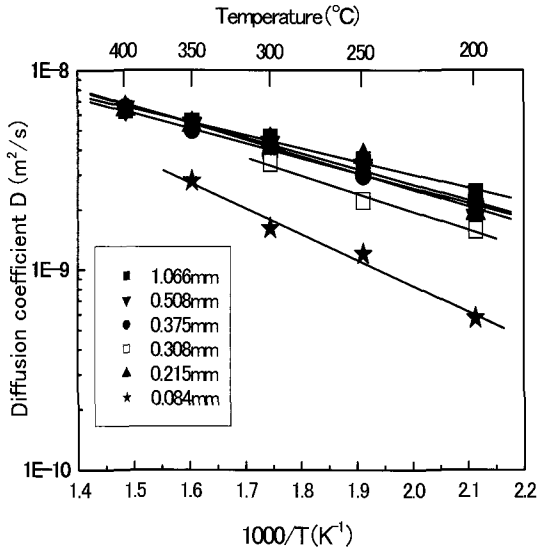

Fig.1 Diffusion coefficients of V-15Ni membranes prepared by polishing

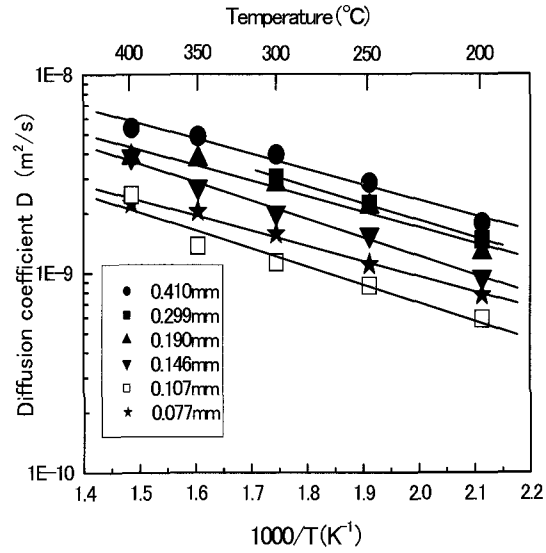

Fig.2 Diffusion coefficients of V-15Ni membranes prepared by rolling

Figure 1. The thinnest specimen, 84 μm thick, showed a steeper curve than the other specimens, suggesting increases in activation energy for diffusion. This was likely because the strain produced while processing the specimens had a larger effect in thinner specimens.

The diffusion coefficients of V-15Ni specimens that were rolled to adjust the thickness are shown in Figure 2. No differences in curve inclination are shown between specimens, but the thinner the specimens, the smaller the diffusion coefficient in general, resulting in differences in the exponential term in appearance. A possible cause of the differences was that the intensively rolled specimens received large deformation which prevented removal of the oxidized layer by mechanical polishing and so the layer remained on the surface, which extended the apparent diffusion distance hydrogen and affected the time lag and the resultant diffusion coefficients. The actual causes, however, have not been clarified.

The hydrogen permeability of the V-15Ni specimens that were polished to adjust the thickness is shown in Figure 3. The figure also shows the hydrogen permeability of Pd-25Ag (0.493 mm) for comparison. The V-15Ni showed higher hydrogen permeability than Pd-25Ag, which is already used in practice, especially at low temperatures such as 200°C. The 84-μm thick specimen showed high hydrogen permeability but not at low temperatures, suggesting that the strain induced

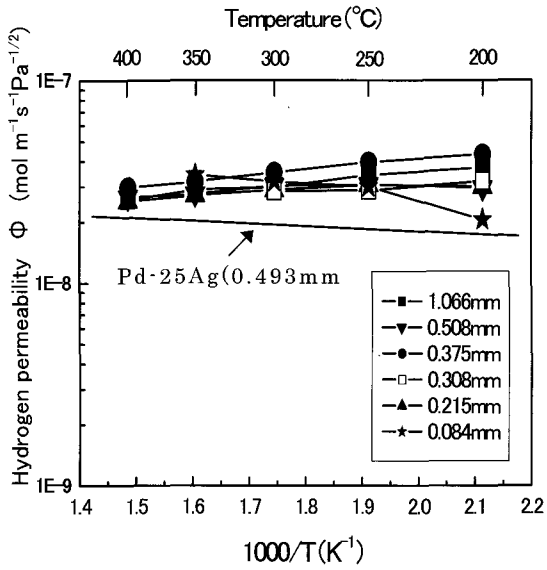

Fig.3 Hydrogen permeability of V-15Ni membranes prepared by polishing

by polishing affected hydrogen permeability.

The hydrogen permeability of the V-15Ni specimens that were rolled to adjust the thickness is shown in Figure 4. Thinner specimens showed lower hydrogen permeability. This was likely because the rolled sheet was not flat and mechanical polishing could not remove the oxidized layer. Thus, the apparent hydrogen permeation area was reduced, and the effect was larger in thinner specimens.

The hydrogen permeability of the V-15Ni specimens

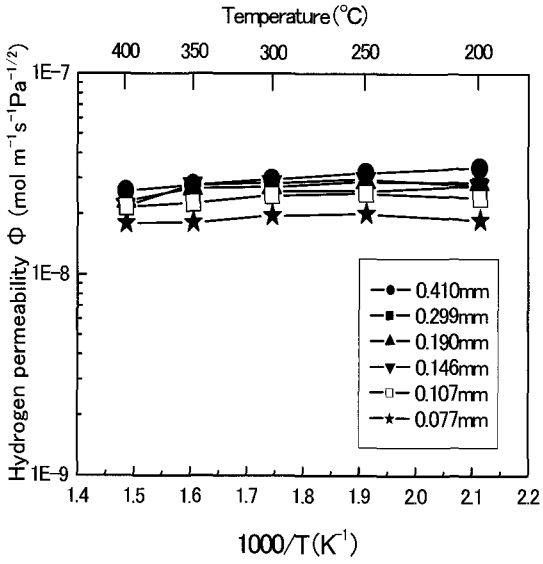

Fig.4 Hydrogen permeability of V-15Ni membranes prepared by rolling

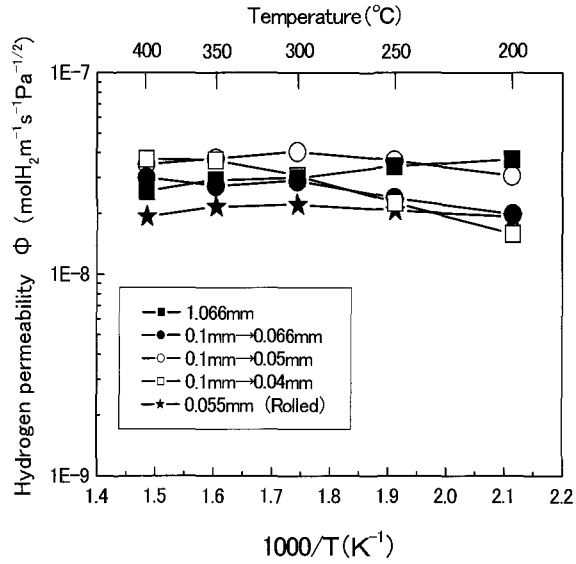

Fig.5 hydrogen permeability of V-15Ni membranes prepared by rolling to 0.1mm and then thoroughly polished

that were cold rolled to a thickness of 0.1 mm and then thoroughly polished to further reduce the thickness is shown in Figure 5. The figure also shows the permeability of specimens prepared by cold rolling to 55 μm and polished so that the buff was in contact with the specimen surface as much as possible. The test revealed that even thin membranes can show high hydrogen permeability when the oxidized layers are carefully removed from the surface.

The relationship between the membrane thickness and hydrogen flux measured is shown in Figure 6. In specimens cold rolled to adjust the thickness, the flux did not increase in proportion to the inverse of the membrane thickness for thickness of less than 0.15 mm. The other specimens, which were either polished or rolled to 0.1 mm and then thoroughly polished to reduce the thickness, showed ideal fluxes, which increased in proportion to the inverse of the thickness. The specimen prepared by rolling to 55 μm and polished carefully with a buff showed higher flux than what was predicted for simply rolled specimens (dashed line). The results suggest that V-15Ni membranes of high hydrogen purification rate can be obtained by rolling to several tens of microns and developing an appropriate method for cleaning the surface.

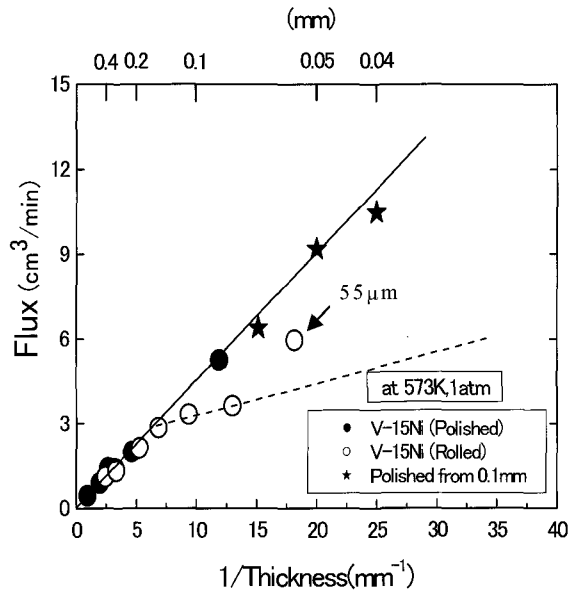

Fig.6 Relationship between membrane thickness and flux of V-15Ni alloy

4. CONCLUSIONS

To investigate the effects of membrane thickness on hydrogen permeation of V-15Ni alloy covered by Pd-25Ag and methods for preparing thin membranes, hydrogen permeation tests were conducted using specimens prepared by polishing and cold rolling at a temperature range of 200℃ to 400℃. The principal results were as follows:

(1) Specimens prepared by adjusting the thickness by polishing and those that were rolled to 0.1 mm and then thoroughly polished showed ideal fluxes at temperatures above 300 ℃ , which increased in proportion to the inverse of the thickness.

(2) Rolling to a thickness below 0.15 mm resulted in lower fluxes than the ideal values. This was likely because the oxidized layer could not be removed by mechanical polishing, thus reducing the apparent hydrogen permeation area of the V-15Ni specimens.

(3) Properly polished specimens that were rolled to 55 μm resulted in high flux. The result suggests that V-15Ni membranes of high hydrogen purification rate can be prepared by rolling to several tens of microns and then properly cleaning the surface.

5. REFERENCES

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