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V–Ni alloy membranes for hydrogen purification

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Abstract

In order to establish technical fundamentals for practical application of V–15%Ni alloy developed for hydrogen purification membrane, deformation behavior and hydrogen permeation performance of Pd-plated cold-rolled and unrolled samples have been examined. Once the solidification microstructure was refined by plastic works at high temperatures, cold rolling could be performed without any difficulty to produce thin strips. Pd-plated membranes machined from a cold-rolled sheet of V–15Ni alloy exhibited slight trapping behavior of hydrogen, resulting in a decrease in apparent hydrogen diffusivity and steady-state hydrogen permeability. Nevertheless, the hydrogen flux was observed to increase inversely in proportion to the thickness of the membrane due to a much greater influence of thinning on the permeation flow. The durability tests showed that hydrogen permeability decreased by 5% in 2 weeks at 573 K and 30% in 1 week at 473 K. The deteriorated permeability was recovered successfully by a baking treatment.

Keywords: Vanadium; Hydrogen; Permeation; Purification; Membrane

1. Introduction

The production of high purity hydrogen gas is an important technical issue, which is related to future energy and environmental problems.

Vanadium is one of the most hydrogen-permeable metals because of its high hydrogen diffusivity and solubility. The intrinsic hydrogen permeability of vanadium is much higher than that of palladium–silver (Pd–Ag) alloys which have been commercially used for hydrogen purification membranes. Some attempts have been reported to use Pd-plated vanadium or other Va metals as hydrogen purification or extraction membranes [1–4]. However, vanadium has not been recognized as a possible membrane material for hydrogen purification due to hydrogen embrittlement problems, especially at low temperatures. We have demonstrated that Pd-plated disks of V–Ni, V–Co and V–Mo alloys maintained high hydrogen permeability even at low temperatures, around 473 K and it showed a good resistance to the hydrogen-induced cracking during hydrogen permeation runs [5–7].

In this paper, hydrogen permeation performance and durability of Pd-coated V–15Ni alloy membrane are reported. Deformation behavior of the alloy at high temperatures is also briefly described.

2. Experimental

Two V–15 mol% Ni alloys with 0.05 mol% Ti and 0.05 mol% Y, respectively, were prepared by arc melting in an argon atmosphere, where Ti and Y were used as deoxidizers. The purities of vanadium, nickel, titanium and yttrium, used as charging materials were over 99.9%. Button ingots of 150 g were obtained by arc melting at least five times. The ingots were homogenized at 1523 K for 1 h under a vacuum below 4×10^{-3} Pa. V–15Ni–0.05Y alloy was used only for a long-period permeation test. V–15Ni–0.05Ti alloy was used for compression test and standard permeation test. Hereafter, the alloys will be simply noted as V–15Ni alloy in the text, since there are no essential differences in the two alloys.

In order to check the plastic workability of the V–15Ni alloy to a thin sheet, high temperature compression tests were carried out at 1373 K and 1523 K at a constant strain rate of 1×10^{-3} s^{-1} under argon atmosphere.

Disk samples of 12 mm in diameter were used for hydrogen permeation tests. Two sets of V–15Ni alloy samples were used for hydrogen permeation tests, i.e. with and without cold rolling. Samples without cold rolling were directly machined from the homogenized ingot, and were thinned to certain thicknesses by mechanical polishing, finished by alumina abrasive of 0.05 μm. The cold rolled samples were prepared as follows. A cut piece from

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the alloy ingot was encapsulated in a steel container and hot rolled at 1323 K to a strip of 5 mm thickness. The strip was then cold rolled to a thickness of 0.3~0.4 mm. Surface oxides were removed using a solution of hydrofluoric acid:nitric acid:lactic acid=1:1:1 in volume. Then, all the V–15Ni alloy samples were processed in the same way as follows. The samples were annealed at 1473 K for 15 min. under a vacuum of 4×10^{-4} Pa and rapidly cooled to obtain a bcc solid solution. They were chemically polished and then quickly placed in an ultra high-vacuum chamber for vacuum deposition of palladium. A palladium overlayer of 0.1 μm thickness was deposited on both sides as a hydrogen dissociation catalyst. Hydrogen permeation was performed in a conventional gas-permeation apparatus described in previous works [5–7] in the temperature range of 423–673 K, using a high purity hydrogen gas. Steady-state hydrogen permeabilities were determined by a mass flow transducer, and apparent diffusion coefficients of hydrogen were determined by the time-lag method. For comparison, hydrogen permeation was also performed for Pd–25Ag samples, prepared from an as-received sheet (thickness=0.505 mm) and a cold rolled sheet (thickness=0.111 mm).

3. Results and discussion

Our previous tensile tests of V–15Ni alloy at room temperature gave the yield strength of 500 MPa [8], which is four times higher than that of pure vanadium. When we attempted cold rolling of as-cast or annealed ingots, cracking from the side surfaces prevented further rolling. However, the alloy possesses relatively good ductility exceeding 20% total elongation, so the cold rolling is expected to be possible, once the solidification microstructure is refined by deformation at high temperatures. Before trying hot rolling, compression tests were performed to investigate the deformation behavior at 1373 and 1523 K.

Fig. 1 shows the stress–strain curves of V–15Ni alloy compression-tested in argon atmosphere at a constant strain rate of 1×10^{-3} s^{-1}. At 1373 K, the yield strength was about 70 MPa and the flow stress gradually decreased as the plastic deformation proceeded to a value of 54 MPa at a total strain of 0.46 where the test was stopped. At 1523 K, the yield strength decreased to 23 MPa, followed by uniform deformation at a constant flow stress. The yield strengths of the alloy were markedly lower at high temperatures than the room-temperature value of 500 MPa. Therefore, hot rolling was expected to be carried out without difficulty. Indeed, hot rolling was carried out with ease; it was possible to decrease the thickness of the alloy block from the initial value of 15–5 mm finally, at a reduction rate of 1 mm per pass at 1323 K.

Once the solidification microstructure was destroyed by hot rollings, the alloy was successfully cold rolled to a thickness of 0.3 mm which was a performance limit of the rolls used in this work without any intermediate annealing. Fig. 2 shows the appearance of the cold-rolled strips of V–15Ni alloy. The small piece shown at the bottom right in Fig. 2 is the alloy piece before cold rolling with a thickness of 5 mm. Some of the samples for hydrogen permeation tests were prepared from these cold-rolled strips.

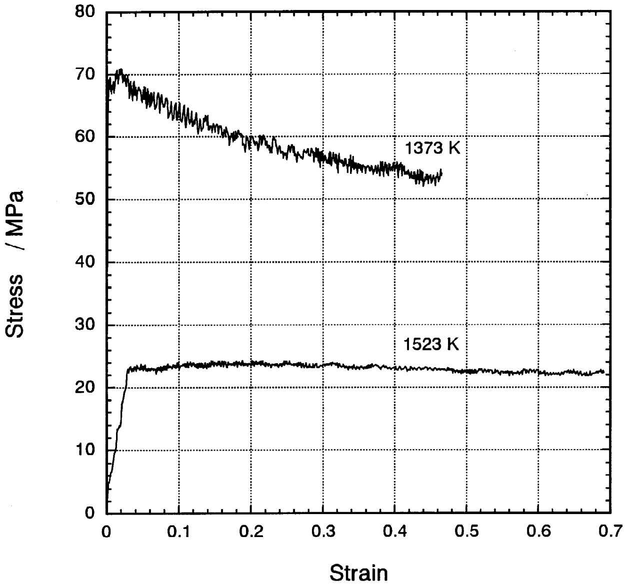

Fig. 1. Stress–strain curves for V–15Ni alloy, compression-tested in argon at a strain rate of 1×10^{-3} s^{-1}.

Fig. 3 shows the temperature dependence of apparent diffusion coefficients for Pd-plated V–15Ni, and Pd–25Ag samples. There are three sets of specimens: unrolled V–15Ni (circles), cold-rolled V–15Ni (squares) and Pd–25Ag (triangles). Each set has two types of samples, thin and thick. The thin sample of Pd–25Ag was cold rolled, whereas the thick one was not. When a comparison is made in each set, thickness dependence is seen where the thin sample exhibits lower apparent diffusivity. This thickness dependence implies that the rate-limiting-step was not simply the hydrogen diffusion process in bulk alloy of the membrane, but surface-related steps affected the whole permeation process. Unrolled V–15Ni alloy sample of 0.138 mm showed 20~30% lower diffusivities than the 1.133 mm sample. Similar tendency was seen in Pd–25Ag samples, where a sample of 0.111 mm thickness showed 20~40% lower diffusivities compared to the 0.505 mm thick sample. This suggests that surface reactions on the palladium overlayer are the main cause of the thickness dependence in V–15Ni samples.

When we compare the unrolled V–15Ni membranes and cold-rolled V–15Ni membranes, we notice the stronger temperature dependence in cold-rolled membranes, indicating hydrogen trapping in cold-rolled samples. Calculated activation energies for hydrogen diffusion, E_D, for cold rolled samples and unrolled samples are about 26 and 14

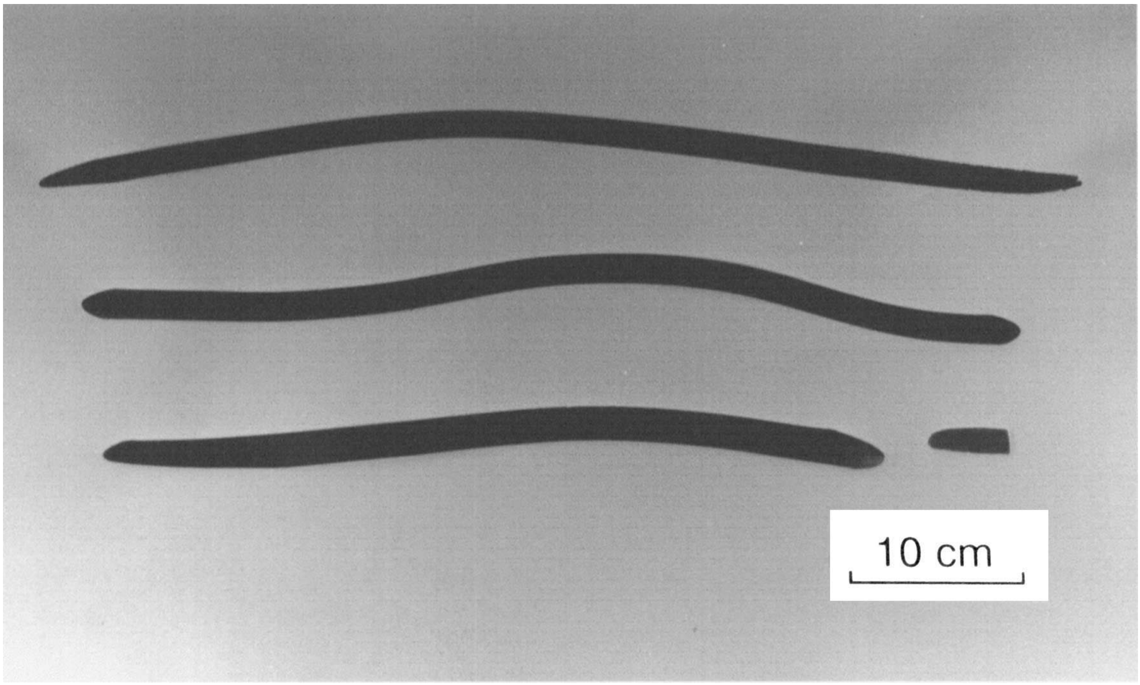

Fig. 2. Appearance of the cold-rolled strips of V–15Ni alloy.

kJ mol^{-1}, respectively. These values agree well with the values for samples with sub-surface trapping [5] and without sub-surface trapping [9], respectively, in our previous works. The removal of oxide layers and/or deformed layers at sub-surface must have been insufficient in cold-rolled samples.

Fig. 4 shows the temperature dependence of hydrogen permeability for Pd-plated V–15Ni, and Pd–25Ag samples. The results from three sets are plotted in the same way as Fig. 3. In all the sets, the two samples exhibit almost identical permeabilities, independent of the thickness. It is in clear contrast to the diffusivity data shown in Fig. 3, where the thickness dependence is obviously seen in each set. It must be noted here that the permeability was determined from the steady state hydrogen flow which was

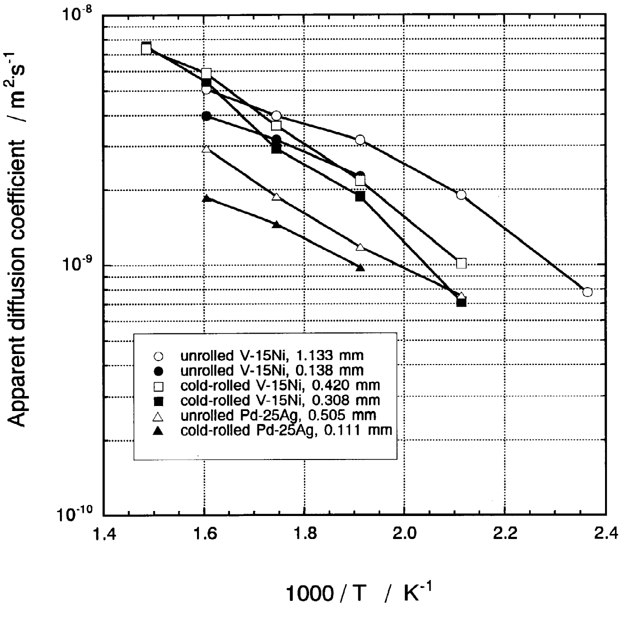

Fig. 3. Temperature dependence of apparent hydrogen coefficients for Pd-plated V–15Ni alloy, cold-rolled (squares) and unrolled (circles), and Pd–25Ag membranes (triangles). Pd–25Ag membranes were used without Pd layer.

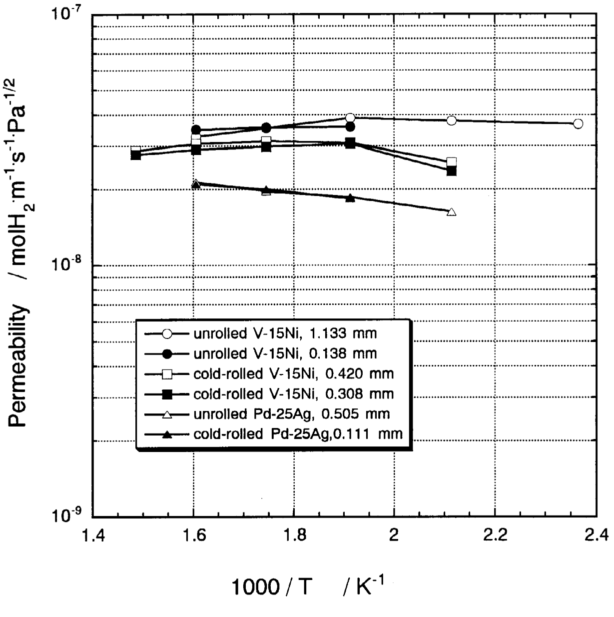

Fig. 4. Temperature dependence of hydrogen permeabilities for Pd-plated V–15Ni alloy, cold-rolled (squares) and unrolled (circles), and Pd–25Ag membranes (triangles).

obtained 5–20 min after the hydrogen pressure was applied, whereas the apparent diffusion coefficient was calculated from the initial transient of the pressure build-up curves at the exit side of the membrane. Thus, the hydrogen permeability was less prone to surface-related steps than diffusion coefficient, because equilibrium of surface reaction was already achieved. Cold-rolled samples of V–15Ni alloy (squares) showed slightly lower permeabilities compared to unrolled samples (circles). As mentioned above, we believe that main origins of the trapping effect lay in oxide layers and/or deformed layers at sub-surfaces [9].

Fig. 5 shows the thickness dependence of the hydrogen permeation flux for Pd-plated V–15Ni alloy membranes at 523 K. It is clearly demonstrated that hydrogen permeation flux increased inversely proportional to the thickness of the membrane at this temperature. Hydrogen permeation flux achieved by Pd-plated V–15Ni alloy membranes was nearly twice that of Pd–25Ag membranes at the same thickness. A higher hydrogen permeation flux is expected to be obtained with further thinning of the alloy.

Membrane durability test has also been performed. Figs. 6 and 7 show the change in hydrogen permeability of a Pd-plated V–15Ni alloy membrane during a continuous permeation operation up to 2 weeks, at 573 and 473 K, respectively. The durability test at 573 K gave little decrease in hydrogen permeability as shown in Fig. 6. The permeability decreased about 5% over a 15-day-long operation. The permeability recovered completely by a simple baking treatment, where air was introduced into the apparatus and kept for a few minutes followed by a vacuum pumping. Fig. 7 shows a noticeable decrease in permeability during the test at 473 K. The permeability decreased about 30% in a week. However, again, the baking treatment was confirmed to be effective as shown in Fig. 7. Since the permeability can be recoverable by the baking treatment, the decrease in permeability is attributed to a contamination of the surface of the palladium overlayer instead of the damage of the membrane.

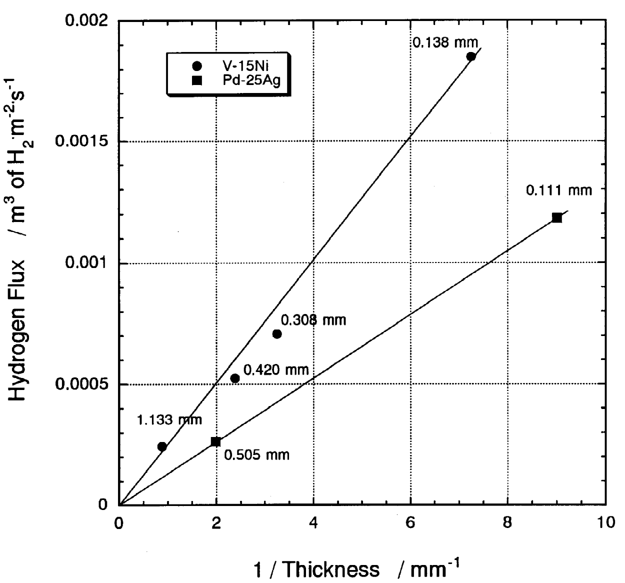

Fig. 5. Thickness dependence of the hydrogen permeation flux for Pd-plated V–15Ni alloy membranes at 523 K.

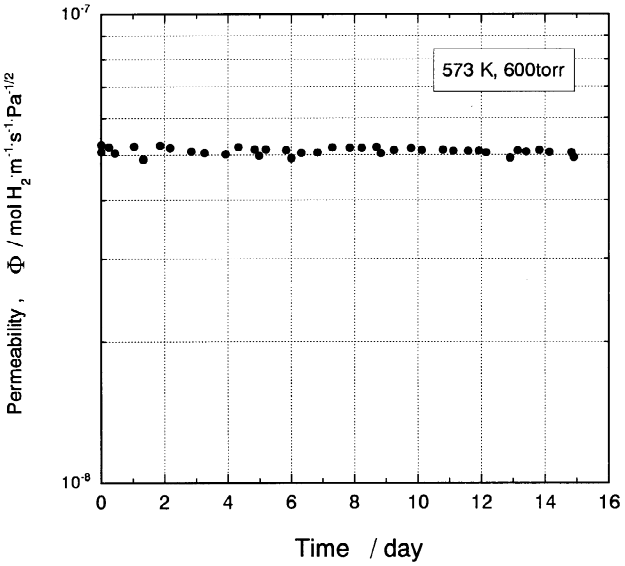

Fig. 6. Change in hydrogen permeability of a Pd-plated V–15Ni alloy membrane during a continuous permeation operation at 573 K for 2 weeks.

4. Conclusions

The high-temperature deformation of V–15Ni alloy was found to be easy and once the solidification microstructure

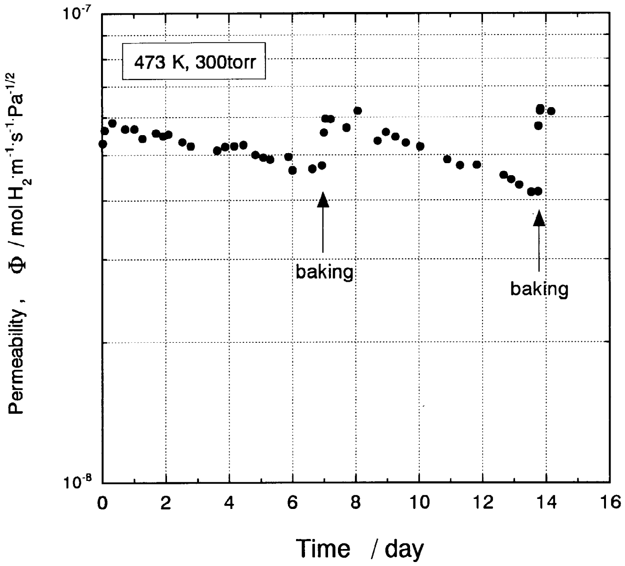

Fig. 7. Change in hydrogen permeability of a Pd-plated V–15Ni alloy membrane during a continuous permeation operation at 473 K for 2 weeks.

was refined, cold rolling was able to be performed to produce a thin strip without any intermediate annealing. Pd-plated membranes machined from cold-rolled strips of V–15Ni alloy exhibited a slight trapping behavior of hydrogen, resulting in a decrease in apparent hydrogen diffusivity and steady-state hydrogen permeability. Nevertheless, the hydrogen flux was observed to increase inversely proportional to the thickness of the membrane due to much greater influence of thinning on the permeation flow. The durability tests showed that hydrogen permeability decreased 5% in 2 weeks at 573 K and 30% in 1 week at 473 K. The baking treatment completely recovered the initial permeability.

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