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Hydrogen permeation and transmission electron microscope observations of V–Al alloys

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Abstract

Hydrogen permeation and transmission electron microscope (TEM) observations were performed for V–Al alloys (10–40 mol% Al). Hydrogen permeability of V–Al alloys decreased with aluminum content, but not in a monotonous manner. Below 20 mol% of aluminum, hydrogen permeability of V–Al alloys decreased linearly with aluminum content. From 20 to 30 mol% of aluminum, hydrogen permeability decreased abruptly. A15 phase which is shown in the V–Al phase diagram was not observed in any samples, quenched from 1373 K or aged at 853 K for 100–350 h. Instead, some precipitates of 200 nm to 1 μm were observed at grain boundaries, sub-boundaries and inside the grains. The amount of the precipitates, however, was too small to explain the significant drop of hydrogen permeability observed in the alloys with more than 20 mol% Al. The long-time permeation test showed that V–10Al sample possessed satisfactory durability to be used as hydrogen purification materials.

Keywords: Vanadium; Aluminium; Hydrogen permeation; Membrane

1. Introduction

The production of high purity hydrogen gas is an important technical issue, which is related to future energy and environmental problems. Membranes of palladium-based alloys have been used commercially for decades to provide high purity hydrogen mainly for laboratory use and semiconductor manufacture. However, palladium-based alloys are usually too costly for large-scale production of high purity hydrogen. Keeping such situations in mind, we developed some vanadium alloys including V–Ni [1,2] for membrane materials to purify and/or separate hydrogen gas instead of palladium-based alloys.

Commercial pure vanadium is produced by electron beam melting (EBM) from V–Al alloys. Then Al element would be one of the main impurities for vanadium-based alloys depending on EBM conditions [3]. The impurities have a great influence on the hydrogen permeation of metals, therefore it is important to know the influence of Al on the hydrogen permeation behavior of vanadium. In a previous work [4], we studied the hydrogen permeation characteristics of V–Al alloys and found that hydrogen permeability of V–Al alloys decreased with the aluminum content, but not in a monotonous manner. Below 20 mol% of aluminum, hydrogen permeability of V–Al alloys decreased linearly with aluminum content. When the Al content increased above 20 mol%, hydrogen permeability decreased abruptly. According to the phase diagram of V–Al system, there exists an A15-structured V_3Al phase between 8 and 38 mol% Al [5].

In this work, hydrogen permeation and TEM observations were performed to make clear whether A15 phase or other precipitates exist and whether they affect the hydrogen permeability of V–Al alloys.

2. Experimental

Pure vanadium (99.9%) and aluminium (99.9%) were used as raw materials. V–Al alloys (10, 20, 25, 30 and 40% Al) were prepared by arc melting in an argon atmosphere. Table 1 lists the results of chemical analysis for Al and residual oxygen. The table indicates that the residual oxygen content decreased as more Al was added. Disk samples were machined directly from the ingots. Then all the disk samples were annealed at 1373 K for 30 min under a vacuum of 3×10^{-4} Pa and rapidly cooled by

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Table 1
Chemical composition of V–Al samples

	Al content (mol%)	Oxygen content (mass%)
V–10Al	9.8	0.0231
V–20Al	20.6	0.0114
V–25Al	26.1	0.0080
V–30Al	29.3	0.0070
V–40Al	39.5	0.0041

argon flow. Some samples of V–20Al, V–25Al and V–30Al were aged at 853 K for 100–350 h under a vacuum of 4×10^{-4} Pa. Both sides of the heat-treated samples were mechanically and chemically polished in sequence. A palladium overlayer of 0.1 μm thickness was deposited on both sides of the disk samples in a physical vapor deposition apparatus. The thickness of the samples were in the range 0.8–2.3 mm. Within this thickness range, the hydrogen diffusion in vanadium alloys would be the rate-limiting step of the whole hydrogen permeation procedure so that the contribution of palladium overlayer and interface-related processes are insignificant [1]. Hydrogen permeation tests were carried out in a conventional gas-permeation apparatus in the temperature range 523–673 K, in the hydrogen pressure range 20–200 kPa, using high purity hydrogen. The steady-state hydrogen permeability was determined by a mass flow transducer.

In addition, the samples before the hydrogen permeation test were analyzed by X-ray diffraction (XRD) and transmission electron microscope (TEM) and atomic force microscope (AFM).

3. Results and discussion

XRD analysis indicated that all the as-prepared V–Al samples were b.c.c. single phase, i.e. solid solution of vanadium regardless the alloys were quenched or aged. Fig. 1 shows XRD patterns for V–25Al, the stoichiometric V_3Al composition. One is for the quenched sample and the other is for the aged sample. XRD revealed no apparent difference in these two samples. Lattice constants were calculated to be 0.3057 nm for the quenched sample and 0.3054 nm for the aged sample. These values are in good accordance with our previous results [4], obeying Vegard's Law. This suggests that the average distance between adjacent interstitial sites, which affects the hydrogen diffusion, changes linearly with Al content.

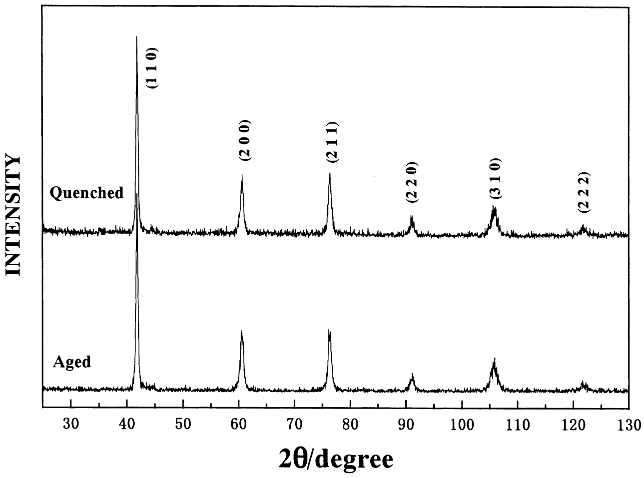

Fig. 1. XRD results of V–25Al alloy after different heat treatment.

Fig. 2 shows the temperature dependence of hydrogen permeability of quenched V–Al alloys. The V–10Al sample showed a high hydrogen permeability of 1.3 to 2.0×10^{-7} mol H_2 m^{-1} s^{-1} $Pa^{-1/2}$. The hydrogen permeability of V–Al alloys decreased with the Al content and reached a value for 30% Al in the range of $0.7–1.8\times10^{-9}$ mol H_2 m^{-1} s^{-1} $Pa^{-1/2}$ at the examined temperature. When the Al content increased to 40%, the hydrogen permeability of V–Al alloy tended to decrease further and was close to the sensitive limits of the experimental apparatus used in this work, so that we could obtain only one plot at 673 K for the V–40Al sample in Fig. 2. We also checked the effects of aging on the hydrogen permeability, resulting in no apparent difference.

Fig. 3 illustrates the variation of hydrogen permeability for V–Al alloys with the solute Al content at 573 and 673 K. Data at 3% Al are reproduced from our previous work [4]. The hydrogen permeability of the V–Al alloys showed good linear relation with Al content below 20% but fell rapidly when the Al content increased further. At 40% Al,

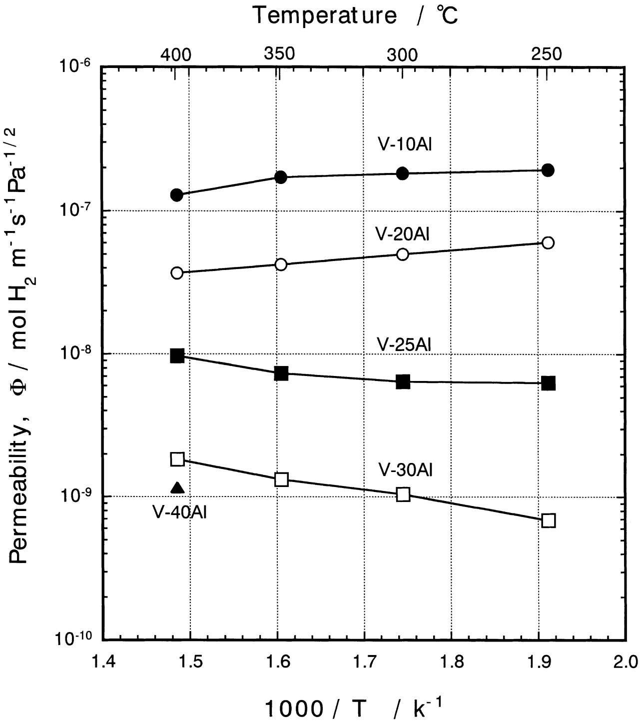

Fig. 2. Hydrogen permeability of V–Al alloys.

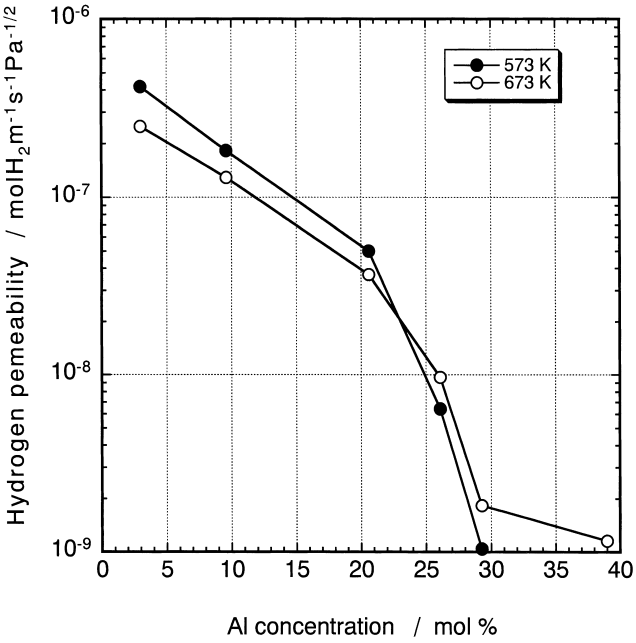

Fig. 3. Al content dependence of hydrogen permeability in V–Al alloys.

the hydrogen permeability decreased but the degree of the permeability drop by Al addition was moderated.

Aiming to elucidate this anomalous behavior of hydrogen permeability, TEM and AFM observations were performed. Fig. 4 shows a typical TEM image of a grain boundary of quenched V–20Al. As shown in the figure, most of the observed grain boundaries were clean and precipitate-free. Fig. 5 shows an AFM image of a grain boundary of aged V–30Al alloy. The sample was slightly etched by a chemical solution, to emphasize the grain boundary. In a wide range of 100 μm, there is no sign of large precipitates at the grain boundary. Instead, some precipitate-like bumps are observed inside the grains. Fig. 6 shows the TEM image of a grain boundary of quenched V–30Al. Two photos were taken with different diffraction conditions for the identical region of the sample, near the center hall of the TEM specimen. Some precipitates of about 200 nm to 1 μm were observed at grain boundaries. Fig. 7 is a TEM image of a sub-boundary observed in the aged V–30Al sample. Plate-like precipitates of about 1 μm in area were observed at the sub-boundary. Using some relatively large precipitates, we attempted the electron diffraction, resulting in a monoclinic structure, with a similar structure of AlV_2C carbide. No sign of A15 phase was obtained.

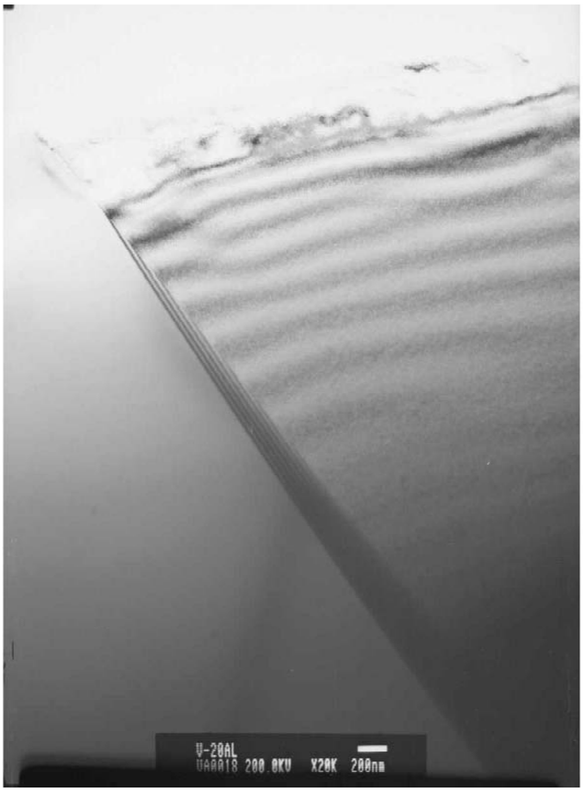

Fig. 4. TEM image of a grain boundary of quenched V–20Al.

We tried all the TEM and AFM observations aiming to clarify whether there is any relation between the anomaly in hydrogen permeability of V–Al alloys and the second phase shown in the phase diagram [5]. Some precipitates were observed at grain boundaries, sub-boundaries and in grains. The amount of those precipitates, however, is too small to explain the significant drop of hydrogen permeability observed in the V–Al alloys with more than 20% Al. Interstitial impurities such as oxygen can trap hydrogen and reduce hydrogen diffusivity [6] and hence permeability. However, in this work, the effects were negligible since the oxygen content decreased with Al content (Table 1). Thus, it is concluded that the reason for a significant fall of hydrogen permeability in V–Al alloys with more than 20% Al lies in the matrix of the b.c.c. phase instead of in a second phase.

Finally, keeping applications of V–Al alloys to the hydrogen separation membranes in mind, we tested the durability of the V–10Al alloy, which exhibits a high hydrogen permeability and a good deformability. Fig. 8 shows the results of a long-time hydrogen permeation test carried out on V–10Al sample at 573 K and under 27 kPa of hydrogen. The hydrogen permeability decreased with time, reaching as low as 22% of the initial value after 136 h. Later, however, after a baking treatment with the introduction of air into the permeation system, the permeability completely recovered to the initial value. This recovery in hydrogen permeability suggests that its initial decrease was not due to permanent damage or change in microstructure, but rather to the concentration of the impurities in the feed gas on the sample surface. The permeability of this sample decreased more rapidly than the permeability of the V–15Ni alloy [2,7]. The hydrogen gas was not purged in our permeation system, and hence higher hydrogen permeability of the sample resulted in the higher rate of the impurity accumulation.

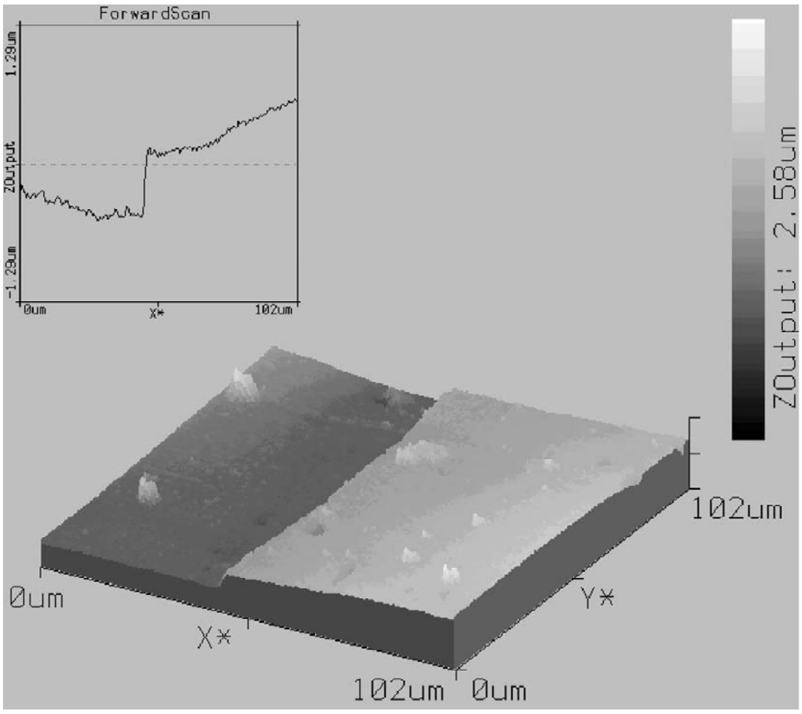

Fig. 5. AFM image of a grain boundary of aged V–30Al alloy.

4. Conclusion

Hydrogen permeation characteristics of V–Al alloys (10 to 40 mol% Al) were investigated. When the amount of Al addition increased above 20 at.%, the hydrogen permeation of V–Al alloys decreased considerably. TEM and AFM observations revealed that the amount of precipitates was too small to explain the significant fall of hydrogen permeability. It was concluded that the reason for a significant fall of hydrogen permeability lay in the matrix of the b.c.c. phase. The long-time permeation test showed that the V–10Al sample possessed satisfactory durability to be used as a hydrogen purification material.

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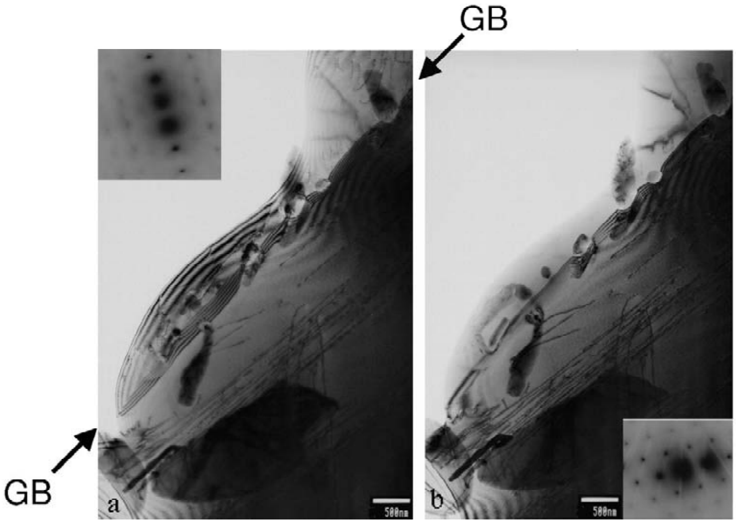

Fig. 6. TEM image of quenched V–30Al.

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Fig. 7. TEM image of a sub-boundary of aged V–30Al.

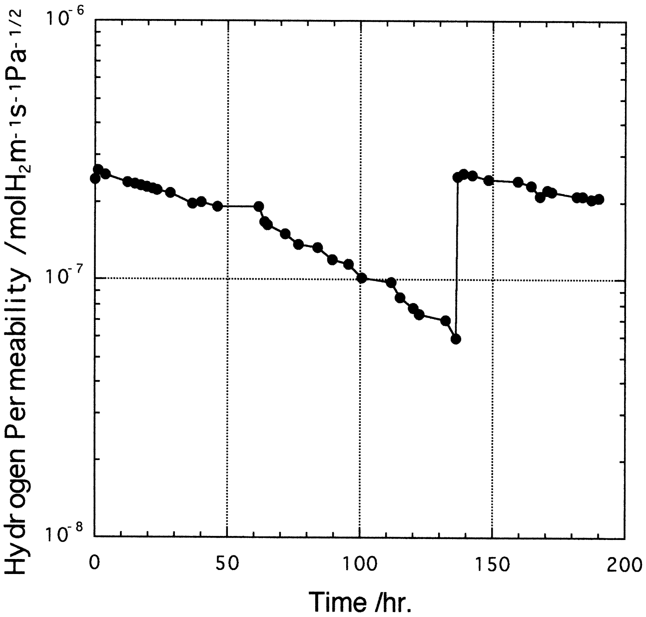

Fig. 8. Time dependence of hydrogen permeability of V–10Al alloy, in long time permeation test at 573 K.

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