

In-situ Observation of Vanadium on Hydrogen Absorption

N. Ohdaira¹, H. Endo¹, M. Kobayashi¹, M. Komaki² and C. Nishimura²

¹Chiba Institute of Technology, Tsudanuma 2-17-1 Narashino Chiba 275-0016 JAPAN,

OHDAIRA.Norio@nims.go.jp, ²NIMS, Sengen 1-2-1 Tsukuba Ibaraki 305-0047 JAPAN

1. Introduction

Hydrogen emits no carbon dioxide when it burns or when energy is taken out from hydrogen fuel cells, and thus is an environment-friendly energy source and a key to preventing global warming. Hydrogen is an important secondary source of energy to support the 21st century, and thus core technologies and related materials should be urgently established to deploy hydrogen energy systems [1].

There is now a growing demand for highly pure hydrogen especially as fuel for fuel cells, which are a promising next-generation type of clean energy system. Highly pure hydrogen is needed because platinum (Pt), which is used as the electrode catalyst of polymer electrolyte fuel cells (PEFC), loses its catalytic activity in the presence of even trace amounts of CO of about 10 ppm, and hence electrode capacity decreases. Thus, technologies for producing highly pure hydrogen need to be urgently developed for the deployment of fuel cells. Highly pure hydrogen of a purity as high as 7N (99.99999%) can be produced using metallic membranes for hydrogen separation, and the only practical membranes available today are made of palladium alloy. However, palladium (Pd) is expensive and has various problems that hinder widespread utilization [2, 3]. The National Institute for Materials Sciences has investigated vanadium (V), whose hydrogen diffusivity and hydrogen solubility are high, and studied the hydrogen permeability and ease of processing and welding vanadium alloy prepared by adding 15 at% of nickel (Ni) [4 - 7]. To enable the alloy membrane to be used in practice, the phenomenon of developing cracks due to hydrogen embrittlement and its crack resistance should be investigated. Actually, easy crack generation was reported for metallic membrane materials based on 5th-group metals [8-10].

An objective of this study was to obtain basic data on the resistance for cracking needed for using the V-15Ni alloy membrane in actual systems. The relationship between

hydrogen concentration and crack generation was investigated by in-situ observation of vanadium and V-Ni alloy at certain temperatures and hydrogen pressures using a microscope equipped with an atmospheric chamber and measuring pressure-composition-isotherms (PCTs).

2. Experimental Procedures

Specimens of pure vanadium and V-15 and % Ni alloy were used. Pure vanadium specimens were prepared by electric discharge machining from a forged mass of commercially available highly pure vanadium (99.9 mass %), cold-rolling, and annealing under a vacuum at 1463 K for 20 minutes. The V-15Ni specimens were prepared by hot rolling and cold rolling, then some were subjected to solution quenching in vacuum at 1573 K for 1 hour. The specimens were mechanically, buff- and chemically polished, and were covered by a layer of Pd-25Ag of about 100 nm thickness on both surfaces by sputtering. The specimens were used for PCT measurement (temperature: 673 to 323 K, hydrogen pressure: 0.001 to 4 MPa) and for in-situ observation under a microscope equipped with a hydrogen chamber at various temperatures (323 to 673 K) and hydrogen pressures (vacuum to 0.1 MPa). After observation, the specimens were taken out from the chamber and were observed by a scanning electron microscope (SEM). To simulate the constraining conditions in the actual permeation process, some V-15Ni specimens were constrained with screws.

3. Results and Discussions

Hydrogen at a pressure of 0.1 MPa was introduced at 573 K to pure vanadium specimens that had not been heat treated. The introduction of hydrogen caused the specimens to expand by about 5% as shown in Figures 1 and 2; at this stage, the specimens showed no cracks. After retaining the hydrogen pressure for 450 seconds to ensure thorough diffusion of

hydrogen, the pressure was suddenly reduced to vacuum. Within several seconds, the specimens fractured as shown in Figure 3.

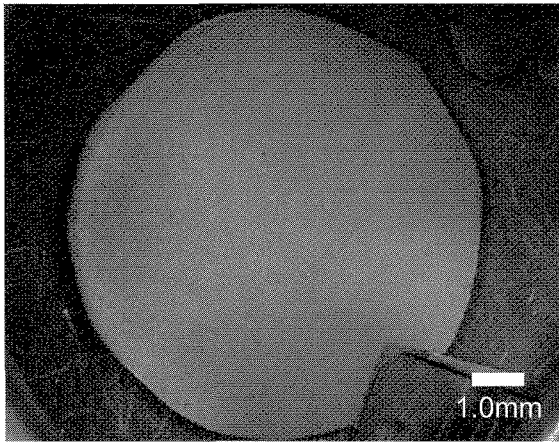


Figure 1 Pure vanadium (573 K, 0 MPa H₂)

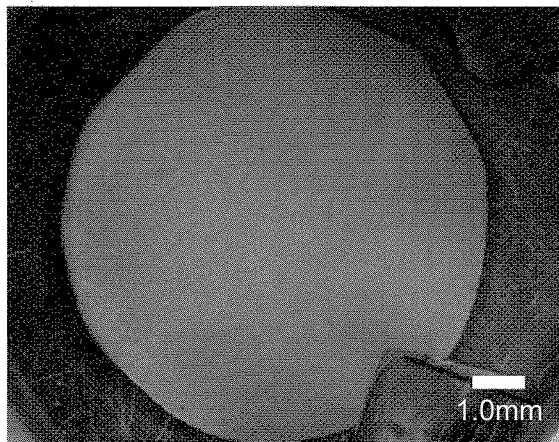


Figure 2 Pure vanadium (573 K, 0.1 MPa H₂)

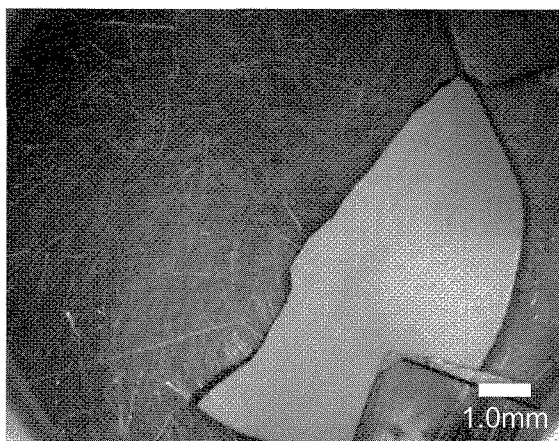


Figure 3 Pure vanadium (573 K, 0.1 – 0 MPa H₂)

Pure vanadium specimens that had been heat treated at 1460 K for 20 minutes were observed at 573 K in exactly the same way. The specimens showed no cracks. When the specimens were observed at a lower temperature of 523 K, the specimens

fractured when the pressure was suddenly reduced to vacuum.

The specimens fractured when the pressure was suddenly reduced to vacuum regardless of whether the specimens had been heat treated. This was likely because vanadium released hydrogen endothermically and the temperature of the specimens dropped when the specimens were exposed to sudden vacuum, causing the specimens to crack. The heat-treated pure vanadium specimens fractured at 523 K and the non-heat-treated specimens fractured at 573 K. This was likely because the non-heat-treated pure vanadium specimens retained the strains produced while it was processed, which facilitated the development of cracks.

In the case shown in Figure 3, the specimen fractured apart; but in the case shown in Figure 4, the specimen developed a crack on the edge at 523 K. When the hydrogen pressure was raised from vacuum to 0.1 MPa, the cracks extended as shown in Figure 5. These results suggest that cracks originated when exposed to sudden vacuum, and the introduction of hydrogen caused the cracks to grow.

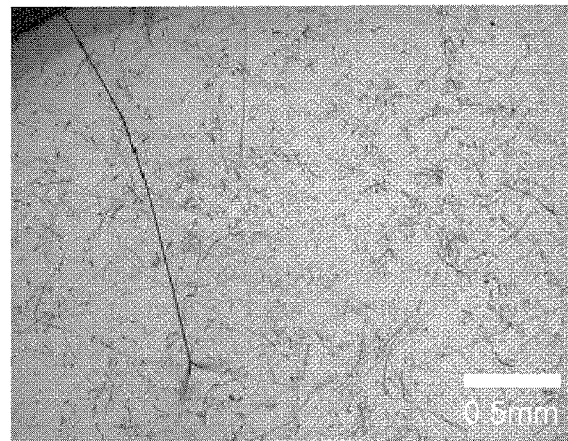


Figure 4 Pure vanadium (523 K, 0 MPa H₂)

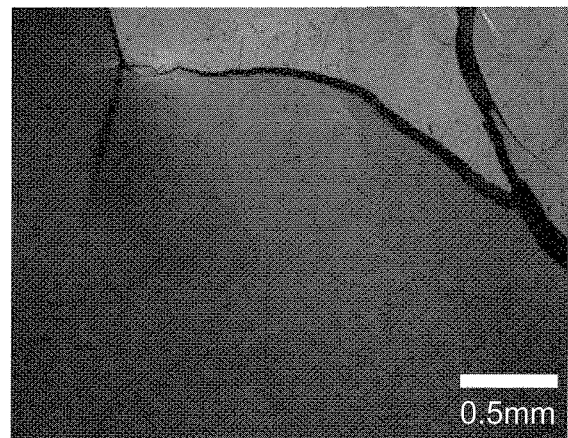


Figure 5 Pure vanadium (523 K, 0.1 MPa H₂)

Then, the temperature was gradually lowered while retaining

the hydrogen pressure at 0.1 MPa. At 428 K, hydrides started to appear as shown in Figure 6, and at 323 K, hydrides accumulated as shown in Figure 7. When the temperature was increased by retaining the hydrogen pressure at 0.01 MPa, the hydrides gradually disappeared as shown in Figure 8.

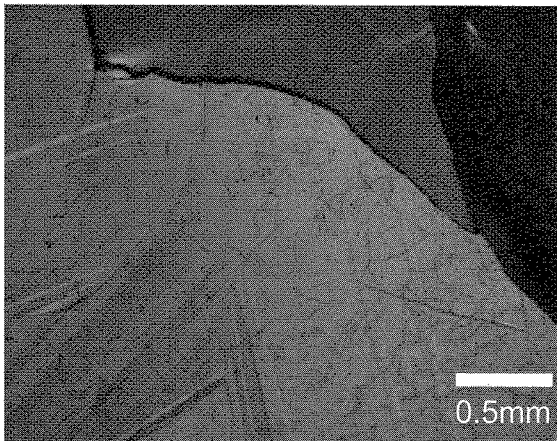


Figure 6 Pure vanadium (428 K, 0.1 MPa H₂)

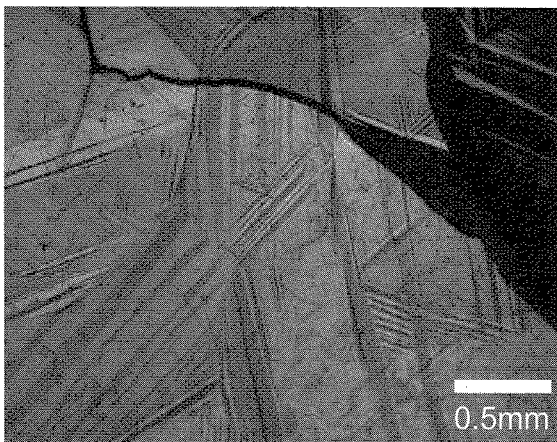


Figure 7 Pure vanadium (323 K, 0.1 MPa H₂)

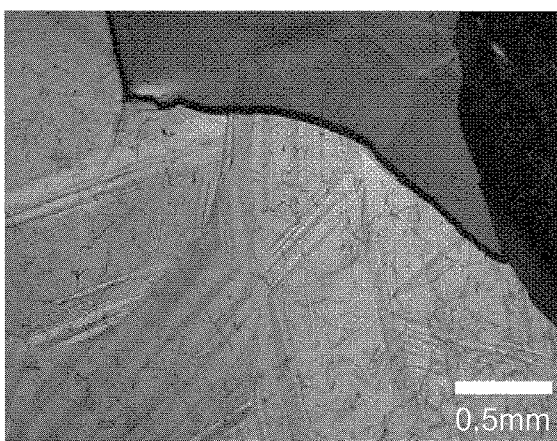


Figure 8 Pure vanadium (453 K, 0.01 MPa H₂)

a hydrogen pressure of 0.05 MPa (Figure 9). Under this optical microscope, no cracks were observed, but when the specimens were taken out and observed under an SEM, the following cracks were observed. As shown in Figure 10, there were cracks where a thermocouple had been attached by spot welding. Figure 11 shows a crack under a washer constrained by a screw. No other cracks were observed in the V-15Ni specimens.

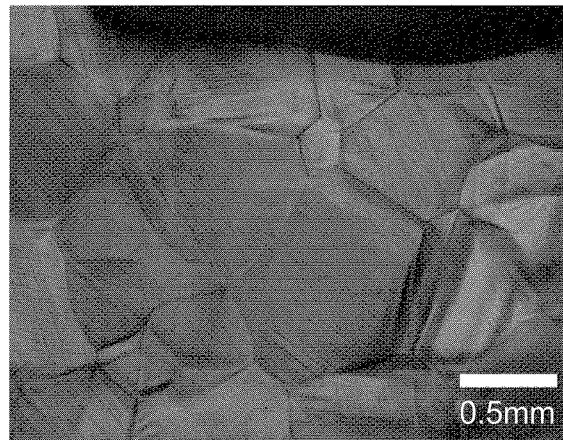


Figure 9 V-15Ni (423 K, 0.1 MPa H₂)

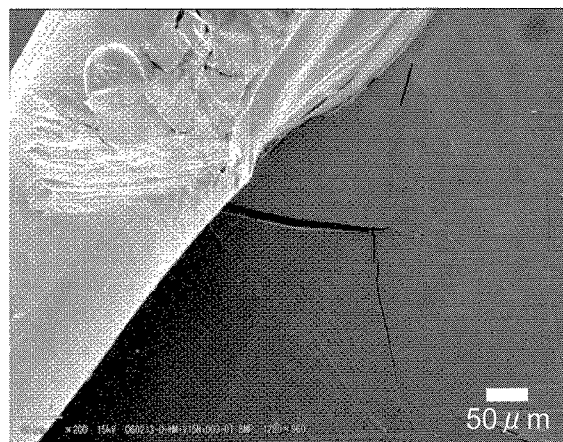


Figure 10 V-15Ni (at thermocouple)

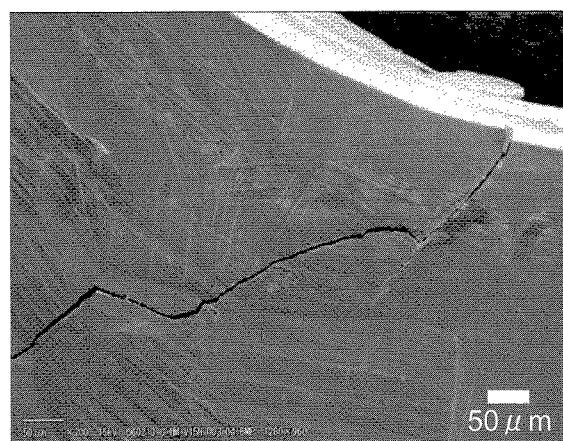


Figure 11 V-15Ni (at constrained region)

V-15Ni specimens started to show deformation at 423 K and

From the results of PCT measurements (Figure 12), the hydrogen concentration (H/M) in the pure vanadium specimens at 523 K and 0.1 MPa, at which cracks developed, was 0.59, and the concentration of hydrogen in the V-15Ni specimens at 323 K and 0.1 MPa, at which no cracks developed other than in the constrained region, was 0.57. Although the hydrogen concentration was almost identical, the pure vanadium specimens fractured, whereas the V-15Ni alloy specimens developed no cracks, suggesting that the addition of Ni increased the resistance against hydrogen-induced cracking.

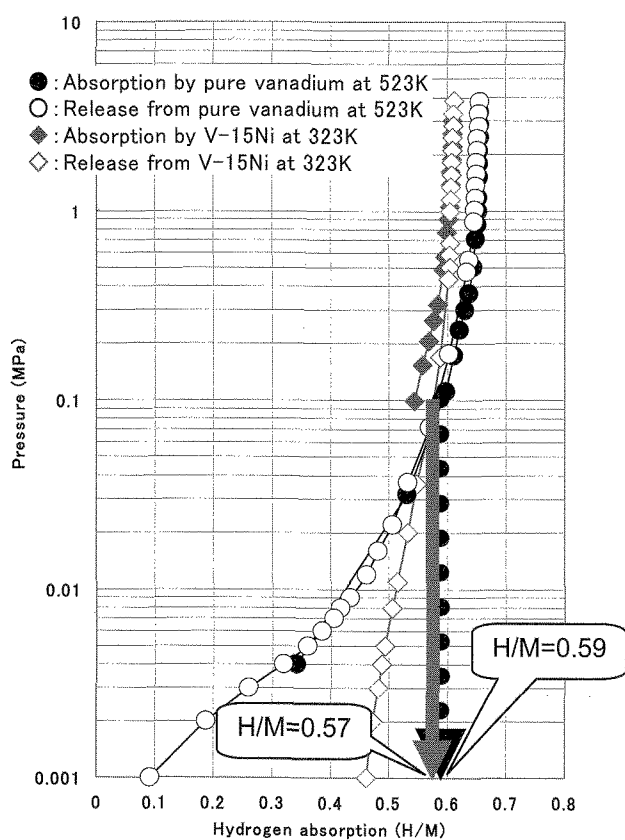


Figure 12 PCT of pure vanadium at 523 K and V-15Ni at 323 K

4. Conclusions

The relationships between crack generation and hydrogen concentration were investigated by combining the results of the in-site observation of pure vanadium and V-15Ni alloy on hydrogen absorption/desorption, and the results of PCT measurements.

The V-15Ni alloy had higher resistance against hydrogen-induced cracking than pure vanadium.

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