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Enhanced hydrogen embrittlement of Pd-coated niobium metal membrane detected by in situ small punch test under hydrogen permeation

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Abstract

The hydrogen embrittlement of pure niobium metal membrane was investigated under a hydrogen atmosphere by using a newly developed in situ small punch apparatus. The boundary for the ductile-to-brittle transition of the palladium-coated pure niobium was determined from a series of the in situ small punch tests. The measured boundary was found to be shifted greatly to the lower hydrogen content region as compared to that of palladium non-coated niobium membrane. The present result will provide us a clue to the design of niobium-based permeable membrane against the hydrogen embrittlement.

Keywords: Pure niobium metal; Hydrogen permeable metal membrane; Hydrogen embrittlement; Ductile-to-brittle transition; Small punch test

1. Introduction

The palladium and its alloys are well known as the hydrogen permeable metal membrane for the separation and purification of hydrogen gas [1]. Nowadays, there has been a great demand for new hydrogen permeable alloys to be substituted for the currently used palladium-based alloys, in order to reduce the material cost and to advance the performances of membrane reformer [2–5]. The hydrogen permeability is defined as the product of the hydrogen diffusivity and the hydrogen solubility. Niobium metal exhibits the higher hydrogen permeability than other metals [6], so it is one of the most promising materials. However, there is still a large barrier to the practical use due to its poor resistance to hydrogen embrittlement.

The hydrogen embrittlement of pure niobium has been investigated by Birnbaum and co-workers [7–9]. The boundary for the ductile-to-brittle transition shown on the Nb–H binary phase diagram was proposed by Gahr and Birnbaum from the results of tensile test under a hydrogen gas atmosphere for the samples without any Pd coating on the surface [9]. According to their boundary, pure niobium is supposed to be ductile in a highly soluble hydrogen state at high temperatures. However, the brittle fracture due to hydrogen embrittlement occurred during the hydrogen permeation through a Pd-coated pure niobium metal membrane. This contradiction suggests that the hydrogen embrittlement of pure niobium has not been understood correctly as yet. Therefore, the dominant factors which cause the hydrogen embrittlement, should be investigated in a quantitative way in order to design a niobium-based permeable metal membrane with strong resistance to hydrogen embrittlement.

In this study, an in situ small punch apparatus was developed in order to measure the mechanical properties of metal

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membranes under either the hydrogen permeation or the constant hydrogen pressure. The condition of the ductile-to-brittle transition for pure niobium metal membrane was investigated quantitatively using this newly developed apparatus.

2. Experimental procedure

2.1. Small punch apparatus

The mechanical properties of the metal membrane specimens are investigated by the small punch (SP) test which is well known as an effective method to estimate a ductile-to-brittle transition phenomenon [10–13]. A schematic diagram is shown in Fig. 1 of the in situ SP test apparatus newly equipped with a gas flow system. The metal membrane specimen is fixed at a lower flange with the die. The atmosphere between the lower and the upper flange is sealed with the bellows tube. The temperature of the specimen is controlled accurately with the ceramic heating resistor and the thermo-couple inserted in a lower flange. The SP rig is mounted on the Instron-type universal test machine, and then a load–deflection curve is measured by punching the specimen with a steel ball of 2.4 mm in diameter. The hydrogen pressure introduced from inlet and outlet ports can be controlled independently in this system.

2.2. Specimen

The niobium metal raw material with the purity of 99.9 mass% was melted in a tri-arc furnace under a purified argon gas atmosphere. The button-shaped ingot of about 30 g was then cold rolled into a plate by approximately 50% reduction in thickness, and annealed in a high purity argon gas atmosphere at 1473 K for 86.4 ks. In addition, the pure niobium rod with the purity of 99.96 mass% was prepared in the shape of 12 mm in diameter and 100 mm in length. This rod-shaped specimen was cold-rolled into a plate with 0.6 mm in thickness, and then annealed under the same condition mentioned above.

The plate-shaped specimens for an in situ SP test were cut from each annealed specimens by using a wire-electric discharge machine. The specimen size was about 0.6 mm × 10 mm × 10 mm. The surface of the specimen was mechanically polished by using the emery abrasive paper and the buff, while dripping a solution of Al_2O_3 powders in water on it. The thickness of the specimen was reduced to approximately 0.5 mm by the final polishing with 0.3 μm Al_2O_3 powders. Subsequently, pure palladium of about 200 nm in thickness was coated on the surface of the specimen, after argon-ion etching by using the RF magnetron sputtering machine. For the comparison, the palladium non-coated specimens were prepared.

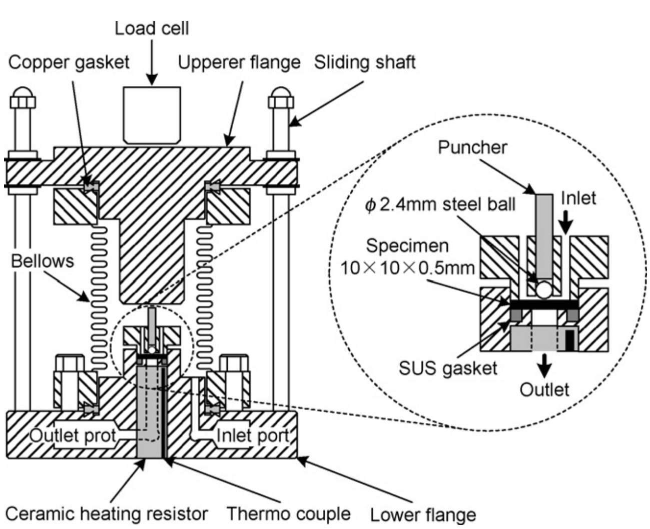

Fig. 1. Schematic illustration of small punch test apparatus equipped with the gas flow system.

Table 1
The conditions of the in situ small punch tests under the hydrogen atmosphere

Symbol	Hydrogen pressure (MPa)		Hydrogen content (H/Nb)		Temperature (K)
	Inlet	Outlet	Inlet	Outlet	
A	0.015	0.005	0.49	0.20	673
B	0.060	0.010	0.66	0.38	673
C	0.002	0.002	0.24	0.24	623
D	0.003	0.003	0.37	0.37	623
E	0.001	0.001	0.06	0.06	673
F	0.005	0.005	0.20	0.20	673
G	0.010	0.010	0.38	0.38	673
H	0.020	0.020	0.24	0.24	733
I	0.030	0.030	0.33	0.33	733

2.3. In situ small punch test

The conditions of the in situ SP tests under the hydrogen atmosphere are shown in Table 1. The equilibrium hydrogen contents, H/Nb, in the specimen were estimated from the applied hydrogen pressure using the hydrogen-composition isotherms of pure niobium measured by Veleckis and Edwards [14]. The hydrogen content of the inlet side surface of the specimen under the test condition B (i.e., H/Nb = 0.66) was close to the boundary content for the ductile-to-brittle transition in the Nb–H phase diagram shown by Gahr and Birnbaum [9]. For all of the other conditions listed in Table 1, the ductile fracture will occur dominantly according to the boundary proposed by them.

In case of the test conditions A and B, the load–deflection curves were measured during hydrogen permeation by setting the hydrogen pressure difference between the inlet and the outlet of the specimen prepared by melting. On the other hand, the load–deflection curves were measured under the constant hydrogen pressure in the test conditions of C to I in order to determine the boundary for the ductile-to-brittle transition. Here, the specimens used were prepared ones from pure niobium rod. These SP tests were performed by holding for one hour after the hydrogen gas was introduced to the apparatus following each test conditions. The loading rate (i.e., the cross-head speed), v, was set at 0.5 mm/min (8.33×10^{-3} mm/s).

3. Results and discussion

3.1. Effect of palladium coating for hydrogen embrittlement

The load–deflection curves of pure niobium metal membrane measured under the test conditions A and B are shown in Fig. 2(b) and (c), respectively. In each figure, the results of the Pd-coated specimen and the Pd non-coated specimen are drawn by as the solid and the dashed curves, respectively. For comparison, the result obtained in vacuum is shown in Fig. 2(a).

The Pd-coated specimen was ductile in vacuum. However, the remarkable brittle fracture due to the hydrogen embrittlement occurred under the test conditions A and B of the Pd-coated specimen. The specimen was fractured just before or after yielding without showing any plastic deflection. These results of the Pd-coated specimen differed largely from the previous experiment by Gahr and Birnbaum [9].

On the other hand, the Pd non-coated specimen was ductile under the test condition A. The ductility was comparable to the result obtained in vacuum. The tiny crack was, however, initiated in the specimen when the applied load reached nearly a maximum value, since a slight drop appeared in the load–deflection curve. As shown in Fig. 2(c), the ductility decreased with

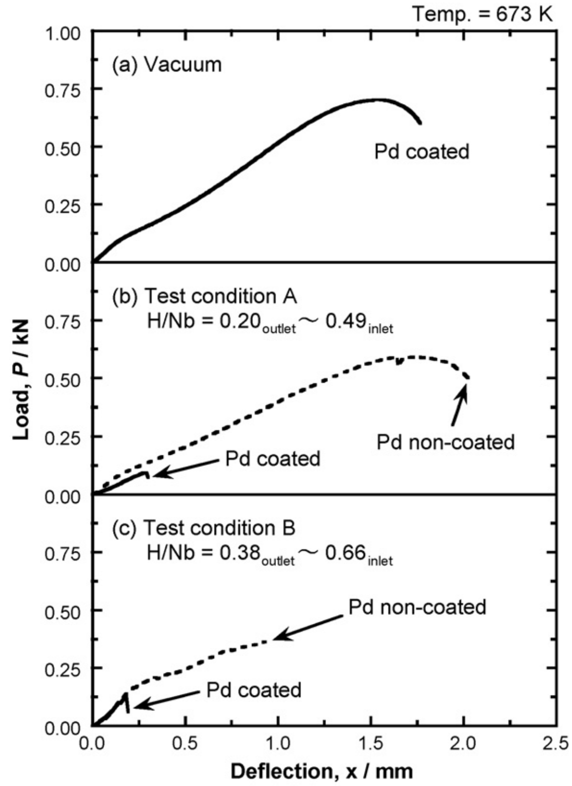

Fig. 2. Load–deflection curves of palladium-coated and palladium non-coated pure niobium membrane measured by the SP test during hydrogen permeation: (a) vacuum atmosphere, (b) inlet = 0.015 MPa and outlet = 0.005 MPa, and (c) inlet = 0.06 MPa and outlet = 0.01 MPa.

increasing hydrogen content. But a certain plastic deflection was still observed before fracture under the test condition B. These results of Pd non-coated specimen were in agreement with the previous experiment [9].

To account for this difference between the Pd-coated and non-coated specimen, an amount of hydrogen permeation, Q (mol/m^2), is shown in Fig. 3 as a function of holding time. These are experimental results of hydrogen permeation tests at 673 K by using the specimen with about 0.5 mm in thickness and about 40 mm^2 in the effective area. The slop of the plotted line means a so-called hydrogen flux, J (mol/m^2 s). In case of the Pd-coated pure niobium, as shown by the solid circles, the hydrogen started permeating through the specimen immediately after applying a hydrogen pressure difference between 0.26 MPa at the inlet and 0.06 MPa at the outlet. However, the hydrogen permeation did not occur in the Pd non-coated specimen despite the holding for one hour after applying a hydrogen pressure difference, as shown in the open circles. The hydrogen permeation was not observed in the Pd non-coated specimen even after about 24 h (86.4 ks), although it was not shown in this figure.

From these results, it was understood that once the membrane surface was coated with palladium by about 200 nm in thickness, hydrogen absorption and permeation were enhanced strongly, resulting in the brittle fracture of the membrane induced by the hydrogen embrittlement. By contraries, the present result of the ductile-to-brittle transition of the Pd non-coated niobium membrane shown in Fig. 2(b) and (c) was in agreement with the

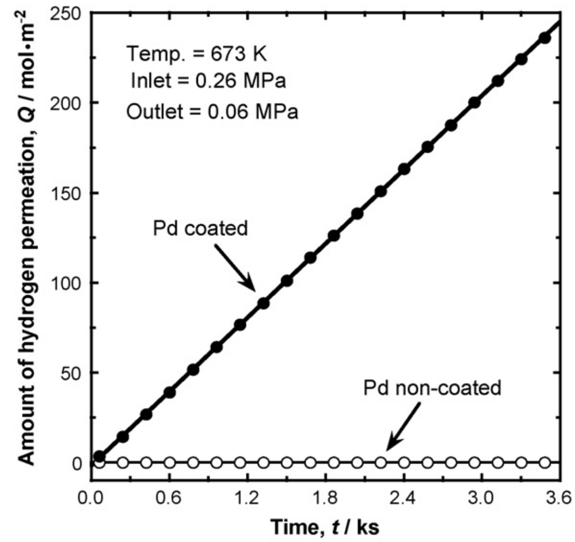

Fig. 3. Change in the amount of hydrogen permeation with holding time at 673 K for Pd-coated and Pd non-coated pure niobium membrane. The hydrogen pressures are 0.26 MPa at the inlet surface and 0.06 MPa at the outlet surface.

experimental results by Gahr and Birnbaum, since the boundary for the ductile-to-brittle transition proposed by them was determined from the tensile test of Pd non-coated niobium under the hydrogen atmosphere [9].

3.2. Change in the ductile-to-brittle transition curve with hydrogen content

The load–deflection curves are shown in Fig. 4 of Pd-coated pure niobium metal membrane measured in the test conditions of E–G (see Table 1). For comparison, the result obtained in vacuum is shown in an alternate long and short dash line. The dashed, dotted and solid curves represent the results of the test conditions E, F and G, respectively.

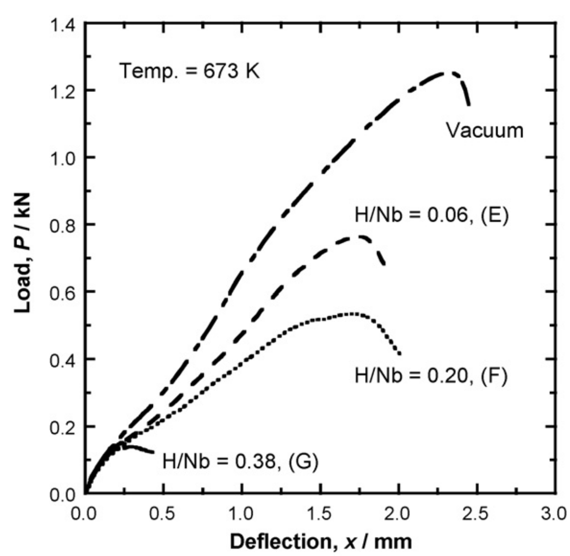

Fig. 4. Load–deflection curves of palladium-coated pure niobium membrane measured by the SP test under the constant hydrogen pressure given in the conditions of E, F and G or in vacuum.

It was found that the maximum and failure load tended to decrease with increasing dissolved hydrogen content, H/Nb. In case of test condition F (H/Nb = 0.20), the slope of the curve changed slightly due to the crack initiation at the deflection around 1.5 mm. Therefore, it was evident that the deflection until the crack initiated, decreased with increasing hydrogen content. The remarkable brittle fracture due to the hydrogen embrittlement was observed under the test condition G (H/Nb = 0.38), and then the specimen fractured without showing any plastic deflection. From these results, it was understood that the boundary for the ductile-to-brittle transition existed in the region of the hydrogen content between 0.20 and 0.38 for H/Nb at 673 K. In addition, when the SP tests were performed at 623 and 733 K, the brittle fracture occurred under the test conditions D (H/Nb = 0.37 at 623 K) and I (H/Nb = 0.33 at 733 K), but the ductile fracture was observed in the test conditions C (H/Nb = 0.24 at 623 K) and H (H/Nb = 0.24 at 733 K), although these results does not shown in the figure.

3.3. Boundary for the ductile-to-brittle transition

The hydrogen pressure-composition isotherms of pure niobium measured at 673 K by Veleckis and Edwards [14] is shown in Fig. 5. However, instead of the hydrogen pressure the square root of the hydrogen pressure is plotted in a vertical axis. The applied hydrogen pressures are also shown as the horizontal dashed lines in this figure to show the test conditions of E, F and G.

The hydrogen solubility in pure niobium is proportional to the square root of hydrogen pressure below 0.001 MPa, as shown by a straight dotted line that passes the origin. The slope of the dotted line expresses the hydrogen dissolution coefficient, K, of pure niobium since the Sieverts law [15] is satisfied at 673 K and below 0.001 MPa. The hydrogen solubility deviates gradually from this dotted line with increasing hydrogen pressure, and hydrogen becomes more soluble above 0.001 MPa. On the measured curve, there appears an inflection point in the pressure range between 0.005 and 0.01 MPa, as indicated by a solid circle. The boundary for the ductile-to-brittle transition appears near this inflection point of the hydrogen dissolution curve when compared the load–deflection curves (F) and (G), shown in Fig. 4 with the horizontal pressure lines (F) and (G), shown in Fig. 5.

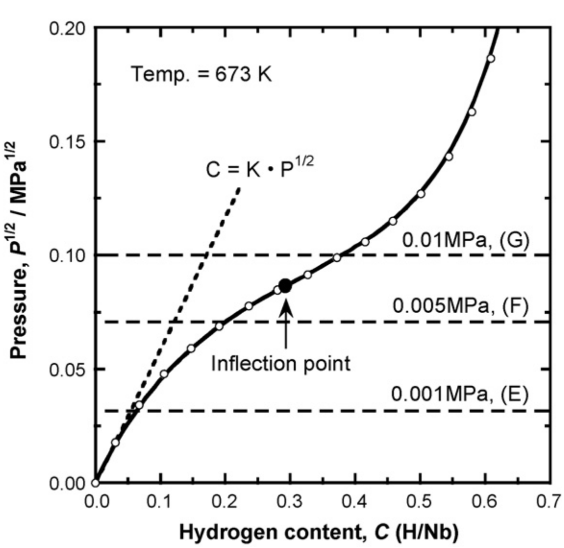

Fig. 5. Hydrogen pressure-composition isotherms of pure niobium at 673 K [14]. The vertical axis is the square root of hydrogen pressure. The constant hydrogen pressures for the conditions of E, F and G are given by the dotted horizontal lines.

The hydrogen content corresponding to the inflection point is plotted in the Nb–H binary phase diagram [16], as shown in Fig. 6. The inflection point was calculated by differentiating an approximated polynomial for the hydrogen-composition isotherms of pure niobium at 623–773 K measured by Veleckis and Edwards [14], as indicated by the open circle and by Lässer et al. [17], as indicated by the open rhombus. The boundary for the ductile-to-brittle transition proposed by Gahr and Birnbaum is also plotted in this figure, as indicated by the alternate long and short dash line. In addition, the results of SP test under the conditions of C to I are plotted by the solid circle for the ductile-fractured specimen and the solid triangle for the brittle-fracture specimen.

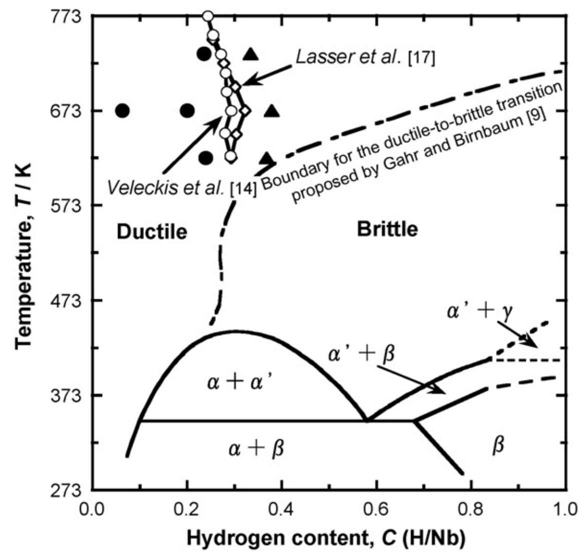

Fig. 6. The boundary for the ductile-to-brittle transition shown on the Nb–H binary phase diagram.

The measured boundary of the palladium-coated niobium metal membrane was found to be shifted greatly to the lower hydrogen content region, as compared to the boundary proposed by Gahr and Birnbaum. It is interesting that the hydrogen content of the inflection point in the hydrogen dissolution curve is in agreement with the boundary for the ductile-to-brittle transition obtained by the present experiment. The inflection point of the hydrogen pressure-composition isotherms is one of the effective indications to estimate the boundary for the ductile-to-brittle transition of palladium-coated niobium metal membrane. The present results renovate a widely accepted concept that pure niobium metal is ductile at high temperatures even in a highly soluble hydrogen state, and hence provide an important clue to design of niobium-based permeable membrane against the hydrogen embrittlement.

4. Conclusion

The boundary for the ductile-to-brittle transition was measured quantitatively by using a newly developed in situ small punch apparatus. The measured boundary of the palladium-coated niobium metal membrane was found to be shifted greatly to the lower hydrogen content region, as compared to that of palladium non-coated membrane.

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