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Development of melt-spun Ni–Nb–Zr–Co amorphous alloy for high-performance hydrogen separating membrane

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Abstract

We produced the Ni–Nb–Zr–Co amorphous membranes by single-roller melt-spinning technique and measured the hydrogen permeation behavior of them. The palladium thin films were deposited on both sides of membranes as catalysts for hydrogen dissociation. The hydrogen permeability of the Ni–Nb–Zr–Co amorphous alloys increased with increasing test temperature and was much larger than that of the conventional Pd–Ag alloy. The durability of the alloys during service was also examined at 573 K and 673 K. As a result, it was found that the permeability decreased significantly with time at 673 K. However, the permeability did not almost decrease at 573 K even after 100 h. Furthermore, we developed the manufacturing technique to fabricate the 100 mm wide hydrogen separating amorphous membranes.

Keywords: Amorphous; Permeation; Melt-spinning; Separation

1. Introduction

Pd-based alloy membranes are adopted in the current designs of fuel reformers in fuel cell systems due to their ability for catalyzing hydrogen dissociation and selective permeation of hydrogen without suffering from hydrogen embrittlement [1,2]. However, the use of the novel metals makes the cost of such membranes unacceptably high for many fuel cell applications. It is therefore desired that alternative membrane alloys with low-cost metals should be developed to replace the Pd-based alloys and to improve hydrogen permeability while reducing the material cost. Recently, many alloy candidates such as amorphous [3–8], V-based [9,10], Ti–Ni–Nb [11] and Ta [12] alloys have been developed as hydrogen permeable membranes.

We have been developing economical high-performance alloys for hydrogen separating membranes. Previously, we investigated the formability, mechanical properties and thermal stability of the Ni–Nb–Zr amorphous alloys [13]. It was found that the hydrogen permeability of the Ni–Nb–Zr amorphous alloy is strongly dependent on the composition of the alloy and increased with increasing Zr content in our previous work [14]. The hydrogen permeability of the melt-spun Ni–Nb–Zr amorphous alloy ribbons was higher than that of pure Pd metal. However, it was difficult to investigate the hydrogen permeability of the amorphous alloys having high Zr content due to severe hydrogen embrittlement during the measurement. Therefore, we produced the Ni–Nb–Zr–Co amorphous alloys and investigated the effect of Co addition to the Ni–Nb–Zr alloys on the suppression of hydrogen embrittlement. As the result, it was found that the Co addition is effective for the suppression of hydrogen embrittlement [15]. In this work, we performed long-time permeation tests to examine the hydrogen permeability and the durability of the Ni–Nb–Zr–Co amorphous alloys.

2. Experimental

Ni–Nb–Zr–Co alloy ingots were prepared by arc-melting the mixture of pure metals with desired compositions in an Ar atmosphere. Melt-spun ribbons were produced by a single-roller melt-spinning technique in an Ar atmosphere. The ribbons for hydrogen permeation measurement were about 20 mm in width and about 50 μm in thickness.

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Pd thin film was deposited on both sides of the specimens by sputtering technique (ULVAC SH-350) to obtain an active catalyst for hydrogen dissociation and recombination during permeation. The Pd deposition was performed under the condition of Rf = 50 W for 200 s in an Ar 0.3 Torr atmosphere. Hydrogen permeation was measured by a conventional gas-permeation technique using pure hydrogen gas at 573 K, 623 K and 673 K under the hydrogen pressure up to 0.5 MPa. The diameter of permeation area was 10 mm. The durability of the hydrogen separating membrane was examined by a long-time hydrogen permeation test using mixed gas at 573 K and 673 K under a constant hydrogen pressure. The mixed gas that we prepared as simulated gas consists of 74% H_2, 15% CO, 10% CO_2 and 1% CH_4. In this work, the mixed gas was used as the feed gas for the long-time permeation tests.

Depth analysis by using AES was carried out with Ar-ion-etching system (PH1650, Perkin-Elmer Inc., USA). The acceleration voltage of electron probe was fixed to 10 kV and the electron probe was focused to about 10 μm. Acceleration voltage of Ar-ion beam was fixed to 3 kV. The ion gun was differentially pumped and the Ar pressure was 5×10^{-3} Pa. The etching rate was about 0.4 nm s^{-1} determined by a silicon-oxide film.

3. Results and discussion

Fig. 1 shows the Arrhenius plots of the hydrogen permeability of $(Ni_{0.6}Nb_{0.4})_{45}Zr_{50}Co_5$ amorphous alloy prepared in this work together with our previous data of Ni–Nb–Zr amorphous alloys. The permeabilities shown in Fig. 1 were measured with pure hydrogen gas. The hydrogen permeability of the Ni–Nb–Zr–Co amorphous alloys increased with increasing test temperature like the Ni–Nb–Zr amorphous alloys. The hydrogen permeability of the $(Ni_{0.6}Nb_{0.4})_{45}Zr_{50}Co_5$ amorphous alloys was as high as that of the conventional Pd–Ag alloys.

Fig. 2 shows the time-dependent change of the hydrogen permeation rates of the melt-spun $(Ni_{0.6}Nb_{0.4})_{55}Zr_{40}Co_5$ amorphous alloys at 673 K. The mixed gas was used in these measurements. The hydrogen pressures of the upper- and the lower-side surfaces of the membrane was 0.25 MPa and 0.1 MPa, respectively. Because the mixed gas including gaseous contaminations, the permeabilities measured in Fig. 2 are smaller than that obtained with pure H_2 gas shown in Fig. 1. As shown in the figure, the rapid decrease of the permeation rates are seen from the start of the test and the sample with Pd layer of 0.15 μm in thickness could not permeate hydrogen after 20 h. The permeation rate of the sample with Pd layer thickness of 0.3 μm decreases more slowly. In order to understand the reason for these deteriorations, the depth profile was of the specimen was investigated.

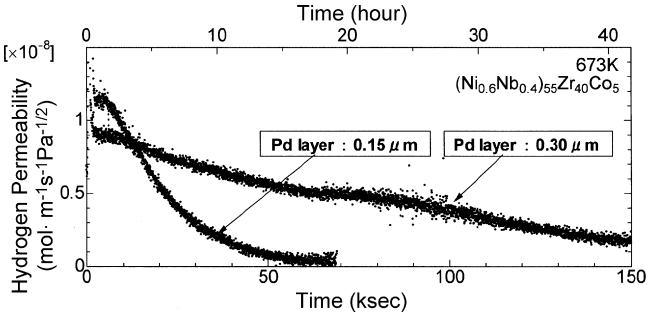

Fig. 2. Time-dependent change of the hydrogen permeabilities of the melt-spun $(Ni_{0.6}Nb_{0.4})_{55}Zr_{40}Co_5$ amorphous alloys at 673 K.

Fig. 3 shows the result of the depth analysis of the $(Ni_{0.6}Nb_{0.4})_{65}Zr_{30}Co_5$ amorphous sample with Pd surface layers before and after the permeation tests at 673 K for 24 h by Auger electron spectroscopy. As shown in the figure, the diffusion of the Pd layer to the inside of the amorphous matrix is clearly observed. Therefore, it is considered that the diffusion of Pd layer relates to the deterioration of the hydrogen permeability. The appearance of carbon (C) on the surface of the specimens would come from carbon monoxide/dioxide (CO/CO_2) and/or methane (CH_4) included in the mixed gas used in this work. Then we checked the crystallinity of the specimens used after the permeation test at 673 K.

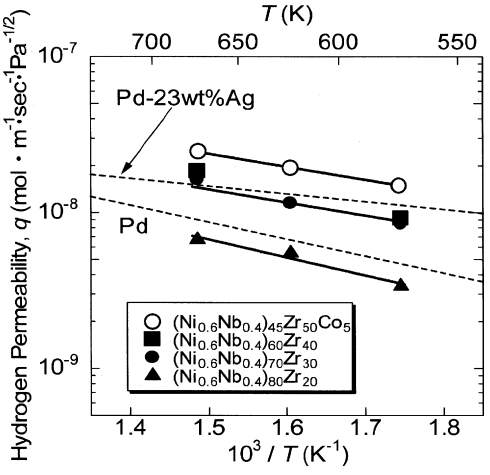

Fig. 1. Arrhenius plots of the hydrogen permeability of $(Ni_{0.6}Nb_{0.4})_{45}Zr_{50}Co_5$ amorphous alloy.

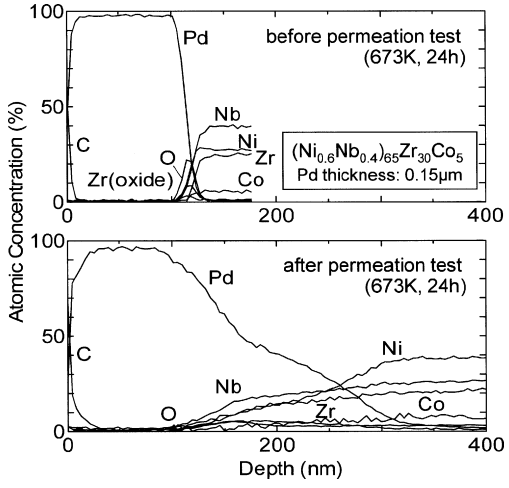

Fig. 3. Auger depth profiles of the $(Ni_{0.6}Nb_{0.4})_{65}Zr_{30}Co_5$ amorphous ribbons with Pd surface layers before and after about 24 h permeation test at 673 K.