Effect of Continuous Hydrogen Charging on Tensile and Fatigue Properties of Amorphous Ni-Zr Alloy Membranes

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Effect of hydrogen charging on mechanical properties in tensile and fatigue tests was investigated for the Ni-Zr amorphous alloy membranes with and without palladium plating. As a result of the tensile test, it was shown that both tensile strength and fracture strain decreased by continuous hydrogen charging in all the specimens. It was also found that palladium plating reduced effectively the hydrogen embrittlement sensitivity. Fatigue properties were also lowered by hydrogen charging. In the specimen without hydrogen charging, fatigue limit was about 600–700 MPa, while in the specimen with hydrogen charging, no clear fatigue limit was observed. Fracture morphology was changed from the vein-like patterns to the shell patterns by hydrogen charging, both after the tensile test and the fatigue test.

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1. Introduction

In order to enhance the lifetime and efficiency of the fuel cell system, several kinds of hydrogen purification method have been developed.1 It is reported2-4 that one of the significant methods to purify hydrogen is to utilize hydrogen permeable metallic membranes since they show high thermal stability and excellent hydrogen selectivity. Up to date, palladium and palladium base alloys have been practically used as the hydrogen permeable membranes.5 It is believed that the reduction of cost to produce the hydrogen permeable membrane is an important issue to proceed efficiently the hydrogen purification system. For such the demand, as another hydrogen permeable membrane materials, amorphous Ni-Zr alloys have been developed since the alloys show excellent hydrogen permeability, mechanical properties and low cost.6,7 It is presumed, however, that the membranes having high strength prone to show high hydrogen embrittlement sensitivity after continuous hydrogen permeation. Thus far, the effect of continuous hydrogen charging on mechanical properties of the Ni-Zr amorphous alloy membranes has not been fully reported,8 probably due to the difficulty in the testing of very thin membranes. Considering the direction for use of the Ni-Zr alloys as hydrogen permeable membranes, however, it will be important to clarify the tensile properties as well as fatigue properties affected by continuous hydrogen absorption. In the present study, tensile and fatigue properties of the Ni-Zr alloy membranes affected by hydrogen charging were examined. The effect of palladium plating on the hydrogen embrittlement sensitivity was also examined.

2. Experimental Procedure

The amorphous Zr_{36}Ni_{64} membrane of about 30 µm in thickness was prepared by the rapid quenching method under an argon atmosphere. Chemical composition of the amorphous Zr_{36}Ni_{64} membranes is shown in Table 1. The test pieces for tensile test are rectangle shaped ones having dimensions of 3 mm in width and gage length of 12 mm. The test pieces for fatigue test are sandglass shaped ones with a minimum width of 2 mm. The shapes of the tensile and fatigue test pieces, which were prepared by cutting, were illustrated in Fig. 1. Some of the unpolished specimen surfaces were plated with thin (100 nm) palladium layers on both sides by means of conventional electroplating (PdEP) or ion plating (PdIP). For comparison, the unpolished specimen without palladium plating was also prepared (normal). Hydrogen charging was conducted electrolytically in a 3 mass%NaCl–0.1 mass%KSCN solution at a current density of 200 A/m² for 0.5 h at room temperature before starting the tensile test or the fatigue test. Hydrogen charging was performed all at room temperature with a view to introducing high amounts of hydrogen. With the change in the specimen dimensions before and after hydrogen charging, volume expansion rate was measured with a laser microscope. In order to protect jigs of the testing machines during hydrogen charging, insulating tapes were attached at both edges of the specimens using glues. The amount of hydrogen gas in the specimens was measured by the thermal desorption analysis

Table 1 Chemical composition of the Ni-Zr amorphous alloy membrane (mass%).

<table>
<thead>
<tr>
<th>Zr</th>
<th>Ni</th>
<th>Ti</th>
<th>Fe</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.2</td>
<td>54.7</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Fig. 1 Specimen shapes for tensile test (a) and for fatigue test (b).
(TDA) using gas chromatography. TDA was done for the specimens after hydrogen charging for 0.5 h to stabilize the hydrogen permeation. Hydrogen evolution from the specimens was detected at 1 min intervals during heating a sample weighed about 0.008 g. High purity argon carrier gas of 99.999% was passed through at 5 min intervals with a heating rate of 100°C/min until the temperature reached 700°C. Hydrogen charging was also done continuously in the course of the tensile or fatigue tests in the same charging condition (200 A/m² for 0.5 h, in 3 mass%NaCl–0.1 mass%KSCN solution). Tensile tests were carried out at an initial strain rate of $1.67 \times 10^{-3}$ s⁻¹, and three different specimens were tested under each experimental condition to ensure the reliability of the results. The fatigue test was carried out by using a micro servo-electromagnetic testing machine with a frequency of 15 Hz and a stress ratio of $R=0$. Fracture surfaces after the tensile and fatigue tests were observed with a scanning electron microscope (SEM).

3. Results and Discussion

3.1 Hydrogen absorption by cathodic hydrogen charging

The TDA curves for the specimens with and without hydrogen charging are shown in Fig. 2. In the specimen without hydrogen charging, thermal desorption of hydrogen was not observed below 400°C. On the other hand, in the hydrogen charged specimens, the thermal desorption of hydrogen appeared as a single peak at 100°C when the specimen surfaces were plated with the palladium layers (PdEP and PdIP), and that appeared at 250°C in the specimen without palladium plating (normal). This result indicates that the hydrogen evolution from the specimen is enhanced because palladium acts as a catalyst to convert molecular hydrogen into atomic hydrogen. It was also clear that the total amount of desorbed hydrogen increased when the palladium was plated on the surface. As for the difference in the method of palladium plating, there was no marked difference in the thermal desorption behavior in the specimens between PdEP and PdIP. The diffusive hydrogen concentration was calculated by integrating the relation between hydrogen desorption rate and heating time below 400°C. The hydrogen concentration in the palladium plated specimens, PdEP and PdIP was 19.4 mol% and 20.3 mol%, respectively, both of which were twice as high as that in the specimen without plating (9.8 mol%). This shows that the absorbed hydrogen amount also increases due to palladium plating when compared to the same hydrogen charging condition. The volume expansion rate by hydrogen charging for 0.5 h was shown in Fig. 3. It is found that the volume expansion rate actually increases by palladium plating, which is in agreement with the increase of hydrogen absorption amount as previously shown in Fig. 2. Macroscopic views of the undeformed specimens after hydrogen charging for 0.5 h are shown in Fig. 4. In the specimen without palladium plating (normal), the corrugation was observed in the specimen surface. It is assumed that the corrugation in the specimen surface (normal) represents the heterogeneity of the hydrogen absorption during hydrogen charging. On the other hand, in the specimen surfaces with palladium plating (PdEP and PdIP), such corrugation was not observed. These results suggest that not only hydrogen absorption amounts but also surface morphology would be variable owing to the palladium plating during hydrogen charging.

3.2 Effect of hydrogen charging on tensile properties

Figure 5 shows the typical stress-strain curves obtained from the tensile test of the Ni-Zr amorphous alloys with and without palladium plating. In the uncharged state, there was no marked differences of the fracture stress and the fracture strain in the specimens with and without palladium plating. Tensile strength was about 2.1 GPa and the fracture strain was about 5% in all the specimens without hydrogen charging. Figure 6 shows the stress-strain curves of the alloys with hydrogen charging. It was clear that the fracture stress as well as fracture strain decreased by hydrogen charging in all the specimens. It was found, however, that the detrimental effect of hydrogen charging was slightly decreased by palladium plating. In order to clarify the detrimental effect of hydrogen charging on tensile properties, hydrogen embrittlement sensitivity was measured by introducing the hydrogen embrittlement sensitivity index $I$, which was defined as follows:

$$I = \frac{\sigma_f - \sigma_{t,0}}{\sigma_{t,0}}$$

where $\sigma_f$ is the fracture stress and $\sigma_{t,0}$ is the tensile strength without hydrogen charging.
Here, $X_0$, $X$ represent the tensile parameters of fracture stress $\sigma$ or fracture strain $\varepsilon$ in the uncharged and hydrogen charged conditions, respectively. Figure 7 shows the changes in the index $I$ in the different specimen conditions. It is obvious that the specimen without palladium plating is highly embrittled by hydrogen charging ($I_\varepsilon = 0.5$ in normal) as compared to the specimens with palladium plating ($I_\sigma = 0.23$ in PdEP, $I_\varepsilon = 0.09$ in PdIP). As indicated earlier in Fig. 4, the surface morphology was changed due to palladium plating after hydrogen charging. It is thus assumed that the decrease of the hydrogen embrittlement sensitivity due to palladium plating would be attributed to the suppression of surface corrugation, which becomes the sites of local stress concentration. Changes in the index values between PdEP and PdIP also suggest that the hydrogen embrittlement sensitivity is
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3.3 Effect of hydrogen charging on fatigue properties

Figure 8 shows the effect of palladium plating on the S-N relation in the specimens without hydrogen charging (normal, PdEP). No clear differences were observed for the fatigue properties in the specimens without hydrogen charging. Both specimens with and without palladium plating indicated the fatigue limit about 600–700 MPa when hydrogen was uncharged. Thus, it is noted that the effect of palladium plating on fatigue properties is small under the testing condition without hydrogen charging. Figure 9 shows the S-N relation in the specimens with hydrogen charging (normal, PdEP). By comparing the results between Figs. 8 and 9, it is obvious that the fatigue lifetime decreases due to hydrogen charging in all the stress amplitude levels. Contrary to the case as previously shown in Fig. 8, no clear fatigue limit was observed when the specimens were hydrogen charged continuously. It was clear that palladium plating was also effective to lower the detrimental effect of hydrogen on fatigue properties, particularly in the high cycle fatigue region above $10^5$ cycles. Similarly to the case in the tensile test as discussed before in the previous section, the improvement of the fatigue properties due to palladium plating would be also attributed to the suppression of surface corrugation, which becomes the sites of local stress concentration. In order to characterize the fatigue properties affected by hydrogen charging and/or palladium plating, the well-known Basquin relation was applied to the testing results in the low cycle fatigue region below $10^5$ cycles. The Basquin relation is expressed as follows:

$$\sigma_a = AN_f^{-b}.$$  

Here, $\sigma_a$, $N_f$ represent the stress amplitude (GPa) and the fatigue lifetime, respectively, and $A$ and $b$ represent the material constants. In the specimens without palladium plating (normal), the relationship between $\sigma_a$ and $N_f$ was expressed as $\sigma_a = 3.47N_f^{-0.140}$ when hydrogen was uncharged, and expressed as $\sigma_a = 2.86N_f^{-0.237}$ when hydrogen was charged. On the other hand, in the specimens with palladium plating (PdEP), that was expressed as $\sigma_a = 3.04N_f^{-0.133}$ when hydrogen was uncharged and expressed as $\sigma_a = 1.77N_f^{-0.164}$ when hydrogen was charged. Since $b$ values exhibit the slope in the S-N relation lines, the detrimental effect of hydrogen charging on fatigue properties was also characterized by the difference of $b$ values in the specimens without hydrogen charging and with hydrogen charging. The reduction ratio of $b$ value in the specimen without palladium plating (normal) was 0.69, and that in the specimen with palladium plating (PdEP) was 0.23. This indicates that the hydrogen embrittlement sensitivity in the specimen with palladium plating is 3 times as low as that without palladium plating for the fatigue properties.

3.4 Fracture surfaces affected by hydrogen charging

Figure 10 shows the fracture surfaces of the specimens (normal) with and without hydrogen charging after the tensile test. The fracture surface in the specimen without hydrogen charging consists of a smooth region produced by large local plastic shearing and a vein-like region produced by plastic instability. On the other hand, in the specimen with hydrogen charging, the fracture surface characterized by the wavy patterns was observed. Similar differences were also identified in the specimen (normal) after the fatigue test as shown in Fig. 11. This morphology in the specimen with hydrogen charging was similar in appearance to Wallner lines, as has been reported in the other amorphous iron-based alloy affected by hydrogen. It is reported that the formation of Wallner lines in the fracture surfaces is brought about by the interference between the stress waves originating from the crack origin. The Wallner lines also represent that the very rapid fracture takes place due to the separation of atomic bonding. Thus, it is assumed that the hydrogen embrittlement in the present Ni-Zr amorphous alloys is also caused by the decrease in the strength of atomic bonding due to continuous hydrogen charging, similarly to the case of other amorphous alloys as reported elsewhere.11,12
4. Summary

Effect of hydrogen charging on mechanical properties of Ni-Zr amorphous alloy membranes was investigated. Obtained results are summarized as follows: (1) Fracture stress and fracture strain decrease by continuous hydrogen charging in the tensile test. (2) Fatigue limit disappears when the continuous hydrogen charging is carried out in the fatigue test. (3) Fracture morphology is changed from the vein-like patterns to shell-like patterns due to the hydrogen embrittlement. (4) Palladium plating is effective to lower the hydrogen embrittlement sensitivity both in the tensile test and the fatigue test. (5) The improvement of the tensile and fatigue properties by the palladium plating would be attributed to the suppression of the corrugation in the specimen surface during hydrogen charging.

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REFERENCES