The Effect of Additional Elements on Hydrogen Permeation Properties of Melt-Spun Ni-Nb-Zr Amorphous Alloys*1

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The (Ni0.4Nb0.4)0.5Zr0.5X (X = Al, Co, Cu, P, Pd, Si, Sn, Ta or Ti) alloy ribbons were produced by the melt-spinning technique. All ribbon specimens were confirmed to have a single amorphous phase by XRD analysis. The crystallization temperatures of the melt-spun (Ni0.4Nb0.4)0.5Zr0.5X (X = Al, P, Pd, Si or Sn) amorphous alloys are higher than that of the (Ni0.4Nb0.4)0.5Zr0.5 amorphous alloy (727 K). Although the hydrogen permeability of the (Ni0.4Nb0.4)0.5Zr0.5X (X = Si, Sn, Ta or Ti) amorphous alloys could not be measured due to severe embrittlement during the permeation test, the (Ni0.4Nb0.4)0.5Zr0.5X (X = Al, Co, Cu, P or Pd) amorphous alloys had high ductility which was enough to measure the permeability. The hydrogen permeabilities of the (Ni0.4Nb0.4)0.5Zr0.5Co and the (Ni0.4Nb0.4)0.5Zr0.5Cu amorphous alloys were 2.46 × 10−8 and 2.34 × 10−8 [mol·m−1·s−1·Pa−1/2] at 673 K, respectively. The (Ni0.4Nb0.4)0.5Zr0.5P amorphous alloy possesses the lowest permeability of 1.36 × 10−8 [mol·m−1·s−1·Pa−1/2] at 673 K among the alloys where the permeability was measured. The reduction of the permeability in the (Ni0.4Nb0.4)0.5Zr0.5P amorphous alloy is thought to be due to a preferential development of Zr-P atomic pairs which may suppress hydrogen solubility and hydrogen diffusivity in the alloy, because the heat of mixing for Zr-P atomic pairs is negatively larger than those of other pairs such as Ni-P and Nb-P. It is concluded that the Ni-Nb-Zr-X (X=Co or Cu) amorphous alloys have high potential to hydrogen permeable membranes.

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1. Introduction

Recently, the improvement of hydrogen purification techniques has been strongly required to increase the lifetime and efficiency of electric power generation of fuel cells. There are various hydrogen purification techniques such as the pressure swing adsorption, the cryogenic separation and the membrane separation. Since the mechanism of hydrogen purification by using a hydrogen permeable membrane is very simple, the continuous production of hydrogen by the membrane is cost-saving and suitable for mass-production. The membrane can be combined with a reformer by which hydrocarbons are decomposed to hydrogen and carbon dioxide. The system is called the membrane-reformer. 1) The membrane alloy which has been practically used is limited to the Pd-Ag alloy. 2) Since Pd metal is extremely expensive, it is important to develop a new membrane alloy with minimum addition or absence of Pd metal for the stable hydrogen supply at lower cost for the coming fuel-cell powered society. 3)

 Previously, we developed the Ni-Nb-Zr ternary amorphous alloys as a new membrane material for hydrogen purification 4) and investigated the formability, mechanical properties and thermal stability of the amorphous alloys. 5) In our previous work, we reported that the melt-spun (Ni0.4Nb0.4)0.5Zr0.5 amorphous alloy possessed hydrogen permeability of 1.3 × 10−8 [mol·m−1·s−1·Pa−1/2] at 673 K. 4) It was also shown that the embrittlement of this alloy system became significant with increasing Zr content during the permeation test, even though the hydrogen permeability

increased with Zr content.

In the present work, the effect of additional element in the Ni-Nb-Zr ternary alloys on hydrogen permeability was investigated with the aim of developing a new membrane material with high hydrogen permeability in the absence of distinct hydrogen embrittlement.

2. Experimental

(Ni0.4Nb0.4)0.5Zr0.5X (X=Al, Co, Cu, P, Pd, Si, Sn, Ta or Ti) alloy ingots were prepared by arc-melting the mixture of pure metals in an Ar atmosphere. Melt-spinning ribbons were produced by a single-roller melt-spinning method in an Ar atmosphere. The ribbons to measure hydrogen permeation were about 20 mm wide and about 50 μm thick.

The amorphicity of the melt-spun ribbon specimens was investigated by X-ray diffractometry (CuKα, 40 kV, 30 mA, hereafter denoted as XRD). The crystallization temperature and melting point of each alloy were examined by differential scanning calorimetry at a heating rate of 0.17 K·s−1. The hardness was measured with a Vickers microhardness tester with a load of 50 g.

Pd thin film was deposited on both sides of the specimen by two methods such as sputtering and electro-less plating as an active catalyst for hydrogen dissociation and recombination during permeation. Hydrogen permeation was measured by a conventional gas-permeation technique at 673 K at the hydrogen pressure up to 0.3 MPa. Sample membranes were mounted in the gas-permeation cell. Pure hydrogen gas was introduced to one side of a membrane and then the flow rate of effluent gas from the other side was measured by a mass flow meter.

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3. Results and Discussion

Figure 1 shows the XRD patterns of the melt-spun alloys prepared in this work. As shown in the figure, no sharp diffraction peak is observed in the 2θ range of 20–80°. This indicates that all alloys possess a single amorphous phase. In our previous work, we pointed out that the X-ray diffraction angle of a halo peak decreased with increasing Zr content. However, the peak position of the alloys prepared in this work remains unchanged presumably because the Zr content was fixed to 50 at%.

Figure 2 shows the relationship between the crystallization temperature, \( T_c \) and the melting point, \( T_m \) of each alloy. The \( T_c \) of the \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{X}_{5}\) amorphous alloy is 727 K. Additions of Pd, non-metals (P, Si) and amphoteric (Al, Sn) are effective to raise \( T_c \) because the \( T_c \) of the \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{X}_{5}\) amorphous alloy is 778 K, which is higher by about 50 K than that of the \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{Sn}_{5}\) amorphous alloy. Among the additional elements to the \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{Sn}_{5}\) amorphous alloy in the present work, the addition of Al causes the lowest \( T_m \) of 1194 K. In addition, Ta having the highest \( T_m \) of 3258 K, did not affect \( T_c \) of the \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{Sn}_{5}\) amorphous alloy.

For hydrogen permeation measurement, Pd thin film was deposited on both sides of the specimens by sputtering and by electro-less plating. As shown in Table 1, the hydrogen permeability of the melt-spun \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{X}_{5}\) \((X=\text{Si}, \text{Sn}, \text{Ta and Ti})\) amorphous alloys could not be measured due to severe embrittlement during the measurement. Consequently, we examined the permeability of the melt-spun \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{X}_{5}\) \((X=\text{Al}, \text{Co}, \text{Cu}, \text{P} \text{ and Pd})\) amorphous alloys.

Figure 3 shows the hydrogen permeability of the melt-spun \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{X}_{5}\) \((X=\text{Al}, \text{Co}, \text{Cu}, \text{P} \text{ and Pd})\) amorphous alloys. It was difficult to measure the permeability of \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{X}_{5}\) \((X=\text{Al} \text{ and P})\) alloys with Pd thin film coated by the sputtering technique. Although the reason is not clear, it is thought that the conditions of Pd thin film deposition by using electro-less plating, particularly, the temperature change may be relatively mild compared to those by sputtering. As shown in the figure, the permeabilities of the \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{Co}_{5}\) and \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{Cu}_{5}\) amorphous alloys are 2.46 \times 10^{-8} and 2.34 \times 10^{-8} [mol·m^{-1}·s^{-1}·Pa^{-1/2}] at 673 K, respectively, which are as high as that of the conventional Pd-Ag alloys. The \((\text{Ni}_{0.6}\text{Nb}_{0.4})_{45}\text{Zr}_{50}\text{P}_{5}\) amorphous alloy possesses the lowest permeability of 1.36 \times 10^{-8} [mol·m^{-1}·s^{-1}·Pa^{-1/2}] among the alloys examined at 673 K in the present study.

In order to study the effect of the alloy composition on mechanical properties of amorphous alloys prepared in the
The alloy has the highest hydrogen permeability among the alloys prepared in this study. No sharp diffraction peak is seen in the alloys prepared in this study. This is because the Zr content strongly affects the permeability of hydrogen affinity which relates to high hydrogen solubility, it is known that Zr atoms possess high hydrogen diffusivity in the alloy, resulting in the decrease in hydrogen permeability.

4. Summary

We examined the formability and hydrogen permeability of the melt-spun (Ni0.6 Nb0.4 Zr50)X5 (X=Al, Co, Cu, P, Pd, Si, Sn, Ta and Ti) amorphous alloys. The results obtained are summarized as follows.

(1) An amorphous single phase was formed in the melt-spun (Ni0.6 Nb0.4 Zr50)X5 (X=Al, Co, Cu, P, Pd, Si, Sn, Ta and Ti) alloys.

(2) The crystallization temperatures of the (Ni0.6 Nb0.4 Zr50)X5 (X=Al, Co, Cu, P, Pd, Si, Sn, Ta and Ti) alloys are higher than that of the (Ni0.6 Nb0.4 Zr50) amorphous alloy.

(3) The permeabilities of the (Ni0.6 Nb0.4 Zr50)X5 amorphous alloys are higher than that of the (Ni0.6 Nb0.4 Zr50) amorphous alloy. The relationship between the permeability and the Vickers hardness for the melt-spun (Ni0.6 Nb0.4 Zr50) amorphous alloys with Pd thin films deposited by sputtering (●) or electro-less plating (○) is shown in Fig. 4. As shown in the figure, there is a tendency for the hydrogen permeability to decrease with increasing the Vickers hardness. The Vickers hardness of the (Ni0.6 Nb0.4 Zr50) amorphous alloy with the lowest permeability possesses the highest hardness.

Here, we discuss the reason why the (Ni0.6 Nb0.4 Zr50) amorphous alloy possesses the lowest hydrogen permeability among the alloys prepared in this study. No sharp diffraction peak is seen in the 2θ range of 20°–80°, indicating that the alloy consists of a single amorphous phase.

Table 2 The list of the mixing enthalpies of the constitutional elements (Ni, Nb and Zr) and the added 4th elements for the (Ni0.6 Nb0.4 Zr50) amorphous alloy.

<table>
<thead>
<tr>
<th>X elements</th>
<th>Heat of mixing [kJ (mole of atoms)^-1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Ni</td>
</tr>
<tr>
<td>Nb</td>
<td>-22</td>
</tr>
<tr>
<td>Zr</td>
<td>-18</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
</tr>
<tr>
<td>Co</td>
<td>-25</td>
</tr>
<tr>
<td>Cu</td>
<td>-23</td>
</tr>
<tr>
<td>P</td>
<td>-81</td>
</tr>
<tr>
<td>Pd</td>
<td>-119</td>
</tr>
<tr>
<td>Si</td>
<td>-91</td>
</tr>
</tbody>
</table>

The hardness of the (Ni0.6 Nb0.4 Zr50) amorphous alloy possesses the highest hardness among the alloys prepared in this study. No sharp diffraction peak is seen in the 2θ range of 20°–80°, indicating that the alloy consists of a single amorphous phase.

The mixing enthalpy of the 4th additional element and the constitutional elements (Ni, Nb and Zr) are summarized in Table 2. Since the mixing enthalpy of Zr-P atomic pairs is relatively lower than those of other pairs such as Ni-P and Nb-P, there may be a tendency for P atoms to gather around Zr atoms. This segregated atomic configuration may be the origin for the reductions of hydrogen solubility and the hydrogen diffusivity in the alloy, resulting in the decrease in hydrogen permeability.
673 K among the alloys examined in the present study probably because of the inhomogeneity in the atomic configurations resulting from much larger negative mixing enthalpy of Zr-P atomic pair as compared with the other pairs of Ni-P and Nb-P.

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REFERENCES