Hydrogen Permeable Nb-Based Amorphous Alloys with High Thermal Stability

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In this work, the Nb-based Nb42Ni40Co18−xZr(x = 0, 4, 12) and Nb42Ni40Co14−xZr(x = 0, 4, 12) amorphous alloy ribbons were successfully prepared by single roller melt-spinning technique. These amorphous alloys exhibit high thermal stability with the crystallization temperature (Tc) exceeding 850 K. It has been found that Tc of the Nb42Ni40Co18 alloy decreased with Zr addition, while hydrogen permeability increased linearly with Zr content. The hydrogen permeability of the Nb42Ni40Co18, Nb42Ni40Co14Zr4, Nb42Ni40Co6Zr12 and Nb42Ni40Co6Zr20 amorphous alloys at 673 K are 0.03 × 10⁻⁶, 0.23 × 10⁻³, 0.69 × 10⁻³ and 1.40 × 10⁻¹ mol·m⁻¹·Pa⁻¹·s⁻¹, respectively. It is noticed that hydrogen permeability of the Nb42Ni40Co6Zr20 alloy is comparable with that of Pd–Ag alloy (1.14 × 10⁻⁹). Meanwhile, permeability of the above mentioned alloy decreased to 60% of the initial value while it still maintains amorphous structure after 24 h long term durability test. Both thermal stability and hydrogen permeability are enhanced by substituting 8 at% Ni with Ta or Ti in the Nb42Ni40Co18 alloy. The present result indicates that the Nb-based amorphous alloys possess the potential of applying as a kind of hydrogen permeable membrane at high temperature. [doi:10.2320/matertrans.MF201310]

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1. Introduction

In order to solve the problems such as energy crisis and environmental pollution caused by excessive consumption of fossil fuels nowadays, people are trying to find other kinds of energy. Among them, hydrogen energy attracts much attention because of its high efficiency and no pollution. For the large scale application of hydrogen energy, a whole system including the production, purification, storage, distribution and utilizing of hydrogen needs to be established. The purification of hydrogen is an important procedure because in many cases such as semiconductor industry and fuel cells, pure hydrogen is necessary. However, the hydrogen produced by steam reforming contains lots of other contamination gases, e.g., O2, N2, CO, CO2, CH4 and so on, which is detrimental for the application of hydrogen. Traditionally, Pd and Pd- alloys have been used as hydrogen permeable membranes to obtain pure hydrogen, especially the Pd–Ag8 and Pd–Cu3 alloys are now commercially available. Since Pd is a noble metal with high price and limited resources, the development of substitute materials with lower cost for hydrogen purification is becoming a very urgent task.

Amorphous alloy is a kind of material without crystalline structure and has very high strength4–7 due to the absence of dislocations. By single roller melt-spinning, thin amorphous alloy membrane can be obtained easily, while the conventional Pd-based alloys need repeated rolling and subsequent annealing to be a thinner membrane.8) During the past few years, there are many papers on hydrogen permeable amorphous alloy membranes.3–21) Table 1 lists the main results on this subject. Hara et al. investigated the hydrogen permeability of Ni–Zr amorphous alloys9) and the effect of Ti or Hf addition.10) Yamaura et al. designed the Ni–Nb–Zr alloy system and found that the hydrogen permeability increased with increasing Zr content11) and that further alloying with Co or Cu is beneficial for the permeability.12–14) Further investigations in the Ni–X–Zr alloys revealed that Ni content should be reduced to improve hydrogen permeability.15) Lee et al. developed the Ni–Nb–Ti–Zr amorphous alloys with improved permeability at higher temperature.17) Qiang et al. discussed the effect of Ta substitution for Nb in the Ni–Nb–Zr alloy and found that Ta is effective in improving its thermal stability without severely deteriorating the permeability.18) It can be seen from Table 1 that some membranes possess permeability comparable with or even better than that of Pd-alloys. So, amorphous alloy may be a potential candidate as a hydrogen permeable membrane in the future, while much research work is still required.

Since amorphous alloy is a kind of metastable material, when the temperature exceeds its crystallization temperature (Tc) it tends to crystallize and the properties associated with the amorphous structure will disappear. Therefore, enhancing the thermal stability of amorphous alloy is very important for...
its practical application.\(^{18-22}\) We can see that most alloys listed in Table 1 are Ni-based alloys and their \(T_x\) are relatively low, resulting that their thermal stability is a little insufficient. So, developing hydrogen permeable amorphous alloys with higher \(T_x\) is meaningful. In this work, we designed the \(\text{Nb}_{42}\text{Ni}_{32}\text{Co}_{6}\text{Zr}_{12}x\) alloy (\(x = 0, 4, 12\)) and \(\text{Nb}_{42}\text{Ni}_{32}\text{Co}_{6}\text{Zr}_{12}x\) \((M = \text{Ta}, \text{Ti}, \text{Zr})\) amorphous alloy membranes as well as Pd-23\%Ag alloy.

### Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>(T_x) (K)</th>
<th>Permeability, (10^{-8} \text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Nb}<em>{42}\text{Ni}</em>{40}\text{Co}_{18})</td>
<td>913</td>
<td>0.05 0.03 — —</td>
</tr>
<tr>
<td>(\text{Nb}<em>{42}\text{Ni}</em>{40}\text{Co}<em>{14}\text{Ta}</em>{4})</td>
<td>894</td>
<td>0.28 0.23 0.17 —</td>
</tr>
<tr>
<td>(\text{Nb}<em>{42}\text{Ni}</em>{40}\text{Co}<em>{12}\text{Ti}</em>{2})</td>
<td>868</td>
<td>— 0.69 0.52 0.42</td>
</tr>
<tr>
<td>(\text{Nb}<em>{42}\text{Ni}</em>{40}\text{Co}<em>{12}\text{Ta}</em>{4}\text{Ti}_{2})</td>
<td>936</td>
<td>— 0.88 0.67 0.47</td>
</tr>
<tr>
<td>(\text{Nb}<em>{42}\text{Ni}</em>{40}\text{Co}<em>{12}\text{Ti}</em>{2}\text{Zr}_{2})</td>
<td>946</td>
<td>— 1.30 1.01 0.75</td>
</tr>
<tr>
<td>(\text{Nb}<em>{42}\text{Ni}</em>{40}\text{Co}<em>{12}\text{Zr}</em>{20})</td>
<td>859</td>
<td>— 1.40 0.95 0.60</td>
</tr>
<tr>
<td>Pd-23%Ag</td>
<td>—</td>
<td>1.14 0.85 0.58</td>
</tr>
</tbody>
</table>

### 2. Experimental

Nb-based \(\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_{x}\) \((x = 0, 4, 12)\) and \(\text{Nb}_{42}\text{Ni}_{32}\text{Co}_{6}\text{Zr}_{12}x\) \((M = \text{Ta}, \text{Ti}, \text{Zr})\) alloys were prepared by arc-melting the mixture of pure metals (purity higher than 99.9\%) under a Ti-getter argon atmosphere, the master alloys were remelted four times for composition homogeneity. By single roller melt-spinning method, we obtained the ribbon samples approximately 10 mm in width and 50 \(\mu\)m in thickness. The samples were polished and sputtered with Pd coating on both sides, the thickness of the coating is about 100 nm. Hydrogen permeability was tested by the conventional gas permeation technique at 573, 623, 673 and 723 K, respectively. The permeation area is about 5 mm in diameter, the lower side pressure was kept to be 0.1 MPa and the upper pressure was up to 0.3 MPa (for the \(\text{Nb}_{42}\text{Ni}_{32}\text{Co}_{12}\text{Zr}_{12}M_8\) \((M = \text{Ta}, \text{Ti}, \text{Zr})\) alloys the maximum pressure was 0.2 MPa).

Microstructure of the ribbon samples was studied by a Rigaku D/max-RB X-ray diffraction spectrometry (XRD) with Cu K\(\alpha\) radiation. Thermal properties of the samples were examined by differential scanning calorimeter (DSC) instrument in an Ar gas flow at a heating rate of 20 K/min.

### 3. Results and Discussion

Figure 1 shows the XRD patterns of the melt-spun Nb-based \(\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_{x}\) \((x = 0, 4, 12)\) and \(\text{Nb}_{42}\text{Ni}_{32}\text{Co}_{6}\text{Zr}_{12}x\) \((M = \text{Ta}, \text{Ti}, \text{Zr})\) alloy ribbons. The XRD spectra are characterized by a broad diffraction halo without any sharp crystalline peaks within the whole scanning range. All the melt-spun samples were identified to possess amorphous structure.

The DSC curves of the melt-spun \(\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_{x}\) \((x = 0, 4, 12)\) and \(\text{Nb}_{42}\text{Ni}_{32}\text{Co}_{6}\text{Zr}_{12}x\) \((M = \text{Ta}, \text{Ti}, \text{Zr})\) alloy ribbons are shown in Fig. 2. The crystallization temperatures \(T_x\) are marked with arrows in Fig. 2 and listed in Table 2. There is no detectable glass transition before crystallization for all the alloys studied. These curves basically comprise of two main crystallization peaks. In the Nb–Ni–Co–Zr quaternary alloys, crystallization temperature \(T_x\) decreased with increasing Zr content. \(T_x\) of the \(\text{Nb}_{42}\text{Ni}_{32}\text{Co}_{6}\text{Zr}_{20}\) alloy (859 K) is 54 K lower than that of...
the Nb_{42}Ni_{40}Co_{18} base alloy (913 K). While T_{x} increased by replacing 8 at% Ni with Ta (936 K) or Ti (946 K) of the Nb_{42}Ni_{40}Co_{18}Zr_{12} alloy (869 K). These T_{x} values are much higher than other amorphous alloys except for a few ones (see Table 1 and Ref. 22). It indicates that the present Nb-based amorphous alloys possess good thermal stability as expected.

Figures 3(a)–(c) shows some representative hydrogen flow rate (F) versus the pressure difference (\Delta p) plots for Nb_{42}Ni_{40}Co_{18}Zr_{12}M_{x} (M = Ta, Ti, Zr) alloys, respectively. That of Nb_{42}Ni_{40}Co_{18}Zr_{12} (x = 0, 4, 12) alloys are not shown here. It is found that the hydrogen flow rate (F) varied nearly linearly with the pressure difference (\Delta p), this indicates that the diffusion of hydrogen atoms in the membrane is the rate-limiting process for the alloys studied.\textsuperscript{11} Hydrogen permeability of the Nb_{42}Ni_{40}Co_{18}Zr_{12} (x = 0, 4, 12) and Nb_{42}Ni_{40}Co_{18}Zr_{12}M_{x} (M = Ta, Ti, Zr) alloys as well as Pd–23%Ag alloy at different temperatures are measured and listed in Table 2. For clarity, Arrhenius plots for Nb_{42}Ni_{40}Co_{18}Zr_{12} (x = 0, 4, 12) and Nb_{42}Ni_{40}Co_{18}Zr_{12}M_{x} (M = Ta, Ti, Zr) alloys as well as Pd–23%Ag standard sample are clearly demonstrated in Fig. 4(a)–(f), the Nb_{42}Ni_{40}Co_{18} base alloy is not included as the data is too low. From Fig. 4 and Table 2 it is found that the hydrogen permeability of the Nb-based alloys increased as the temperature increases. Permeability for the Nb_{42}Ni_{40}Co_{18}, Nb_{42}Ni_{40}Co_{18}Zr_{4}, Nb_{42}Ni_{40}Co_{18}Zr_{12}, Nb_{42}Ni_{40}Co_{18}Zr_{12}Ta_{8}, Nb_{42}Ni_{40}Co_{18}Zr_{12}Ti_{8}, and Nb_{42}Ni_{40}Co_{18}Zr_{20} amorphous alloys and the Pd–23%Ag alloy at 673 K are 0.03 \times 10^{-8}, 0.23 \times 10^{-8}, 0.69 \times 10^{-8}, 0.88 \times 10^{-8}, 1.30 \times 10^{-8}, 1.40 \times 10^{-8} and 1.14 \times 10^{-8} \text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}, respectively. The present permeability of Pd–23%Ag alloy is a little bit lower than Haras’s result.\textsuperscript{9} This might be attributed to the different measurement equipment. It is worth to mention that hydrogen permeability of the Nb_{42}Ni_{40}Co_{18}Zr_{12}Ti_{8} and Nb_{42}Ni_{40}Co_{18}Zr_{20} alloys is higher than the Pd–23%Ag alloy in this study. It is also comparable with other amorphous alloys listed in Table 1.\textsuperscript{9,20}

According to Fick’s first law and the Sievert’s law, the hydrogen flow rate F through the membrane can be described by the following equation:\textsuperscript{11,21}

\[
F = \frac{P \cdot (\sqrt{p_1} - \sqrt{p_2})}{L} = \frac{D \cdot K \cdot (\sqrt{p_1} - \sqrt{p_2})}{2L},
\]

where F represents the hydrogen flow rate (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}), P is the hydrogen permeability (\text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}), L is the thickness of the membrane (m), D is the diffusion coefficient (\text{m}^2 \cdot \text{s}^{-1}), K is the hydrogen absorption coefficient (mol^{-1} \cdot \text{Pa}^{-1/2}), and p_{1}, p_{2} are the hydrogen pressure of the upper and lower side (Pa), respectively.

From the above equation, it is clear that the hydrogen permeation is controlled by both hydrogen absorption and hydrogen diffusion. From Fig. 4 and Table 2, it can be found that hydrogen permeability of the Nb_{42}Ni_{40}Co_{18} alloy is greatly enhanced by replacing Co and Ni with Zr. Hydrogen
permeability increased with higher Zr content on the overall. The correlation between the permeability and Zr content is more clearly demonstrated in Fig. 5. From Fig. 5, hydrogen permeability of the Nb–Ni–Co–Zr alloy almost increases linearly with Zr content. Similar trend was also observed in Ni–Nb–Zr system. As is reported by Aoki et al., the hydrogen absorption in the Ni–Zr system increased dramatically with Zr addition. Harris et al. also reported that hydrogen tends to stay between tetrahedral interstitial sites surrounded by Zr4 atoms rather than Zr3Ni1 or Zr2Ni2 sites. The increase of hydrogen permeability with Zr addition may also be attributed to an improved hydrogen absorption in the Nb–Ni–Co–Zr system.

It is noticed from Fig. 4 and Table 2 that by substituting 8at% Ni with Ta or Ti in the Nb42Ni40Co6Zr12 alloy, the hydrogen permeability is also increased. The reason may lie in that Ta and Ti belong to the early transition metal (ETM), while Ni belongs to late transition metal (LTM). The ETMs commonly have higher affinity with hydrogen than the LTMs. By addition of Ta or Ti and reduction of Ni content, hydrogen absorption property of the Nb42Ni40Co6Zr12 alloy is increased, resulting in the improvement of hydrogen permeability. This is in consistent with our previous result in Ni–X–Zr alloys.

Moreover, from Fig. 1 it is clearly seen that the halo peak position is slightly shifted to lower angle with the increasing in Zr content in the quaternary Nb–Ni–Co–Zr alloys. By replacing 8 at% Ni with Ti or Ta in the Nb42Ni40Co6Zr12 alloy, the peak angle also become smaller. This peak shift is related with the increase in average distance between atoms according to Jiao’s work. From the geometric point of view, it is reasonable because the atomic radius of Zr (0.160 nm) is much larger than Ni (0.125 nm) and Co (0.125 nm). The atomic radius of Ti (0.146 nm) and Ta (0.143 nm) is also larger than Ni (0.125 nm). The introduction of larger atoms (Ta, Ti and Zr) leads to an increase in the average distance between atoms, the expansion of amorphous structure may be beneficial for hydrogen to pass through. In this way, the hydrogen permeation property is also enhanced.

As is demonstrated in Fig. 4 and Table 2, the Nb42Ni13Co6Zr20 alloy possess good hydrogen permeability comparable with that of Pd–23%Ag alloy, also it is the highest among the Nb-based amorphous alloys studied (at 673 K), so we further investigate its long term durability together with structural change before and after permeation test to see its practical performance.

Long term durability of the amorphous Nb42Ni32Co6Zr20 alloy membrane was performed by a 24 h permeation test at 673 K under a constant upper pressure of 0.2 MPa, the result is shown in Fig. 6. It can be seen that during the first few hours the permeability decreased slightly, and it remained nearly unchanged later on. The permeability after 24 h is 60% of the initial value. In contrast, both (Ni0.6Nb0.4)55Zr40Co5 amorphous alloy and the (Ni0.6Nb0.4)70Zr30 amorphous alloy degrade rapidly over time. The present result indicates that the Nb42Ni32Co6Zr20 alloy membrane is very stable during the long term performance.

Figure 7 shows the XRD spectra of the Nb42Ni13Co6Zr20 alloy membrane (a) Pd sputtered and (b) after 24 h permeation test.
Fig. 8 AES depth profile of Pd-coated Nb$_{42}$Ni$_{32}$Co$_{6}$Zr$_{20}$ alloy membrane after 24 h permeation test.

Figure 8 shows the AES depth profile of the Nb$_{42}$Ni$_{32}$Co$_{6}$Zr$_{20}$ alloy membrane after 24 h permeation test. From Fig. 8 we can see that the ratio of Nb, Ni, Co and Zr remain unchanged compared with the nominal composition, while the total amount decreased due to oxygen. This means that an oxidation layer formed after a 24 h long term permeation test, it will lead to a barrier for hydrogen to pass through. Meanwhile it is noticed that some Pd diffuse into the membrane, the depth is about 100 nm. As a result, the catalytic property is damaged. Both oxidation and interdiffusion of Pd into the membrane are responsible for the property degradation after 24 h long term permeation test, as shown in Fig. 6.

4. Conclusions

In this work, Nb-based Nb$_{42}$Ni$_{40}$Co$_{18}$Zr$_{12}$ and Nb$_{42}$Ni$_{32}$Co$_{6}$Zr$_{12}$M$_{8}$ (M = Ta, Ti, Zr) amorphous alloy ribbons were successfully prepared by single roller melting-spinning technique. They all exhibit high thermal stability with the crystallization temperature ($T_{x}$) exceeding 850 K. $T_{x}$ decreased while the hydrogen permeability increased with Zr addition in the Nb–Ni–Co–Zr quaternary alloy system. Both $T_{x}$ and the hydrogen permeability increased by substituting 8 at% Ni with Ta or Ti in the Nb$_{42}$Ni$_{40}$Co$_{18}$Zr$_{12}$ alloy. Hydrogen permeability at 673 K for the Nb$_{42}$Ni$_{32}$Co$_{6}$Zr$_{12}$Ti$_{8}$ and Nb$_{42}$Ni$_{32}$Co$_{6}$Zr$_{20}$ amorphous alloys are 1.30 × 10$^{-8}$ and 1.40 × 10$^{-8}$ mol·m$^{-1}$·s$^{-1}$·Pa$^{-1/2}$, respectively, higher than that of the Pd–23%Ag alloy (1.14 × 10$^{-8}$). In addition, permeability of the Nb$_{42}$Ni$_{32}$Co$_{6}$Zr$_{20}$ amorphous alloy decreased to 60% of the initial value while it still maintains amorphous structure after 24 h long term durability test. The degradation is attributed to oxidation and Pd interdiffusion. The present result indicates that the Nb-based amorphous alloys possess the potential of applying as a kind of hydrogen permeable membrane at high temperature.

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