Hydrogen Permeable Nb-Based Amorphous Alloys with High Thermal Stability

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In this work, the Nb-based Nb₄₂Ni₄₀Co_{18-x}Zr_x (x = 0, 4, 12) and Nb₄₂Ni₃₂Co₆Zr₁₂M₈ (M = Ta, Ti, Zr) amorphous alloy ribbons were successfully prepared by single roller melt-spinning technique. These amorphous alloys exhibit high thermal stability with the crystallization temperature (T_x) exceeding 850 K. It has been found that T_x 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 Nb₄₂Ni₃₂Co₆Zr₂₀ amorphous alloys at 673 K are 0.03×10^{-8} , 0.23×10^{-8} , 0.69×10^{-8} and 1.40×10^{-8} mol·m⁻¹·s⁻¹·Pa^{-1/2}, respectively. It is noticed that hydrogen permeability of the Nb₄₂Ni₃₂Co₆Zr₂₀ alloy is comparable with that of Pd-23%Ag alloy (1.14×10^{-8}). 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 Nb₄₂Ni₄₀Co₆Zr₁₂ 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.

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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,¹⁾ 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-Ag²⁾ 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.⁹⁻²¹⁾ 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

Table 1 Crystallization temperature (T_x) and hydrogen permeability of the amorphous alloy membranes as compared with Pd₇₇Ag₂₃ alloy.

Composition	T_x (K)	Permeability (673 K), $\times 10^{-8}$ mol·m ⁻¹ ·s ⁻¹ ·Pa ^{-1/2}	Year
Ni-Zr ⁹⁾	833	0.12 (at 623 K)	2000
Ni-(Ti, Hf)-Zr ¹⁰⁾	~820	<0.12	2002
Ni-Nb-Zr ¹¹⁾	800-910	0.11-1.30	2003
Ni-Nb-Zr-(Co, Cu) ¹²⁾	720-740	2.34-2.46	2004
Zr-Al-Co-Ni-Cu ¹³⁾	<800	1.13	2004
Ni-Nb-Zr ¹⁴⁾	<800	1.59	2005
Ni-Ti-Zr ¹⁵⁾	<750	1.05	2005
Ni-Nb-Ti-Zr ¹⁷⁾	903	2.50-2.89 (at 773 K)	2008
Ni-Ta-Zr ¹⁸⁾	865	0.86	2009
Ni-Nb-Ta-Zr-Co ¹⁹⁾	820	0.97	2010
Ni-Nb-(Ta)-Zr ²⁰⁾	800-900	1.40 (at 723 K)	2011
Pd ₇₇ Ag ₂₃ ⁹⁾	—	1.5 (at 623 K)	2000

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 (T_x) 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

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Table 2 Composition, thermal property and hydrogen permeability of the $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) amorphous alloy membranes as well as Pd-23%Ag alloy.

Composition	T_x (K)	Permeability, $\times 10^{-8} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}$			
		723 K	673 K	623 K	573 K
$\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18}$	913	0.05	0.03	—	—
$\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{14}\text{Zr}_4$	894	0.28	0.23	0.17	—
$\text{Nb}_{42}\text{Ni}_{40}\text{Co}_6\text{Zr}_{12}$	868	—	0.69	0.52	0.42
$\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{Ta}_8$	936	—	0.88	0.67	0.47
$\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{Ti}_8$	946	—	1.30	1.01	0.75
$\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{20}$	859	—	1.40	0.95	0.60
Pd-23%Ag	—	—	1.14	0.85	0.58

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 $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) alloys based on the following considerations: Niobium (Nb) based amorphous alloy is seldom reported; meanwhile Nb is an element with high melting temperature and possesses good hydrogen permeation property in crystalline state. So, we investigated the properties of Nb-based $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) alloys to see whether it can be made amorphous or not and whether it is suitable for hydrogen permeation or not. We designed the ternary $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18}$ alloy as a base alloy by replacing Ta with Nb in the $\text{Ta}_{42}\text{Ni}_{40}\text{Co}_{18}$ alloy, which was reported to form a bulk metallic glass with a critical diameter of 2 mm.²³ By substituting Co with Zr, quaternary $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) alloys are obtained. Further substitution of Ni with Ta, Ti and Zr leads to the $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) alloys. They were listed in Table 2.

2. Experimental

Nb-based $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) 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 μm 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 $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) 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 $\text{Cu K}\alpha$ 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.

Fig. 1 XRD spectra of the $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) alloy ribbons.

Fig. 2 DSC curves of the $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) alloy ribbons.

The depth profile and compositional variations of the Pd-coated Nb-based amorphous alloy after hydrogen permeation was measured by ULVAC-PHI, Inc. type Auger electron spectroscopy (AES).

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 $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) 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 $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($\text{M} = \text{Ta}, \text{Ti}, \text{Zr}$) 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

Fig. 3 Hydrogen flow rate (F) vs. the pressure difference ($\Delta\sqrt{p}$) for $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($M = \text{Ta}, \text{Ti}, \text{Zr}$) alloys.

the $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18}$ base alloy (913 K). While T_x increased by replacing 8at% Ni with Ta (936 K) or Ti (946 K) of the $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_6\text{Zr}_{12}$ 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 ($\Delta\sqrt{p}$, $=p_1^{1/2} - p_2^{1/2}$) relationship at different temperatures for the $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($M = \text{Ta}, \text{Ti}, \text{Zr}$) alloys, respectively. That of $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) alloys are not shown here. It is found that the hydrogen flow rate (F) varied nearly linearly with the pressure difference ($\Delta\sqrt{p}$), this indicates that the diffusion of hydrogen atoms in the membrane is the

Fig. 4 Arrhenius plots of the $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($M = \text{Ta}, \text{Ti}, \text{Zr}$) amorphous alloys as well as Pd–23%Ag alloy.

rate-limiting process for the alloys studied.¹¹⁾ Hydrogen permeability of the $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 0, 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($M = \text{Ta}, \text{Ti}, \text{Zr}$) alloys as well as Pd–23%Ag alloy at different temperatures are measured and listed in Table 2. For clarity, Arrhenius plots for $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18-x}\text{Zr}_x$ ($x = 4, 12$) and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{M}_8$ ($M = \text{Ta}, \text{Ti}, \text{Zr}$) alloys as well as Pd–23%Ag standard sample are clearly demonstrated in Fig. 4(a)–(f), the $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18}$ 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 $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18}$, $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{14}\text{Zr}_4$, $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_6\text{Zr}_{12}$, $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{Ta}_8$, $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{Ti}_8$ and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{20}$ amorphous alloys and the Pd–23%Ag alloy at 673 K are 0.03×10^{-8} , 0.23×10^{-8} , 0.69×10^{-8} , 0.88×10^{-8} , 1.30×10^{-8} , 1.40×10^{-8} and $1.14 \times 10^{-8} \text{ mol.m}^{-1}\text{s}^{-1}\text{Pa}^{-1/2}$, respectively. The present permeability of Pd–23%Ag alloy is a little bit lower than Hara's result.⁹⁾ This might be attributed to the different measurement equipment. It is worth to mention that hydrogen permeability of the $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{12}\text{Ti}_8$ and $\text{Nb}_{42}\text{Ni}_{32}\text{Co}_6\text{Zr}_{20}$ alloys is higher than the Pd–23%Ag alloy in this study. It is also comparable with other amorphous alloys listed in Table 1.^{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,^{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 ($\text{mol.m}^{-2}\text{s}^{-1}$), P is the hydrogen permeability ($\text{mol.m}^{-1}\text{s}^{-1}\text{Pa}^{-1/2}$), L is the thickness of the membrane (m), D is the diffusion coefficient (m^2s^{-1}), K is the hydrogen absorption coefficient ($\text{mol.m}^{-3}\text{Pa}^{-1/2}$), 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 $\text{Nb}_{42}\text{Ni}_{40}\text{Co}_{18}$ alloy is greatly enhanced by replacing Co and Ni with Zr. Hydrogen

Fig. 5 Hydrogen permeability at 673 K vs. Zr content in the Nb–Ni–Co–Zr quaternary alloy system.

Fig. 6 Long term durability (24 h) test of the Nb₄₂Ni₃₂Co₆Zr₂₀ alloy for hydrogen permeation at 673 K under a constant pressure of 0.2 MPa.

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^{11,14)} system. As is reported by Aoki *et al.*,²⁴⁾ the hydrogen absorption in the Ni–Zr system increased dramatically with Zr addition. Harris *et al.*²⁵⁾ 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 8 at% 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.²¹⁾ 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.¹⁵⁾

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.²⁶⁾ 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).²⁷⁾ 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 Nb₄₂Ni₃₂Co₆Zr₂₀ alloy possess good hydrogen permeability compara-

Fig. 7 XRD spectra of the Nb₄₂Ni₃₂Co₆Zr₂₀ alloy membrane (a) Pd sputtered and (b) after 24 h permeation test.

ble 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 (Ni_{0.6}Nb_{0.4})₅₅Zr₄₀Co₅ amorphous alloy¹⁶⁾ and the (Ni_{0.6}Nb_{0.4})₇₀Zr₃₀ amorphous alloy²⁰⁾ 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 Nb₄₂Ni₃₂Co₆Zr₂₀ alloy membrane (a) Pd sputtered and (b) after permeation test. There is no peak related to the crystallization of the membrane, which means that the membrane still possess its amorphous structure. Meanwhile, the peaks of Pd shifts to lower angle a little bit after the permeation test, this is caused by the hydrogen solution in Pd, leading to a slightly expanded lattice.¹⁷⁾

Fig. 8 AES depth profile of Pd-coated Nb₄₂Ni₃₂Co₆Zr₂₀ alloy membrane after 24 h permeation test.

Figure 8 shows the AES depth profile of the Nb₄₂Ni₃₂-Co₆Zr₂₀ 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 Nb₄₂Ni₄₀Co_{18-x}Zr_x ($x = 0, 4, 12$) and Nb₄₂Ni₃₂Co₆Zr₁₂M₈ (M = Ta, Ti, Zr) amorphous alloy ribbons were successfully prepared by single roller melt-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 Nb₄₂Ni₄₀Co₆Zr₁₂ alloy. Hydrogen permeability at 673 K for the Nb₄₂Ni₃₂Co₆Zr₁₂Ti₈ and Nb₄₂Ni₃₂Co₆Zr₂₀ amorphous alloys are 1.30×10^{-8} and $1.40 \times 10^{-8} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}$, respectively, higher than that of the Pd–23%Ag alloy (1.14×10^{-8}). In addition, permeability of the Nb₄₂Ni₃₂Co₆Zr₂₀ 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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