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Hydrogen Permeation Properties of Pd-Coated $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ Amorphous Membrane

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Abstract. The hydrogen permeation properties of the Pd-coated $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ amorphous membranes have been investigated at 673 and 723K for 720 hours (1 month). Values of the hydrogen permeability during these long term tests were found to be reduced of about 50 and 30 % at 673 and 723K, respectively. The reduction in the hydrogen permeability could be correlated to the change in the composition of the coating as well as at the interface between Pd coating and Ni-based amorphous membrane.

Introduction

The unique structure of metallic amorphous alloys provides them with exceptional physical (magnetic), chemical (corrosion), and mechanical (strength) properties, which make them attractive candidate materials for aerospace and advanced military applications, sporting goods, medical, electronic and micro/nano-electro mechanical devices [1]. Owing to growing concerns about global warming and depletion of the natural resources, the potential of amorphous metallic glass alloys as functional and structural materials for an hydrogen society have been investigated [2,3]. It has been shown that Ni-based metallic glasses exhibit hydrogen permeation similar to that of Pd metal and alloys. Zr-containing $Ni_{60}Nb_{40}$ composition demonstrated the best performance so far in terms of maximum hydrogen permeability. Shimpo *et al.* reported for $(Ni_{0.6}Nb_{0.4})_{95-x}Zr_xCo_5$ amorphous alloys with $30 \leq x \leq 50$ at.% values of hydrogen permeability at 400°C in the range 1-3 x 10^{-8} $mol.m^{-1}s^{-1}Pa^{-1/2}$, which are similar to those of Pd-Ag alloys [4]. However tests performed for up to 1.5 10^5 sec indicated a reduction of the hydrogen permeability that has been attributed to a contamination of the Pd surface and a structural change induced by the diffusion of Pd. More recently Ta was introduced in the $Ni_{60}Nb_{40}$ amorphous alloys to enhance the stability of the amorphous structure at high temperature [5-8]. Using mixed gas to simulate conditions encountered in methanol steam reforming high values of the hydrogen permeability were reported by Yamaura *et al*. for the $(Ni_{0.6}Nb_{0.4})_{70}Zr_{25}Ta_5$ [6] and $Ni_{40}Nb_{20}Zr_{30}Ta_5Co_5$ [9] amorphous alloy compositions.

In order to demonstrate the durability of such alloy systems, the hydrogen permeability of the $Ni_{37.5}Nb_{27.5}Zr_{25}Ta_5Co_5$ amorphous alloy was investigated using pure H_2 at 673 and 723K for tests performed up to 720 hours.

Experimental Procedures

$Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ ribbons of 30 mm width and ~30-35 μm thickness were prepared using single roller melt-spinning technique under vacuum by AMO Ltd, Korea. Hydrogen permeability tests were performed at 673 and 723K by means of with a conventional gas-permeation technique at a hydrogen pressure of 0.2 MPa using pure H_2 (6N). For that purpose, a thin layer of about 150 nm thick Pd coating was preliminarily deposited by RF magnetron sputtering on both sides of the ribbons for facilitating the dissociation and recombination of the H_2 molecules [5]. The structure and thermal stability of the Pd-coated ribbon before and after permeation tests were determined using, respectively, X-ray diffraction (XRD) and a differential scanning calorimeter (DSC) (Perkin-Elmer) at a heating rate of 0.33 $K.s^{-1}$, in the temperature range of 473 to 923 K. Auger electron spectroscopy (AES) analyses were performed before and after hydrogen permeation test to study the possible change of the thickness of the Pd layer and the composition at the interface coating/membrane.

Results and Discussion

Although the composition investigated in this study is slightly different than the one developed by Yamaura *et al.* [9], i.e., higher Nb content and lower Zr content, the ribbons were also fully amorphous as indicated that the XRD (Figs.1a) and DSC traces (Fig.2a). For that alloy composition, Tg was about 830 K and Tx about 860 K (Table 1), which are slightly larger values than those reported by Yamaura *et al.* [9] owing to the higher Nb content and conversely lower Zr content. The reduced value of ΔTx (= Tx – Tg) can also be explained by the excessive content of Nb that certainly reduced the glass formability of that alloy system.

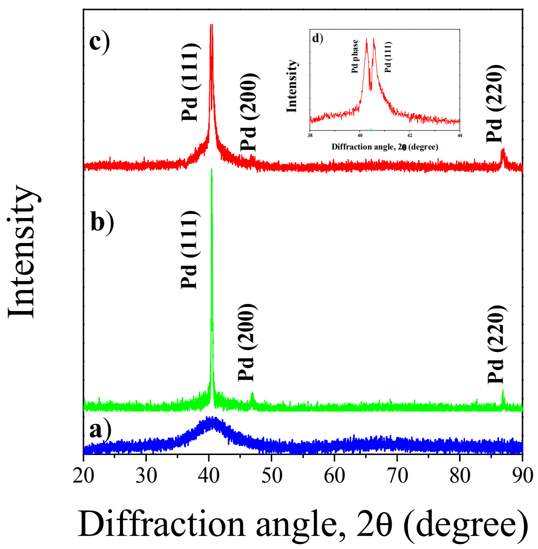

Fig.1 XRD traces of the $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ amorphous ribbons; a) as-spun, b) after Pd coating, c) after permeation test at 673 K, and d) detail of c).

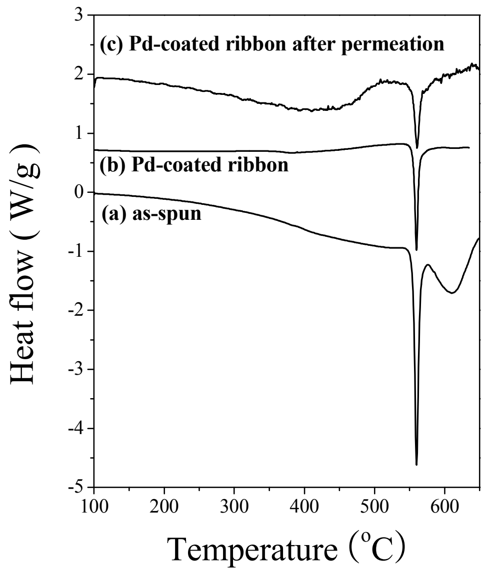

Fig.2 DCS traces of the amorphous ribbons of composition $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$; a) as-spun, b) after Pd coating, and c) after permeation test at 673K.

Table 1 Thermal characteristic of the $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ amorphous ribbons

	Tg (K)	Tx (K)	ΔTx (K)	ΔHx (J/g)
as-spun ribbon	532.7	560.3	27.6	39.2
Pd coated ribbon before permeation test	533.1	560.0	26.9	33.2
Pd coated ribbon after 24 hours permeation test		560.6		29.8

Fig.3 shows the hydrogen permeation data obtained at 673 and 723 K for test performed during 720 hours. The initial values of hydrogen permeation were about 0.8 and 1.6 10^{-8} $mol.m^{-1}.s^{-1}.Pa^{-1/2}$, which are comparable to those of Pd-Cu alloys. However, for both temperatures, the hydrogen permeability decreased moderately without reaching stable values. The larger decrease of the hydrogen permeation obtained at 673 K in comparison to test performed at a higher temperature cannot be explained so far, but can result a lack of reproducibility in the ribbon preparation. The reduction in the performance obtained by Yamaura *et al.* on $Ni_{40}Nb_{20}Zr_{30}Ta_5Co_5$ amorphous alloys

[9] was attributed to a contamination of the surface of Pd layer inducing a reduction of the catalytic activity together with a possible degradation of the glassy structure during permeation test performed at high temperature, resulting from a diffusion of Pd element from the surface layer into the amorphous matrix. In order to confirm such effect, the structure of the amorphous membrane after hydrogen permeation has been analyzed by XRD, DSC and AES.

The XRD and DSC traces of the $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ ribbons before and after permeation tests are presented in Fig.1 and 2, respectively. The sharp peaks in the XRD traces (Figs.1b and 1c) correspond to those of the Pd coating layer. No noticeable change in the XRD traces could be observed after permeation test except the presence of a additional peak near the (111) Pd (Figs.1c and 1d). This split of the Pd peak might results from the existence of two Pd phases; a pure Pd phase and a Pd-rich phase of a slightly larger lattice parameter.

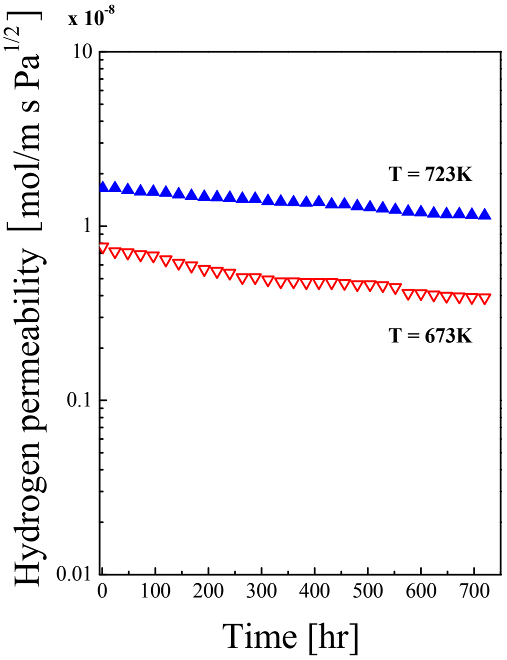

Fig.3 Variation of the hydrogen permeability with the time for tests performed at 673 and 723 K.

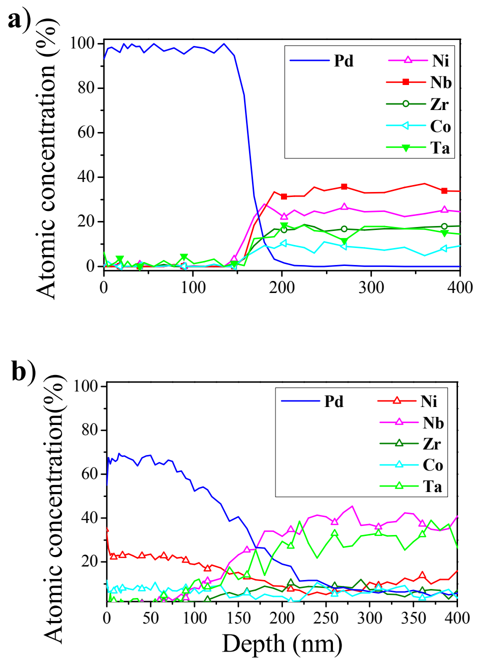

Fig.4 Auger depth profiles of the Pd-coated $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ amorphous ribbons; a) before, and b) after permeation at 673 K.

The DSC traces of the Pd-coated ribbons before and after hydrogen permeation are shown in Fig.2b and 2c, respectively. It can be noticed that the crystallization temperature did not change however the (slight) reduction of the enthalpy of crystallization suggests a moderate modification of the amorphous structure during hydrogen permeation test. Further analyses should be performed by transmission electron microscopy.

The depth profile measured by AES for the Pd-coated $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ ribbons before permeation test is shown in Fig.4a. After permeation test, as shown in Fig.4b, a slight modification can be observed with a reduction of the thickness of the Pd layer accompanied by a diffusion of Pd inwards the ribbon and an outward diffusion of Ni. The outward diffusion of Ni can be explained by the small atomic size of that element, and its presence in the Pd layer can certainly explain the continuous reduction of the catalytic properties during hydrogen permeation. In addition the change of the atomic composition at the interface between coating and amorphous ribbon can induce two possible structural modifications. The incorporation of Pd is believed to affect the local atomic arrangement around each atom by increasing the atomic packing that would result in a decrease of the hydrogen diffusion rate either because of a reduction of the free volume or a larger number of trap sites [10,11]. Moreover, as indicated from the changes in thermal properties, a slight crystallization might be expected that would also affect the hydrogen diffusion rate throughout the membrane.

Summary

The hydrogen permeation tests performed at elevated temperature on Pd-coated $Ni_{37.5}Nb_{27.5}Zr_{25}Co_5Ta_5$ ribbons for 720 hours indicate good performance in term of hydrogen permeability and durability. However these tests performed using pure hydrogen exempt of contaminant revealed a reduction of the hydrogen permeability of about 50 % and 30 % for tests performed at 673 and 723 K, respectively. That reduction in the hydrogen permeability has been correlated to a inwards diffusion of Pd and outward diffusion of Ni that affected the catalytic properties and modified the local atomic arrangement of the amorphous phase.

Acknowledgements

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References

[1] M. Miller, P. Liaw: Bulk Metallic Glasses, An Overview (Springer, 2007)

[2] N. Itoh, W.C. Xu, S. Hara, H.M. Kimura, T. Masumoto, Journal of Membrane Science, Vol.139 (1998) p.29.

[3] S. Hara, K. Sakaki, N. Itoh, H.M. Kimura, K. Asami, A. Inoue, Journal of Membrane Science, Vol.164 (2000) p.289.

[4] Y. Shimpo, S. Yamaura, M. Nishida, H.M. Kimura, A. Inoue, Journal of Membrane Science, Vol.286 (2006) p.170.

[5] K.B. Kim, K.D. Kim, D.Y. Lee, Y.C. Kim, E. Fleury, D.H. Kim, Materials Science and Engineering A, Vol.A449-451 (2007) p.934.

[6] S. Yamaura, M. Yokoyama, H.M. Kimura, A. Inoue, International Journal of Nuclear Hydrogen Production and Applications, Vol.2 (2009) p.69.

[7] S. Jayalakshmi, Y.G. Choi, Y.C. Kim, Y.B. Kim, E. Fleury, Intermetallics, in press, doi:10.1016/j.intermet.2010.03.001.

[8] S. Yamaura, A. Inoue, Journal of Membrane Science, Vol.349 (2010) p.138.

[9] S. Yamaura, H. Kimura, A. Inoue. Y. Shimpo, M. Nishida, S. Uemiya, Journal of the Society of Materials Science, Japan, Vol.57 (2008) p.1031.

[10] R. Kirchheim, Progress in Materials Science, Vol. 32 (1988) p.261.

[11] Y. Sakamoto, K. Baba, W. Kurahashi, K. Takao, S. Takayama, Journal of Non-Crystalline Solids, Vol.61/62 (1984) p.691.