The preparation and hydrogen brittleness resistance of Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ metallic glass ribbons

Xiaoqing Du*, Xiaoqiu Ye, Qingbo Ren
Institute of Materials, China Academy of Engineering Physics, No.9 Huafeng Xincun, Mianyang, Sichuan 621908, China
*Corresponding author. E-mail: xqingd@126.com.

Abstract. Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ metallic glass ribbons as wide as 10mm were prepared by splat quenching. Structure was identified with X-ray diffraction (XRD) spectrums from the conventional X-ray diffractometer and also short wavelength X-ray stress analyzer. The results confirm fully amorphous structure of the ribbons. Multiple H$_2$ adsorption and desorption cycles under a pressure of 100kPa were carried out in the metallic glass ribbon and also pure palladium membrane for comparison. The former didn’t show any cracks after more than 10 cycles, and thermal desorption spectroscopy (TDS) measurement confirms that hydrogen was adsorbed abundantly in the metallic glass ribbon. Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ metallic glass ribbons demonstrate excellent hydrogen brittleness resistance.

1. Introduction
The unique atomic structure characterization [1] and extraordinary mechanical properties (high elasticity and hardness, potential for high fracture toughness, and superior corrosion resistance) [2-7] of metallic glasses provide them a great potential in hydrogen-related applications. And there are metallic glasses which have been reported to be outstanding on hydrogen permeability [8-11]. Palladium and its alloy films are presently used in commercial processes as excellent hydrogen permeation membranes due to their high hydrogen permeability. Therefore, it’s considered that Pd-based metallic glasses are of great potential in hydrogen permeability.

Since hydrogen brittleness would be an important issue in all hydrogen-related applications, we carried out experiments to check hydrogen brittleness resistance of Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ metallic glass which possesses a relatively high $T_x$ (crystallization temperature, the point at which the glassy structure is beginning to crystallized) of 691K among the Pd-based metallic glasses [12-14]. High $T_x$ means the glassy structure remains until a high temperature, which would enlarge the applications very much.

This paper is to present the very first results of our systematic study on hydrogen-related applications of Pd-based metallic glasses.

2. Methods
Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ metallic glass ribbons (fig.1) were prepared by arc melting and copper roller spinning, the thickness and width of which are about 100μm and 10mm, respectively. The alloy compositions represent nominal atomic percentage. Ingots of Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ alloy were prepared by arc melting the mixtures of constituent elements in titanium gettered argon (with a purity of above 99.99%) protection atmosphere for more than 3 times to guarantee the chemical homogeneity, and the purities of Pd, Cu...
and Si are all higher than 99.9wt%. Then the alloy ribbons were prepared by melt-spinning on a copper roller.

Figure 1. Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ metallic glass ribbons

Structure identification of the ribbons was carried out by means of conventional X-ray diffractometer using the Cu Kα radiation ($\lambda=1.541\text{Å}$) and also short wavelength X-ray stress analyzer using the W Kα radiation ($\lambda=0.209\text{Å}$).

Then, cycled H$_2$ adsorption and desorption experiments were carried out to test hydrogen brittleness resistance, and also comparing experiments in pure palladium (99.9wt%) membrane. Samples were cut to small clips (about 3mm in width and 5mm in length) and put into a stainless steel chamber with a glass observation window on the top, then the chamber was pumped down to a vacuum level better than 10$^{-3}\text{Pa}$, and the samples were then heated at 200°C and kept for 2h with the pumping continuing to make them activated. After that, samples were cooled to room temperature and hydrogen with a pressure of 100kPa was charged into the system and kept for more than 1h to react with samples. Then, the samples were heated to 200°C again to make the hydrogen adsorbed desorb and the system was pumped to the best vacuum. Then cooled the samples to room temperature again and repeated this cycle. The samples were observed in real time using an optical microscope during the whole cycles. Hydrogen adsorption capacity of the metallic glass ribbon was studied with the method of thermal desorption spectroscopy (TDS). During the TDS experiment, there is a vacuum better than 10$^{-5}\text{Pa}$ before we heated the sample and the heating rate is 10°C/min.

3. Results and discussion

3.1. Structure characterization

Structure analysis results from the conventional XRD and short wavelength X-ray stress analyzer are shown in fig.2a and c, respectively. Since W Kα radiation used in the short wavelength X-ray stress analyzer has a very short wavelength which is 0.209Å, it has higher energy and is able to pass through the ribbon with a thickness of about 100μm (as shown in fig.2d) to confirm its internal structure. Similarly, the conventional XRD obtains only the surface structure information as shown in fig.2b. Spectra in fig.2a and c are in good agreement and both contain only a broad and continuous diffraction hump which suggests the fully amorphous nature of the ribbon, confirming the Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ alloy ribbons to be fully amorphous ones.
Figure 2. Structure analysis of Pd\textsubscript{71.5}Cu\textsubscript{12}Si\textsubscript{16.5} metallic glass ribbons

(a) and (c) are XRD spectrums by the conventional XRD and short wavelength X-ray stress analyzer respectively, and corresponding optical pathway diagrams are shown in (b) and (d).

3.2. Hydrogen brittleness resistance

Hydrogen adsorption-desorption cycles as many as 10 times were carried out in Pd\textsubscript{71.5}Cu\textsubscript{12}Si\textsubscript{16.5} metallic glass ribbon, as is shown in fig.3(a-c). There isn’t any hydrogen-induced cracks appeared. In the 10th cycle, we kept the sample in hydrogen for 16h, and its surface topography showed nothing different (fig.3d). After that, we heated the sample to desorb all the hydrogen adsorbed and charged D\textsubscript{2} (100kPa) instead into the system. This is because deuterium and hydrogen are isotopes and show similar properties, and the subsequent TDS experiment is more sensitively to deuterium, resulting in a better signal-to-noise ratio.
Figure 3. Images of Pd\textsubscript{71.5}Cu\textsubscript{12}Si\textsubscript{16.5} metallic glass ribbon during the hydrogen adsorption-desorption cycles

a is image the moment this ribbon was put in the stainless steel chamber; b, c are images after it was immersed in hydrogen atmosphere for more than 1h in the 2\textsuperscript{nd} and 10\textsuperscript{th} cycle, respectively; d is image after 16h in hydrogen in the 10\textsuperscript{th} cycle.

Figure 4. Images of pure palladium membrane during the H\textsubscript{2} adsorption and desorption cycles

a, b, c are images in the first cycle, d is image in the second cycle, e and f are images 16h in hydrogen in the 2\textsuperscript{nd} cycle showing the same place with different magnification.

Hydrogen adsorption-desorption cycles were also carried out in pure palladium membrane for comparison, as shown in fig.4. There is slight destruction in the first cycle, as signed with red circles in fig.4a-c. However, a large amount of cracks appear when we kept it in hydrogen for as long as 16h in the second cycle, and the surface become coarse which leads to the blur images (the cracks are
demonstrated more clearly in fig.5). Arrows in fig.4d-f are used to indicate the same place in these three images.

![Figure 5. SEM images of pure palladium membrane before (a) and after (b) the hydrogen adsorption-desorption cycles](image)

TDS experiment was carried out to measure hydrogen adsorption capacity, so that we can confirm if hydrogen is indeedly adsorbed in the metallic glass ribbon. As is shown in fig.6, TDS spectrum of the ribbon showed a single desorption peak at 101°C with a value higher enough than that of the background, suggesting deuterium is adsorbed abundantly and so it is with hydrogen [15].

![Figure 6. TDS spectrum of deuterium in the Pd71.5Cu12Si16.5 metallic glass ribbon](image)

Since Pd71.5Cu12Si16.5 metallic glass ribbon is able to adsorb hydrogen abundantly and bear many cycles of hydrogen adsorption and desorption without any destruction at all, it’s concluded to be very excellent in hydrogen brittleness resistance and would be suitable for hydrogen-related applications.

As is known, metallic glasses don’t form hydrides [15] and there aren’t dislocations to interact with hydrogen, plus with their enticing mechanical properties, it is the unique structure characterization that endues them with the excellent hydrogen brittleness resistance.

4. Conclusions

Pd71.5Cu12Si16.5 metallic glass ribbons with fully amorphous structure were prepared. These ribbons beared more than 10 cycles of hydrogen adsorption and desorption without any destruction under a hydrogen pressure as high as 100kPa, and TDS measurement showed that hydrogen was adsorbed in
the ribbon abundantly. That is, Pd$_{71.5}$Cu$_{12}$Si$_{16.5}$ metallic glass ribbons show excellent hydrogen brittleness resistance which is of big significance in applications of hydrogen-related fields.

Acknowledgments
I’m particularly grateful to Y. X. Geng for his help in the sample preparation and also Y. M. Wang and J. B. Qiang for the useful discussion.

References
[1] Ma E. Tuning order in disorder. Nat Mater 2015;14:547-552.
[2] Inoue A, Zhang T, Takeuchi A. Bulk amorphous alloys with high mechanical strength and good soft magnetic properties in Fe-TM-B system. Appl Phys Lett 1997;71(4):464-466.
[3] Inoue A, Shen BL, Chang CT. Super-high strength of over 4000MPa for Fe-based bulk glassy alloys in [(Fe$_{1-x}$Co$_x$)$_{0.75}$B$_{0.2}$Si$_{0.05}$]$_9$Nb$_4$ system. Acta Mater 2004;52: 4093-4099.
[4] Qin CL, Zhang W, Asami K, Kimura H, Wang XM, Inoue A. A novel Cu-based BMG composite with high corrosion resistance and excellent mechanical properties. Acta Mater 2006;54:3713-3719.
[5] Liu YH, Wang G, Wang RJ, Zhao DQ, Pan MX, Wang WH. Super plastic bulk metallic glasses at room temperature. Science 2007;315:1385-1388.
[6] Inoue A, Shen BL, Koshiba H, Kato H, Yavari AR. Cobalt-based bulk glassy alloy with ultrahigh strength and soft magnetic properties. Nat Mater 2003;2:661-663.
[7] Plummer J. Is metallic glass poised to come of age?. Nat Mater 2015;14:553-555.
[8] Kondratyev VV, Gapontsev AV, Voloshinskii AN, Obukhov AG, Timofeyev NI. The hydrogen diffusion in disordered systems. Int J Hydrogen Energ 1999;24: 819-824.
[9] Paglieri SN, Pal NK, Dolan MD, Kim SM, Chien WM, Lamb J, Chandra D, Hubbard KM, Moore DP. Hydrogen permeability, thermal stability and hydrogen embrittlement of Ni-Nb-Zr and Ni-Nb-Ta-Zr amorphous alloy membranes. J Membrane Sci 2011;378:42-50.
[10] Dolan MD, Dave NC, Ilyushechkin Ay, Morpeth LD, McLennan KG. Composition and operation of hydrogen-selective amorphous alloy membranes. J Membrane Sci 2006;285:30-55.
[11] Ding HY, Zhang W, Yamaura SI, Yao KF. Hydrogen permeable Nb-based amorphous alloys with high thermal stability. Mater Trans 2013;54(8): 1330-1334.
[12] Nishiyama N, Inoue A. Stability and nucleation behavior of glass-forming Pd-Cu-Ni-P alloy with a critical cooling rate of 0.067K/s. Intermetallics 2002;10:1141-1147.
[13] Hu X, Ng SC, Feng YP, Li Y. Glass forming ability and in-situ composite formation in Pd-based bulk metallic glasses. Acta Mater 2003;51:561-572.
[14] Lu IR, Gorler GP, Fecht HJ, Willneckier R. Investigation of specific heat and thermal expansion in the glass-transition regime of Pd-based metallic glasses. J Non-Cryst Solids 2000;274:294-300.
[15] Schroeder HW, Koster U. Hydrogen embrittlement of metallic glasses. J Non-Cryst Solids 1983;56:213-218.