Rare Metal Materials and Engineering
Volume 47, Issue 12, December 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(12): 3629-3633.

ARTICLE

Hydrogen-Related Properties of the $Pd_{71.5}Cu_{12}Si_{16.5}$ Metallic Glass

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Abstract: The $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass was synthesized as wide ribbons by arc melting and copper roller spinning. The structures were determined by X-ray diffraction patterns using the conventional X-ray diffractometer and short wavelength X-ray stress analyzer, and the fully glassy state of the ribbons is confirmed. Multiple hydrogen absorption and desorption cycles at room temperature under 100 kPa were carried out on the samples. No destruction after more than 10 cycles is observed, which demonstrates good hydrogen embrittlement resistance. The hydrogen permeation properties of the $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass and its crystallized counterpart were further tested using a direct permeation method. In the supercooled liquid region, the hydrogen permeation rate is obviously higher for the metallic glass form, which could be explained by the increasing free volumes introduced during isothermal stage in this range.

Key words: metallic glass; amorphous materials; X-ray diffraction; hydrogen embrittlement; hydrogen permeation properties

As is known, the metallic glasses possess extraordinary mechanical properties (high elasticity, large hardness, high fracture toughness, and superior corrosion resistance)[1-3], which allow them to accommodate more hydrogen atoms without failure. And their unique internal structure[4] would be an advantage for hydrogen transport. Thus, the metallic glasses can be considered as promising functional materials used in hydrogen-related industry. On the other hand, palladium and its alloy films are widely used in commercial processes as hydrogen permeation membranes due to their outstanding hydrogen permeability[5-7]. Therefore, it is naturally expected that the Pd-based metallic glasses would be of great potential in hydrogen permeation membranes, since this material integrates the advantages of both the palladium alloy films and metallic glasses.

Studies on Pd-based metallic glasses were mostly focused on their preparation[8-10], structure[11,12], mechanical properties[13-15], and crystallization[16-18], but little work was carried out on their hydrogen permeability. Prochwicz et al[19] did some work on $Pd_{33}Ni_{52}Si_{15}$. They found this metallic glass showed comparable flux of hydrogen diffusing with clean palladium membrane in similar conditions in the temperature range of 294~358 K. And it didn't show deformation during the repeated hydriding process, which is an obvious advantage compared with palladium membrane. In the present paper, we studied hydrogen embrittlement resistance and hydrogen permeability of $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass, which has a relatively high T_x (crystallization temperature, the point at which the glassy structure is beginning to crystallize) among the Pd-based metallic glasses. High T_x means the glassy structure can be remained to a high temperature, which would enlarge the temperature range of the application.

We found that the metallic glass exhibits good hydrogen absorption and desorption performance as expected. No destruction or deterioration is observed during the experiments, implying the hydrogen embrittlement resistance of this metallic glass is rather good. And it shows much higher hydrogen permeation rate than its crystalline form in the supercooled liquid region. The mechanism of absorption and diffusing of hydrogen in this metallic glass is to be further discussed in our later work.

1 Experiment

Received date: December 24, 2017
Foundation items: National Natural Science Foundation of China (21401173); National Magnetic Confinement Nuclear Fusion Program (2015GB109002)
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The $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbons were prepared by arc melting and copper roller spinning. The thickness and width of the samples are about 100 μm and 10 mm, respectively. The Pd, Cu, and Si with purities all higher than 99.9 wt% were mixed in a ratio of 71.5:12:16.5. The ingots of $Pd_{71.5}Cu_{12}Si_{16.5}$ alloy were prepared by arc melting the mixtures of constituent elements under titanium purified argon (with a purity of above 99.99%) protection atmosphere for more than 3 times to guarantee the chemical homogeneity. Then the alloy ribbons were prepared by melt-spinning on a copper roller.

The structure of the ribbons was determined by conventional X-ray diffractometer (XPERT-PRO, Panalytical instrument) using the Cu-Kα radiation (λ=0.1541 nm) and short wavelength X-ray stress analyzer (XL-1, newly developed by China Academy of Engineering Physics) using the W-Kα radiation (λ=0.0209 nm).

The glass transition and crystallization temperatures were evaluated from the DSC curves which were measured in a DSC-Q2000 TA instrument. The experiment was undertaken under a nitrogen atmosphere and a reference pan of alumina was adopted. The heating rate was 20 K/min between room temperature and 823 K.

Then, the hydrogen absorption and desorption experiments were carried out circularly to test the hydrogen embrittlement resistance of the metallic glass ribbon. The samples were cut to small clips (about 3 mm wide and 5 mm long) and put into a stainless steel sample chamber with a quartz glass observation window on the top. Then the chamber was pumped down to a vacuum level <10^{-3} Pa. In order to activate the samples, they were heated to 473 K for 2 h and the vacuum was maintained during the heating process. After that, the samples were cooled down to room temperature. The hydrogen with a pressure of 100 kPa was charged into the chamber and kept for more than 1 h. Next, the samples were heated to 473 K again to make the absorbed hydrogen atoms desorb and the system was pumped to the based vacuum (~10^{-3} Pa). Then the samples were cooled down to room temperature again and the hydrogen absorption-desorption procedure was repeated for ten times. The samples were observed in real time using an optical microscope during the whole experiments.

The hydrogen permeation properties at different temperatures of the $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbon and its crystallized counterpart were tested in a home-made permeation system using direct permeation method, which means hydrogen with a certain pressure at one side of the metal membrane diffuses to the other side (in vacuum) as a result of concentration difference. At first, we measured the permeation rates of the metallic glass when it was heated below its crystallization temperature T_x (691 K) from room temperature. Second, when it was heated above the crystallization temperature, the permeation rates for the crystalline form were obtained in the cooling process. The samples were kept isothermal for more than 30 min at every testing temperature, and the permeation rates were tested every 10 min during this process. Finally, the hydrogen permeation rate is an average of the three measured values.

2 Results and Discussion

2.1 Structure and mechanical properties

Structural analyses from the conventional XRD and short wavelength X-ray stress analyzer are shown in Fig.1a and 1b, respectively. The short wavelength X-ray stress analyzer has higher energy and is able to pass through the metallic glass ribbon with a thickness of about 100 μm. In the present study, we just used it to confirm the internal structure of the samples, because the conventional XRD can access only the surface structure information. The patterns shown in Fig.1a and 1b are consistent with each other. As is seen in this figure, both patterns contain only diffuse diffraction humps which suggest the $Pd_{71.5}Cu_{12}Si_{16.5}$ alloy ribbon is in a fully glassy structure.

The DSC curve (Fig.2) shows a clear glass transition before crystallization. The glass transition temperature T_g and crystallization temperature T_x are estimated to be 651 and 691 K, respectively, which agree quite well with Ref. [20]. These two temperatures were used to choose the hydrogen permeation temperatures later. These phase transition temperatures are a bit high among the reported Pd-based metallic glasses[21-23]. Thus, it is suggested that the $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbons can work under severer condition

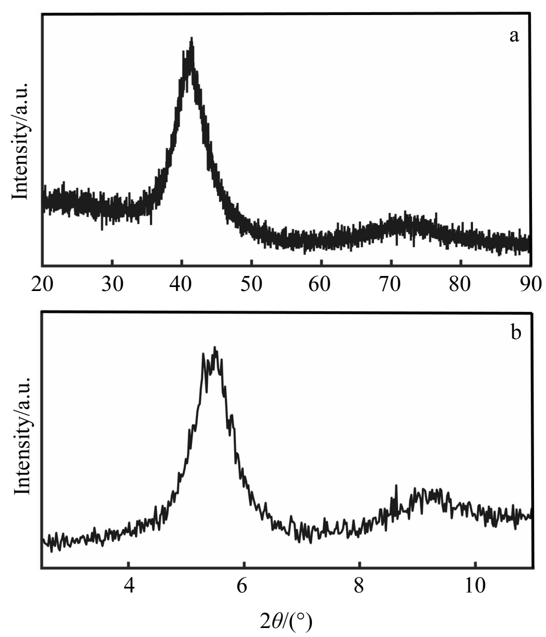

Fig.1 Structural analysis of $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbons obtained by the conventional XRD (a) and short wavelength X-ray stress analyzer (b)

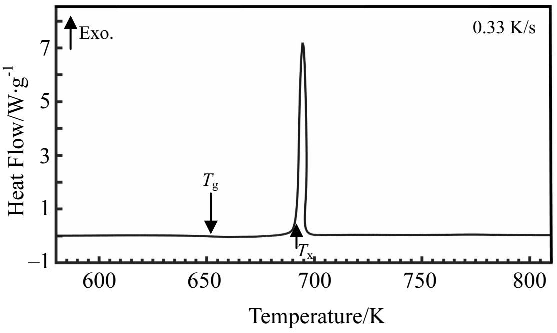

Fig.2 DSC curve of the $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbon

(higher temperature) while their glassy structure is kept.

The metallic glass ribbon can be folded 180° without fracture, indicating good toughness. The Vickers hardness of the ribbon was measured to be 5020 MPa on average, which is much bigger than that of the crystalline Pd-based alloy film (about 3500 MPa[24]). These data indicate the comprehensive mechanical properties of this metallic glass ribbon are excellent, which would be favorable in hydrogen-related applications.

2.2 Hydrogen embrittlement resistance

Hydrogen absorption and desorption cycles were performed up to 10 cycles in the $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbon, as shown in Fig.3. The ribbon was immersed in hydrogen atmosphere (100 kPa) for more than 1 h in each cycle at room temperature. According to the optical imaging, there aren't any hydrogen-induced cracks occurring during the cycles. After the 10th cycle, we maintained the hydrogen atmosphere for 16 h, and observed the surface topography again. It is apparent that the difference is trivial (Fig.3d). The experiments were repeated, and the results show nothing different. For comparison, a large number of cracks appear in the pure palladium membrane just in the second similar cycle. The $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbon does not show any destruction at all after many cycles of hydrogen absorption and desorption, indicating that it has good hydrogen embrittlement resistance and would be suitable for hydrogen-related applications, such as hydrogen purification and separation.

The good hydrogen embrittlement resistance can be explained as follows. As is well known, metallic glasses have a unique internal structure, i.e., short-range order (SRO). This structure can eliminate many defects such as grain boundaries and dislocations which always exist in traditional crystalline alloys, and lead to higher mechanical strength. The SRO structure contains much more inner space, which allows more hydrogen admitted. The higher mechanical strength of Pd-based metallic glass can also accommodate more hydrogen atoms without changing its structure. These may play an important role in good hydrogen embrittlement resistance of the $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass.

2.3 Hydrogen permeation properties

Hydrogen permeation experiments were carried out at 473, 573, 623, 673, and 723 K. The permeation rates (ϕ) were collected. Since the hydrogen permeation rate is temperature-dependent, we plotted its Arrhenius form in Fig.4. As we can see, the metallic glass ribbon shows a slightly lower hydrogen permeability than its corresponding crystallized one at low

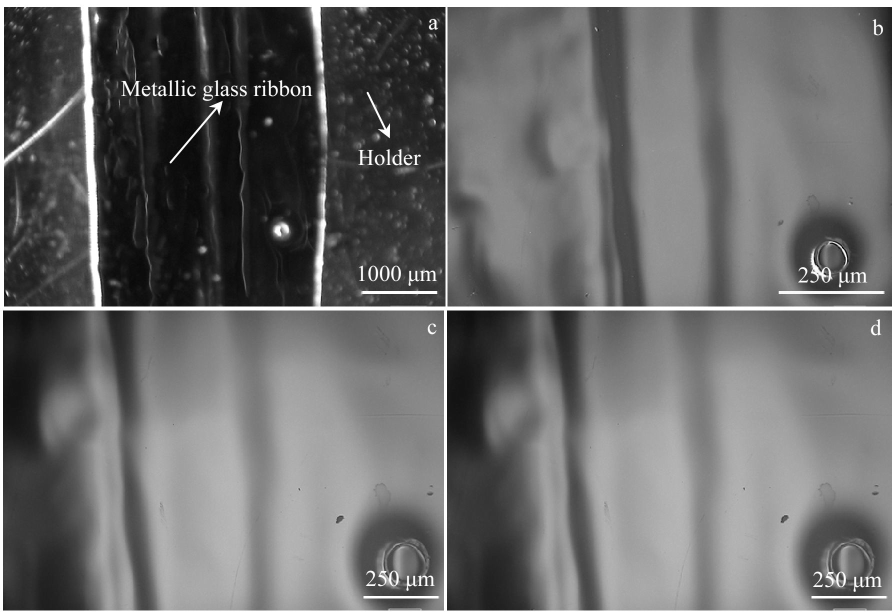

Fig.3 Optical images of $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbon during the hydrogen absorption and desorption cycles: (a) initial ribbon, (b) after 2 cycles, (c) after 10 cycles, and (d) after 10 cycles and immersed in H_2 atmosphere for 16 h

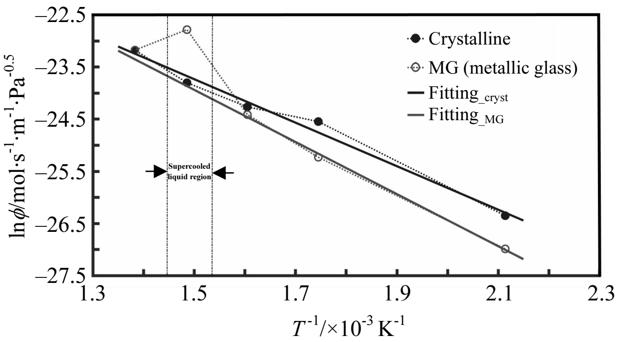

Fig.4 Arrhenius plots of the hydrogen permeation rates ϕ

temperatures (T<673 K), but there is a significant jump at 673 K which is in the supercooled liquid region of this metallic glass (651~691 K). Clearly, the activation energy of hydrogen permeation for the metallic glass ribbon form is slightly bigger than the one for the crystalline phase from the slopes of the straight lines in Fig.4. In other words, the hydrogen atoms in the metallic glass ribbon need more energy to overcome the migration barrier. Crystalline formed here possesses fairly fine grains (maybe much smaller than 50 nm referring to Ref. [25]), because the processing temperature does not exceed much above T_x, and the processing time (less than 1 h) is not long enough for the grains to grow up[25]. These fine grains supply a large number of grain boundaries, which become excellent diffusing channels for hydrogen, thereby reducing its migration barrier, and then improving the permeability[26]. Thus, the lower hydrogen permeability of the metallic glass ribbon at low temperatures is explained. The singularity is at T=673 K, when the metallic glass ribbon was equivalently annealed in the supercooled liquid region and a high density of free volumes was introduced[27]. The increasing free volumes will host more hydrogen atoms and supply the rapid transport channel for them, finally resulting in the dramatic increase in hydrogen permeability. At 723 K, the metallic glass ribbon crystallized into a nanocrystalline structure as described above. Compared with the increased boundaries, the introduced free volumes show much stronger effect on the hydrogen permeability improvement. As a consequence, the hydrogen permeability decreases as the temperature reaches 723 K.

3 Conclusions

1) The $Pd_{71.5}Cu_{12}Si_{16.5}$ metallic glass ribbon with fully glassy structure experiences more than 10 cycles of hydrogen absorption and desorption without any destruction at all, indicating good hydrogen embrittlement resistance.

2) The metallic glass ribbon has a much higher hydrogen permeation rate than its crystallized counterpart in the supercooled liquid region.

3) The $Pd_{71.5}Cu_{12}Si_{16.5}$ or other appropriate Pd-based metallic glasses with high thermal stability, good hydrogen embrittlement resistance and distinctive hydrogen permeability will be potential materials for hydrogen separation applications.

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$Pd_{71.5}Cu_{12}Si_{16.5}$ 金属玻璃的氢相关性能

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摘　要： 通过电弧熔炼、铜辊甩带的方法制备了 $Pd_{71.5}Cu_{12}Si_{16.5}$ 金属玻璃的宽带样品。通过常规 X 射线衍射仪和短波长 X 射线应力分析仪的 X 射线衍射谱确定了样品的完全非晶态结构。在室温、100 kPa 压力条件下，对样品进行了多次的吸、放氢循环实验。经过 10 次以上的循环后，样品没有发生破坏，表现出良好的抗氢脆性能。通过气体直接渗透的方法进一步测试了 $Pd_{71.5}Cu_{12}Si_{16.5}$ 金属玻璃及其同成分晶态合金的氢渗透性能。在金属玻璃的过冷液相区温度范围内，其氢渗透率明显高于晶态相，这一结果由金属玻璃在该区间内的等温保持引入了更多的自由体积进行解释。

关键词： 金属玻璃；非晶态材料；X 射线衍射；氢脆；氢渗透性能

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