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Influence of the palladium coating on the hydrogen embrittlement of $Ni_{61}Nb_{33}Zr_6$ amorphous tapes obtained by melt spinning

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Abstract. The current work is focused towards the properties of $Ni_{61}Nb_{33}Zr_6$ amorphous alloy for use in hydrogen-related energy applications. The master alloys were prepared by arc melting using high purity metals in a Ti-gettered argon atmosphere. The alloys were melted several times to improve homogeneity. The ingots were induction-melted under a argon atmosphere in a quartz tube and a graphite crucible, injected through a nozzle onto a Cu wheel to produce rapidly solidified amorphous ribbons. The characterization of the amorphous ribbons was done by X-ray diffraction, DSC analysis and hardness tests. The hydrogen charging was done electrochemically for low temperature tests and by heating in a hydrogen atmosphere at different temperatures in the case of the high temperature tests. It was found that the palladium plating reduces the hydrogen embrittlement limit by 50 ℃.

Introduction

The amorphous alloys have been proposed for hydrogen separation membranes, because amorphous alloys absorb generally hydrogen without forming metallic hydride and show good mechanical properties. However, since amorphous alloys are thermally unstable, using them as dense, hydrogen permeation membrane at elevated temperatures is very hard. Maintaining an amorphous alloy close to its glass transition temperature will trigger crystallization, decrease of the hydrogen permeability and ultimately its mechanical failure. From this point of view it at utmost importance to have a Tg as high as possible.

Generally, Ni-Nb amorphous alloys have high Tx [1] and according to Inoue [2] it could be further improved by adding more elements to the alloy. Zirconium on the other hand has excellent hydrogen permeability and in general improves the glass forming ability of the alloys [3]. On the other hand, increasing the zirconium content will lead to the reduction of the Tg, so, an optimal balance of these two issues must be found. Different nickel niobium alloys are studied [4, 5] which could be used as a separation membrane.

The studied alloy has a supercooled liquid region of ~ 50K, which would allow it to be shaped by hot-pressing in this temperature range. The purpose of this paper is to evaluate hydrogel embrittlement behavior of the amorphous $Ni_{61}Nb_{33}Zr_6$ alloy and identifying a temperature range in which the alloy could be used as the hydrogen separation membrane from this point of view.

Experimental

The master alloy ($Ni_{61}Nb_{33}Zr_6$) was prepared by arc melting using high purity materials in a Ti-gettered argon atmosphere. The alloys were melted several times in order to improve homogeneity. The alloy ingot was induction-melted under a high-purity argon atmosphere in a quartz crucible and injected through a nozzle onto a rotating Cu wheel to produce amorphous

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tapes. The obtained tapes were 4 mm wide and approximately 50 μm thick. The rotation speed used during the present experiments was 32 m/s. The amorphous nature of the ribbons was investigated by X-ray diffraction using a Shimadzu XRD – 6000 diffractometer and CuKα1 radiation. The samples behavior on heating was investigated by differential scanning calorimetry (SETARAM Labsys system) at the heating rate of 40 K/min. The ultimate tensile strength of the tapes was estimated from the Vickers micro-hardness measurements (40 *gf*. applied for 15 seconds) as UTS = HV*10/3 [MPa].

The palladium layer was deposited by thermal evaporation in a base pressure of $5*10^{-6}$ torr. The hydrogen embrittlement behavior was studied by heating the palladium coated and uncoated samples in flowing hydrogen to different temperatures (250℃, 300℃, 350℃, 400℃, 450℃, 500℃, 540℃ and 580℃). Heating to higher temperatures would result in the crystallization of the tapes.

The critical bending strain was determined by measuring the radius of curvature at which fracture occurs in a bending test between two parallel plates. The strain is then calculated using the following equation: $= \frac{t}{2r-t} \cdot 100\ [\%]$, where r is the bending radius and t is the sample thickness.

Results and discussions

The amorphous structure of the sample is confined by XRD measurement. The X-ray diffraction pattern shown in Fig. 1a presents a broad maximum (FWHM = 6.3°) characteristic for glassy structures.

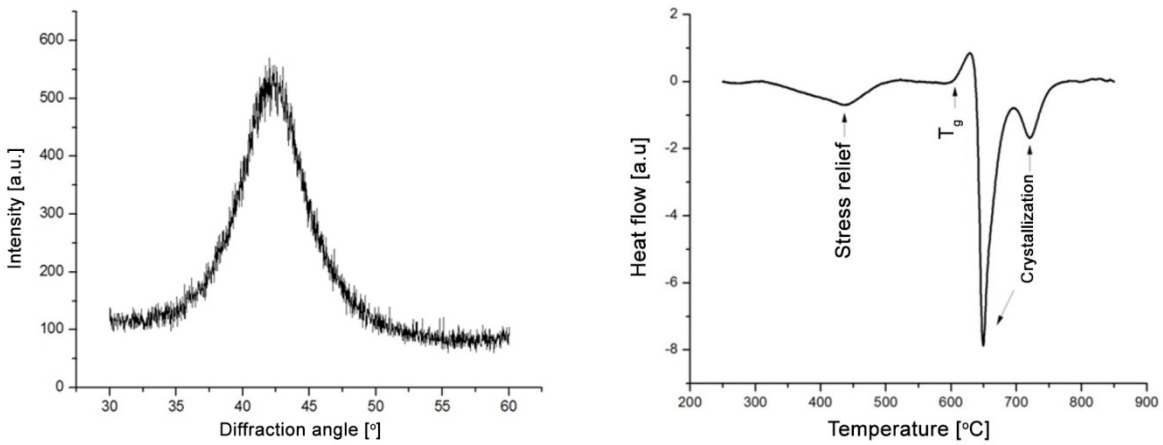

Fig. 1. X-ray diffraction pattern (a) and DSC curve (b) of the as cast tapes.

DSC measurements were performed to determine the thermal transformations that took place in the material and to approximate the thermal stability. The DSC heating curve of an amorphous material presents certain critical temperatures such as: glass transition temperature (T_g), crystallization temperatures (T_X and T_P) and melting temperature (T_S and T_1). The amorphous material remains in vitreous state until the T_X temperature is reached. The crystallization of the amorphous material is indicated by the presence of exothermic peaks, their number depending on the number of crystallization steps through which the material undergoes. The DSC curve presented in Fig. 1b, shows at 420 °C a structural relaxation followed by a glass transition (Tg at 601 ° C and two crystallization steps (T_{x1}= 638 °C and T_{x2}= 702 °C). From the combined analysis we can conclude that these tapes are x-ray amorphous structures.

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Another advantage of the amorphous structure is the outstanding mechanical properties. Although not as precise, the ultimate tensile strength evaluation from the hardness measurements is a simple and strait forward way to go since even if the samples are prepared by grinding and polishing, there will still remain edges on the margins that act as tension concentrators, leading to an erroneous measurement. In table 1 the microhardness measured using the Vickers method is summarized.

Table 1. Microhardness and estimated UTS of the selected tape.

HV0.04/15 [daN/mm^2]	Rm [MPa]	HV_{med} [daN/mm^2]	Rm_{med} [MPa]
958	3193	835	2783
805	2683		
741	2473		

The obtained values are similar to those presented in the literature for a similar alloy ($Ni_{62}Nb_{33}Zr_5$), the alloy that has the best glass forming ability in this alloy family but has a smaller supercooled liquid region than the studied composition [6].

To evaluate the hydrogen embrittlement resistance and the Pd coating's influence on the embrittlement coated and uncoated Pd samples were heated in flowing hydrogen atmosphere and then subjected to bending tests.

Table 2. The critical bending parameters at different hydrogen charging temperatures.

Temperature [℃]	Critical bending diameter [mm]		Deformation [%]	
	Pd coated	without Pd	Pd coated	without Pd
250	0.04	0.04	100	100
300	0.04	0.04	100	100
350	0.04	0.04	100	100
400	0.04	0.04	100	100
450	0.04	1.38	100	1.47
500	2.92	2.28	0.68	0.88
540	5.08	4.03	0.39	0.49
580	8	10.14	0.25	0.19

The samples that permitted bending to 180° were considered to have a deformation of 100%. The critical bending diameters were measured with a precision of 0.01 mm and presented in table 2 correlated with the deformation at the testing temperatures. From Fig. 2 is evident that the alloy starts to embrittle at 400 ℃ for the uncoated alloy and 450 ℃ for the palladium-coated alloy. As the temperature increases the critical bending radius are also increases suggesting a stronger

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embrittlement as the temperature rises. Based on these measurements one can speculate that the upper temperature limit of this alloy should be in the 400 - 450 ℃ area.

X-ray diffraction measurements were performed on both types of hydrogen-loaded alloys at 450 ℃ to assess the effect of the absorbed hydrogen on the alloy structure. Measurements were made on samples heated to this temperature because the palladium-free alloy had embrittled, and the palladium-coated layer did not.

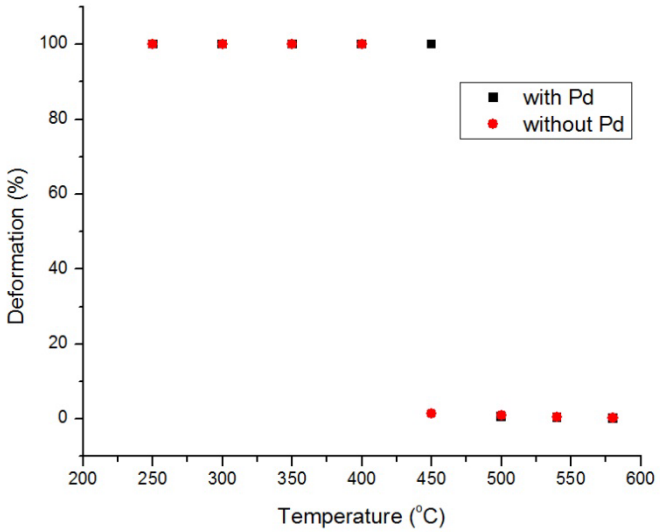

Fig. 2. Embrittlement resistance of coated and uncoated samples.

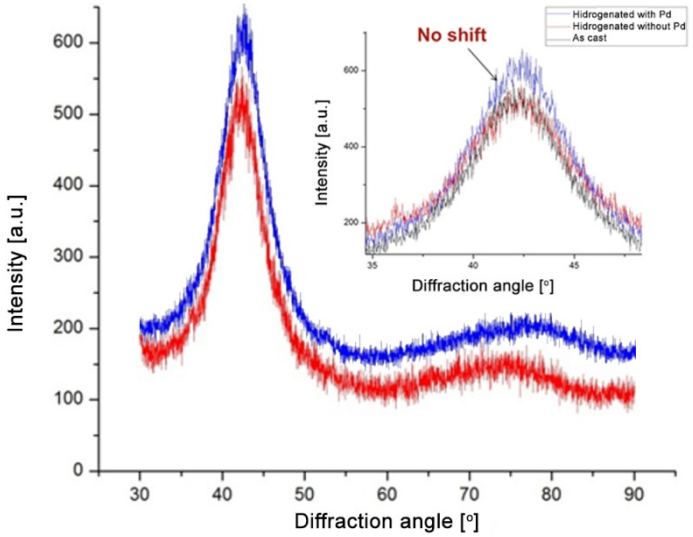

Fig. 3. X-ray diffraction patterns on hydrogen-loaded tapes with and without Pd layer.

The X-ray diffraction patterns presented in Fig. 3 for the samples charged with hydrogen and in the initial state. No shift in the peak position is visible. Also, stable hydrides were not formed during the tests; these observations are in good agreement with the corresponding binary phase diagrams.

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Fracture in the case of bending tests is of brittle nature in both cases, specific to metallic glasses; although some localized plastic flows may be observed on the fracture surface of the samples. In the case of metallic glasses their deformation is achieved by two mechanisms: at high temperatures by viscous flow and at ambient temperature (T <0.5Tg) by twinning, the deformation being in the shear bands [7].

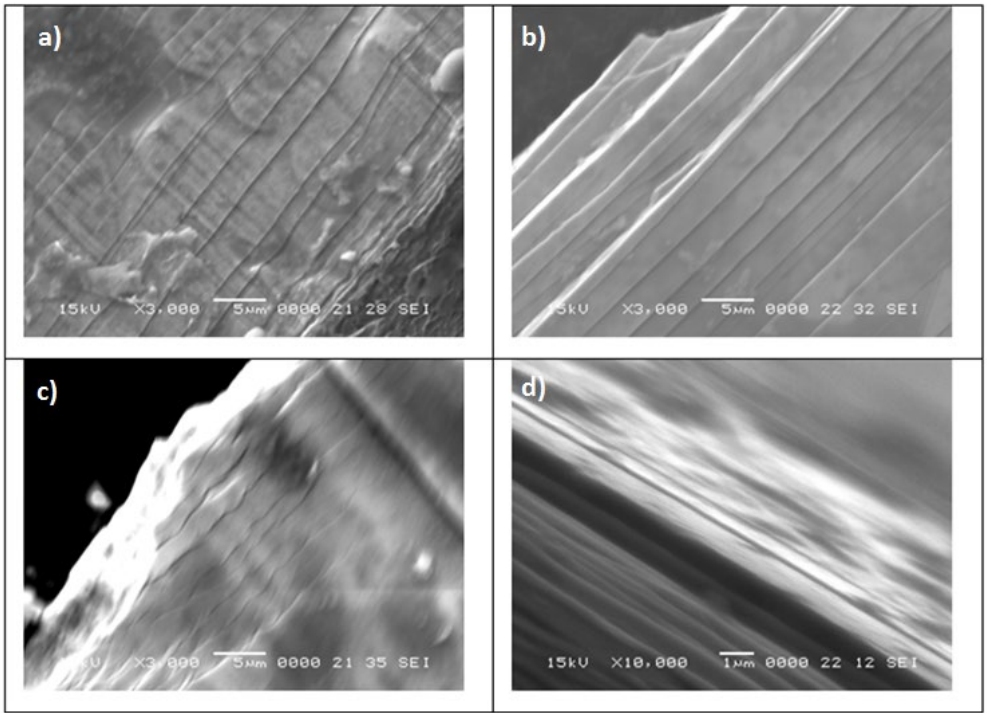

Fig. 4. Fracture surfaces after bending tests.

These materials seem to be fragile, although there are significant local deformations in the rupture. The width of such bands has a width of some micrometers and they appear in the direction of maximum applied tension. The slip occurs in a narrow area (~ 10nm) due to the local temperature increase, the mechanical work performed is proportional to its displacement [8].

The presence of these bands suggests the existence of a plastic deformation zone of thickness s on both surfaces of the strip as shown in Fig. 4. The displacement generated by the shear stresses relaxes the adjacent area, and another slip system cannot be formed close to it. This effect results in the sliding strips being spaced according to their length [8].

The sliding strips for hydrogen heated samples at 400 ℃ or 450 ℃ are deep (~ 1μm) however when heated to 540 ℃ they are significantly shallower. This suggests that the mechanical work consumed to reduce the tensions was lower in this case. This observation is also consistent with the shorter distance between the sliding strips.

If some bands slid more than others during bending, the sliding plane turns into a crack when its displacement exceeds a critical value. According to R. D. Conner et al. [7], in a metallic glass in which the displacement and the distance between the sliding strips is greater, the crack is generated and propagated more easily. This statement is in a slight contradiction with the present observations, but the presence of hydrogen in the structure has an embrittling effect on the material. In samples heated to temperatures below 450 ℃, the amount of hydrogen is too low to

produce fragility. In the present case the most likely mechanism of hydrogen embrittlement is decohesion.

Summary

The influence of the palladium coating on the hydrogen embrittlement behavior of the $Ni_{61}Nb_{33}Zr_6$ amorphous ribbons was studied in the present paper. X-ray amorphous ribbons 4 mm wide was obtained by rapid solidification. Some of these were Pd coated to improve hydrogen dissociation and recombination. These ribbons presented a slightly higher embrittlement resistance determined by bending tests. This better behavior can be attributed to the lower quantity of residual hydrogen in these samples and a lower decohesion force acting between the atoms.

Fracture in both cases is of brittle nature, although some localized plastic flows are present on the fracture surface of the samples in the form of deformation bands. The final fracture surface is generated when the deformation bands displacement exceeds a critical value.

Further tests are needed to demonstrate the alloys long term stability and an improvement of the structural stability is desired in order to increase the maximum theoretical operating temperature.

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