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Hydrogen Permeability of Glass-Forming Ni-Nb-Zr-Ta Crystalline Membranes

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A crystalline form of a glass-forming Ni-Nb-Zr-Ta alloy was studied as a hydrogen permeation membrane working in the temperature range from 573 K to 773 K. The crystalline membrane composed of an Nb-rich phase in an $Ni_{10}Zr_7$ matrix demonstrated a hydrogen permeation property superior to the membrane of the same chemical composition with an amorphous structure and the values of the hydrogen permeability were found to exceed those of the Pd-based membranes. However, the mechanical stability deteriorated significantly such that all membranes failed during hydrogen permeation. This indicates a larger sensitivity to hydrogen embrittlement in comparison with the same alloy in an amorphous state.

Keywords: alloys, amorphous materials, casting, embrittlement, scanning electron microssopy (SEM)

1. INTRODUCTION

While several sustainable and non-polluting energies are emerging to replace those based on petroleum products, fuel cells have appeared as the most efficient method of generating energy for transportation and residential needs. However, the potential of a hydrogen energy-driven society is dependent on the cost of hydrogen production, which is still not competitive when compared with that of gasoline. Among the existing methods, the use of non-porous membranes has received much interest due to the simplicity of this technique in producing high purity hydrogen and the possibility to extend the technique to large production volumes [1]. While palladium metals and alloys have been proposed as potential membrane materials for the separation and purification of hydrogen, research activities in the USA and Japan have recently led to the development of cheaper materials [2-4]. Although elements from Group 5 of the periodic table of elements provide high values for hydrogen permeability, these metals and their alloys still suffer from hydrogen embrittlement [1,5,6]. As an alternative to crystalline materials, studies performed by Inoue's group have demonstrated encouraging performance for Ni-Nb-Zr based metallic amorphous alloys [7-9]. Furthermore, recently developed compositions have hydrogen permeability values similar to those of Pd-based membranes [7-10] while some of these compositions exhibit excellent durability as well [11].

Another approach to design non-palladium-based alloys is to consider the metallic membranes composed of a two-phase microstructure with a phase permeable to hydrogen with a dendritically solidified structure embedded in a crystalline matrix. Encouraging properties have been recently reported for V-, Nb-, and Ta-based duplex phase alloys [12-14], particularly with excellent resistance to hydrogen embrittlement for some compositions.

It is well known that alloys with a glass-forming ability (that is, alloys forming amorphous structures via rapid solidification) are usually found near eutectic compositions. This study was undertaken in order to investigate the hydrogen permeability in its crystalline state of an alloy forming an amorphous structure. For this purpose, the $Ni_{42}Nb_{28}Zr_{25}Ta_5$ alloy was prepared via vacuum casting and its hydrogen permeability values are compared with those of the alloy in the fully amorphous structure that have been published elsewhere [10].

2. EXPERIMENTAL PROCEDURE

$Ni_{42}Nb_{28}Zr_{25}Ta_5$ membranes with a 12 mm diameter and 0.5 mm thickness were fabricated via wire cutting from a 25 g cast ingot with a truncated conic shape that was prepared using a vacuum arc melting machine. In order to investigate the possible effect of the structure on the hydrogen permeability, 0.5 mm thick membranes were sliced

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perpendicular and parallel to the axis of the ingots. Hydrogen permeability tests were performed in the temperature range of 573 K to 773 K using a conventional gas pressure of 0.2 MPa (2 bar absolute) with pure H_2 (UHP grade with 6N purity). For that purpose, a thin layer of Pd with a thickness of approximately 150 nm was deposited via RF magnetron sputtering after the reactive ion etching (RIE) treatment on both sides of the membrane in order to accelerate the dissociation and recombination of the hydrogen molecules on the inlet and outlet sides, respectively. The membranes were sealed between two Cu gaskets and evacuated prior to the test. The membranes were heated to a predefined testing temperature for 30 min before introducing the hydrogen gas. The hydrogen flux was measured for 60 min using a gas chromatography. Then, the hydrogen pressure was reduced followed by the temperature being increased by 50 degrees. The experiments were performed until the temperature reached 773 K and then the temperature was reduced via furnace cooling. The structure of the membranes before and after the permeation tests were observed using a scanning electron microscopy (SEM) equipped with an energy-dispersive spectrometry (EDS) and were analyzed using X-ray diffraction (XRD).

3. RESULTS

In comparison with the broad peak obtained for the amorphous ribbon [10], the XRD trace of the crystalline alloy, shown in Fig. 1, is characterized by sharp diffraction peaks identified as those of the bcc Nb(Ta) (ICDD reference codes 35-0789 and 04-0788 for Nb and Ta, respectively) and orthorhombic $Ni_{10}Zr_7$ phases (ICDD 47-1027). The microstructure of the $Ni_{42}Nb_{28}Zr_{25}Ta_5$ crystalline alloy observed in the SEM images is shown in Fig. 2. As suggested by the XRD trace, the structure is composed of two dominant composition phases: 74 ≤ Nb ≤ 85 at.%, 8.5 ≤ Ta ≤ 16.6 at.%, 5.4 ≤ Ni ≤ 9.4 at.%, 0 ≤ Zr ≤ 1.3 at.% for the Nb-Ta rich dendritic phase and 56 ≤ Ni ≤ 59.1 at.%, 34.8 ≤ Zr ≤ 35.4 at.%, 0.5 ≤ Ta ≤ 5.5 at.%, 0 ≤ Nb ≤ 8.4 at.% for the Ni-Zr rich matrix as analyzed using the EDS. The observation at a higher magnification as shown in Fig. 2(b) revealed a fine eutectic structure. Due to the high melting point of the Nb and Ta elements, the primary phase first formed during the solidification with a dendritic structure, while the eutectic was solidified later at a lower temperature.

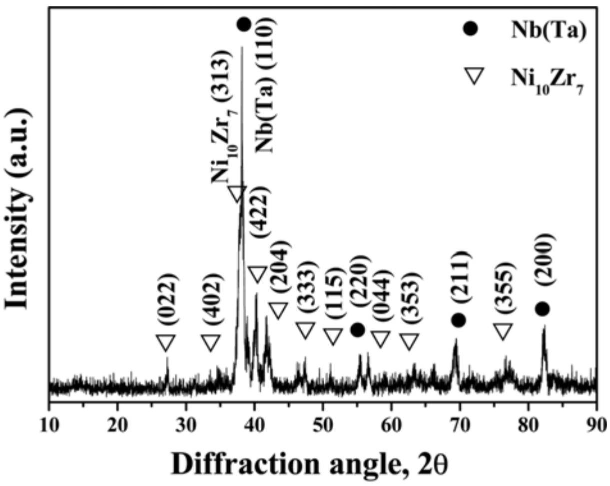


Fig. 1. XRD trace of the crystalline $Ni_{42}Nb_{28}Zr_{25}Ta_5$ membrane.


(a) (b)

Fig. 2. SEM images of the crystalline $Ni_{42}Nb_{28}Zr_{25}Ta_5$ membrane: (a) cross-sectional view and (b) cross-sectional view under higher magnification.

The results of the permeation tests performed in the temperature range of 573 K to 773 K are presented in Fig. 3 and are compared with the results of the amorphous ribbons with the same composition [10]. The hydrogen permeability values of the alloy in the crystalline state are found to be larger than those of the alloy in the amorphous state, particularly around 673 K. The difference in the hydrogen permeation properties can be attributed to the difference in the membrane structure.

The mechanism of hydrogen permeability in metallic amorphous structures is not well understood yet. Earlier works have demonstrated that the hydrogen permeability

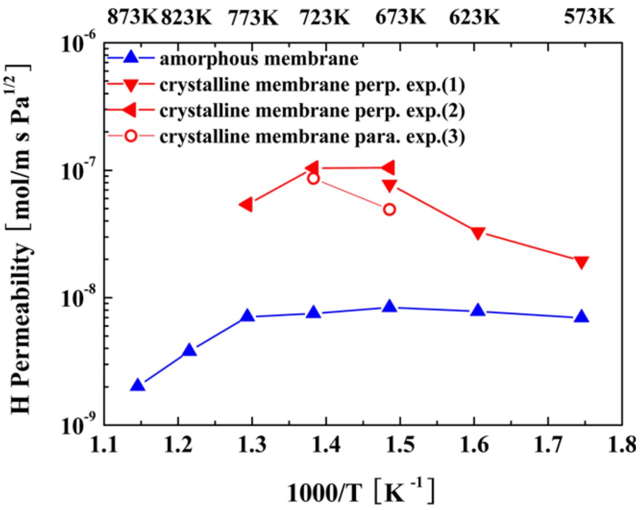


Fig. 3. Values of the hydrogen permeability for the crystalline $Ni_{42}Nb_{28}Zr_{25}Ta_5$ membranes and comparison values obtained from amorphous membranes [10].

of metallic glasses is strongly dependent on the constituent elements and alloy composition [7,15-18]. Oji *et al.* have reported that the local structure around the constituent elements in Ni-Nb-Zr-H amorphous alloys varied significantly with variations in the Zr content [19], which is believed to affect the hydrogen diffusion path and thus the permeability.

In duplex phase alloys, such as those composed of a bcc primary phase embedded in a crystalline matrix, hydrogen is believed to diffuse through the permeable phase composed of bcc Group 5 elements with a dendritic solidified structure of which the hydrogen permeability values are approximately one order of magnitude higher than those of Pd-based alloys at 673 K. In addition to the composition, the diffusion rate is dependent on the morphology and continuity of the dendrite as well as the interface with the matrix [20]. The high hydrogen permeability values of the $Ni_{42}Nb_{28}Zr_{25}Ta_5$ crystalline alloy, which are similar to those of the $Ni_{30}Nb_{40}Zr_{30}$ alloy [21], are believed to result from the duplex structure of the cast alloy.

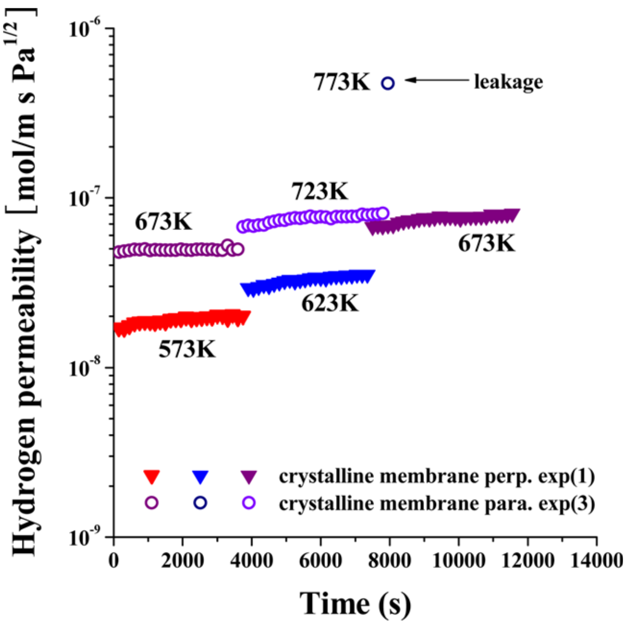


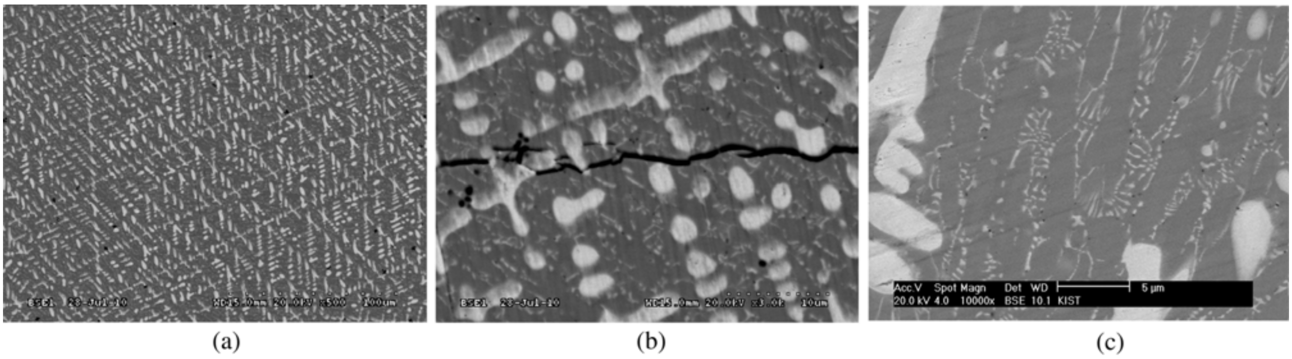
Fig. 4. Variation of the hydrogen permeability with time for the crystalline $Ni_{42}Nb_{28}Zr_{25}Ta_5$ membranes.

Although the $Ni_{42}Nb_{28}Zr_{25}Ta_5$ crystalline membrane demonstrated high hydrogen permeability values, all samples failed during permeation tests when the temperature was increased or decreased (Fig. 4). In contrast, the membranes with an amorphous structure did not fail during permeation tests, even after 463 hours at 673 K [22]. The mechanisms of the hydrogen embrittlement in various amorphous alloys have recently been reviewed [23], and the high resistance of the $Ni_{42}Nb_{28}Zr_{25}Ta_5$ amorphous alloys to hydrogen embrittlement was attributed to the large number of Zr rich tetrahedral sites that can be occupied by hydrogen atoms without inducing significant dilatation of the amorphous structure [10].

Figures 5(a) and (b) show the microstructure of the $Ni_{42}Nb_{28}Zr_{25}Ta_5$ crystalline membrane after the hydrogen permeation test. No significant change can be observed in the microstructure, and the chemical compositions of both phases analyzed via EDS were similar to those of the membrane before the hydrogen permeation, except that the hydrogen concentration cannot be detected. A thorough investigation of Fig. 5(b) suggests that the crack is primarily propagated through the matrix and along the dendrite-matrix interface.

4. DISCUSSION

The comparison of the hydrogen permeation properties of crystalline Ni-Nb-Zr-Ta with those of the amorphous counterpart revealed the strong influence of the microstructure on the hydrogen permeability and resistance to hydrogen embrittlement. The duplex alloy composed of a permeable dendritic phase in the matrix displays a high hydrogen permeability but a poor resistance to hydrogen embrittlement. In contrast, membranes made using the same alloy composition with an amorphous structure have a lower hydrogen permeability but demonstrate superior resistance to hydrogen permeability. Although the hydrogen permeability performance is not as impressive, amorphous membranes



(a) (b) (c)

Fig. 5. SEM images of a crystalline $Ni_{42}Nb_{28}Zr_{25}Ta_5$ membrane after hydrogen permeation: (a) low magnification, (b) high magnification showing the crack propagation, and (c) high magnification showing details of the eutectic.

have demonstrated the mechanical integrity that is required for such applications. The improved structural stability of the amorphous membranes compared with those of crystalline membranes was also noted by Dolan *et al.* [24].

Despite the high hydrogen permeability value, the poor resistance to hydrogen embrittlement of the crystalline alloys made using Group 5 elements has been the limiting factor for the development of Pd-free membranes for the production of low cost, high purity hydrogen. The embrittlement induced by the hydrogen in bcc Group 5 elements is generally attributed to the excessive dilatation of the atomic lattice and the formation of hydride. The XRD of the Pd-coated samples before and after the hydrogen permeation are shown in Figs. 6(a) and (b), respectively. No significant change can be detected; however, the position of the peaks for the Nb(Ta) and $Ni_{10}Zr_7$ phases were found to have shifted slightly towards lower diffraction angles suggesting a dilatation of both phases. The shift in the position of the peaks suggests a dilatation of approximately 0.28 % and 0.30 % for Nb(Ta) and $Ni_{10}Zr_7$ phases, respectively. In contrast, the position of the peaks of the Pd coating layer was less pronounced with a dilatation of only 0.02 %. The large dilatation of the $Ni_{10}Zr_7$ intermetallic phase, a somewhat brittle phase, might be one reason for the premature failure of the membrane during the hydrogen permeation.

For the hydrogen permeation tests performed on the membranes made from crystalline $Ni_{30}Nb_{40}Zr_{30}$ alloy, i.e. an alloy with a higher Nb content [21], cracks were found to propagate through the Nb-rich dendrite indicating that most hydrogen atoms were diffusing through the dendrites. For the alloy investigated in this work, an Nb-rich phase is present in the eutectic phase (Fig. 5(c)). Wong *et al.* [21] suggested that this Nb-rich phase contributes to the diffusion of hydrogen through a percolation effect in the matrix. This can also explain why the hydrogen permeability in the crystalline Ni-Nb-Zr-Ta is high even though the volume fraction of the dendritic phase is only approximately 25 %. Hence, the presence of the Nb-rich phase in the eutectic phase appears to have a harmful effect because it provides a by-passing diffusion path through the matrix for the hydrogen. As hydrogen tends to diffuse through a percolated path made from an Nb-rich phase in the eutectic, the dilatation of the $Ni_{10}Zr_7$ phase suggests that the hydrogen atoms are trapped in the matrix. These results provide two important details. Firstly, the resistance to hydrogen embrittlement of the membrane with a duplex structure can be enhanced by limiting the hydrogen diffusion through a continuous permeable dendritic phase. Thus, the structure of the matrix should be carefully controlled; in particular, the presence of an Nb-rich phase in the eutectic should be avoided. Secondly, membranes with an amorphous structure have an excellent combination of hydrogen permeability and resistance to hydrogen embrittlement, which positions them as potential candidates to replace Pd-based alloys.

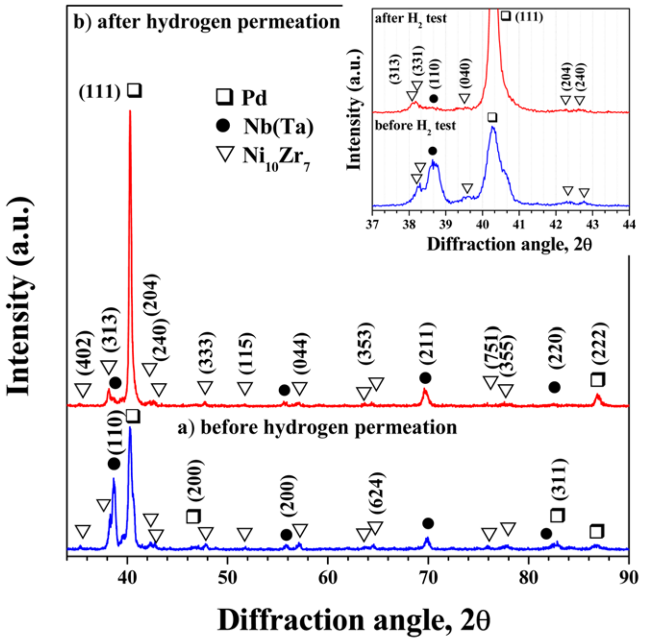


Fig. 6. XRD traces of the Pd-coated crystalline $Ni_{42}Nb_{28}Zr_{25}Ta_5$ membranes: (a) before, and (b) after hydrogen permeation (for Pd element: ICDD reference code 87-0645). Inset: detail of the diffraction pattern in the range 2θ = 37°–44°.

5. CONCLUSION

The hydrogen permeability of the $Ni_{42}Nb_{28}Zr_{25}Ta_5$ crystalline membranes was found to be superior to that of membranes with an identical composition prepared in an amorphous state. This property was attributed to the fast permeability of hydrogen through the Nb-rich phase. However, the premature failure of the crystalline membranes during the hydrogen permeation tests outlined the sensitivity of the duplex alloy on the hydrogen embrittlement. This mechanical instability was attributed to the presence of an Nb-rich phase in the eutectic phase through the promotion of the hydrogen diffusion within the matrix and inducing dilatation. It is interesting to note that the amorphous structure has less hydrogen permeability and better mechanical stability. This might suggest that the bcc elements with a high hydrogen permeability can contribute as a constituting element in an amorphous structure that has acceptable permeability and mechanical stability.

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