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Hydrogen permeability and microstructure of rapidly quenched Nb–TiNi alloys

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ABSTRACT

Effect of annealing on structure, microstructure and hydrogen permeability of rapidly quenched $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloy ribbons were investigated by X-ray diffractometry (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and the gas flow method. Crystalline (Nb, Ti) and TiNi phases coexisted with the amorphous phases in the as-quenched $Nb_{30}Ti_{35}Ni_{35}$ alloy, while only crystalline (Nb, Ti) and TiNi phases were formed in the as-quenched $Nb_{40}Ti_{30}Ni_{30}$ alloy. Both the as-quenched alloys were too brittle to measure their hydrogen permeability, but they became ductile by annealing above 1173 K and showed the microstructure consisting of the crystalline (Nb, Ti) phase embedded in the crystalline TiNi matrix. The volume fraction of the (Nb, Ti) phases in the Nb–TiNi alloys increased with increasing Nb content. Hydrogen permeability at 673 K, i.e. $\Phi_{673\,K}$ of the crystalline $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloys was 1.1×10^{-8} and 1.9×10^{-8} ($molH_2/m/s/Pa^{0.5}$), respectively, which were comparable with that of Pd. The present work has clearly demonstrated that the rapid quenching technique and subsequent annealing process are useful and attractive method for the preparation of hydrogen permeable Nb–TiNi alloy membrane.

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1. Introduction

Pd and its alloys are presently used in the membrane reactor for separation and purification of hydrogen gas [1]. However, since Pd is very expensive and a rare metal, which give rise to the high cost of hydrogen production, alternative hydrogen permeation alloys containing less or no Pd are strongly desired. Recently, we have found out that Nb–TiNi alloys consisting of the bcc-(Nb, Ti) solid solution and the B2-TiNi intermetallic compound show large ductility, large rolling workability, high hydrogen permeability and large resistance to hydrogen embrittlement [2,3]. Such experimental results indicate that the Nb–TiNi alloys are anticipated to be potential non-Pd based hydrogen permeation alloys.

Hydrogen flux (J) permeating through the alloy membrane is in inverse proportion to its thickness, so that preparation of thin alloy membrane is very important for the effective hydrogen purification. It is well known that thin amorphous alloy ribbons are generally obtained by the rapid quenching of the eutectic alloys using a single-roller melt spinning machine. The hydrogen permeation alloys on the basis of amorphous Ni–Zr [4] and Nb–Ni–Zr alloys [5] have been proposed, because amorphous alloys absorb generally hydrogen without forming metallic hydride and show good mechanical properties. However, since amorphous alloys are thermally unstable, using of them as the hydrogen permeation alloy membrane at elevated temperatures is very hard. On the other hand, the present authors have proposed that the rapid quenching should be used as a means to prepare the alloy ribbon [6]. The above-mentioned Nb–TiNi hydrogen permeation alloys consist of the eutectic {(Nb, Ti) + TiNi} and the primary (Nb, Ti) phases [2]. The present authors have prepared the amorphous alloy ribbon by the rapid quenching of the eutectic crystalline $Nb_{20}Ti_{40}Ni_{40}$ alloy, and hydrogen permeability at 673 K, i.e. $\Phi_{673\,K}$ of the amorphous $Nb_{20}Ti_{40}Ni_{40}$ alloy is almost same as the corresponding crystalline alloy [6–8]. The crystalline $Nb_{20}Ti_{40}Ni_{40}$ alloy obtained by crystallization of the amorphous alloy, consisted of the TiNi and the (Nb, Ti) phases, is ductile, but its Φ is too low in comparison to that of pure Pd [6–8]. We have reported that Φ of the arc melted Nb–TiNi alloys is improved in Nb-rich alloys, which is caused by the increase of the volume fraction of the (Nb, Ti) phase showing high Φ [9]. Therefore, it is expected that Φ of rapidly quenched Nb–TiNi alloys is also improved with increasing Nb content.

In the present work, Nb-rich Nb–TiNi alloys consisting of the eutectic {(Nb, Ti) and TiNi} and the primary (Nb, Ti) phase, i.e. $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloys, are rapidly quenched by using the single-roller melt spinning machine and their structures and microstructures are investigated. Furthermore, effects of

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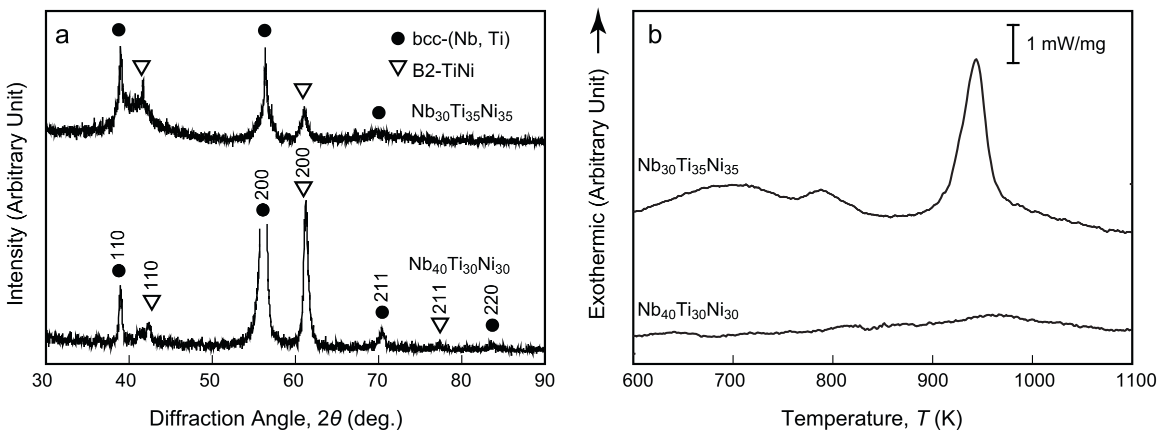

Fig. 1. (a) XRD patterns and (b) DSC curves of the rapidly quenched $Nb_{30}Ti_{35}Ni_{35}$ and the $Nb_{40}Ti_{30}Ni_{30}$ alloys.

annealing on structure, microstructure and hydrogen permeability of these as-quenched alloys are investigated.

2. Experimental

The $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ (mol%) alloy ribbons having 50 mm in width and 30–40 μm in thickness were prepared by a single-roller melt spinning machine in an argon atmosphere. The alloy ribbons were wrapped by a molybdenum foil, and then were enclosed into a quartz tube filled with Ar + 5%H_2 gas. The sample ribbons in the quartz capsule were heat treated in an electric furnace at 1173 K for 10 h, and then quenched into water. Phase identification was carried out by X-ray diffractometry (XRD) using Cu Kα radiation monochromated by graphite. Thermal stability of the as-quenched ribbons was evaluated by differential scanning calorimetry (DSC) heated at the rate of 20 K/min in a flowing Ar atmosphere. Microstructural observation of the samples was carried out by scanning electron microscopy (SEM). After polishing the ribbon samples using a buff, they were coated with Pd of 190 nm in thickness using a magnetron sputtering machine. The sample was sandwiched by two gaskets for hydrogen permeability measurements. Hydrogen permeability measurements were performed at 548–673 K under 0.1–0.35 MPa of high purity hydrogen. The effective membrane area for hydrogen permeation is 24.6 mm^2, which corresponds to the inner diameter of the gasket (5.6 mm). Details of the measurements are described in our previous paper [2].

3. Results and discussion

3.1. Structure and hydrogen permeability of as-quenched $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloy ribbons

Alloy ribbons of 50 mm in width and 30–40 μm in thickness were successfully prepared by rapid quenching. Fig. 1(a) and (b) shows XRD patterns and DSC curves of the as-quenched $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloys, respectively. The Bragg peaks of the as-quenched $Nb_{30}Ti_{35}Ni_{35}$ sample are indexed on the basis of the bcc-(Nb, Ti) and the B2-TiNi phases overlapping with a broad maximum around 42° (a). An exothermic peak is observed in its DSC curve around 950 K (b). Therefore, the as-quenched $Nb_{30}Ti_{35}Ni_{35}$ alloy is concluded to be consisted of both the bcc and B2 and amorphous phases. The present authors have already reported that rapidly quenched eutectic $Nb_{20}Ti_{40}Ni_{40}$ alloy is a single-phase amorphous alloy, and the TiNi phase is firstly crystallized from the amorphous phase around 900 K [8]. The remaining amorphous phase crystallizes into the (Nb, Ti) and the TiNi phases around 950 K. Therefore, the exothermic peak observed around 950 K for the $Nb_{30}Ti_{35}Ni_{35}$ alloy is considered to be caused from formation of the (Nb, Ti) and TiNi phases from the amorphous phase. On the other hand, sharp Bragg peaks on the basis of the bcc-(Nb, Ti) and the B2-TiNi phases are observed in the XRD pattern of the as-quenched $Nb_{40}Ti_{30}Ni_{30}$ alloy (a). Furthermore, no exothermic peak is appeared in its DSC curve (b), suggesting that the as-quenched $Nb_{40}Ti_{30}Ni_{30}$ alloy consists of the crystalline bcc and B2 phases and includes no amorphous phase. It is summarized that $Nb_{20}Ti_{40}Ni_{40}$, $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloys are consisted of the amorphous single phase, the mixture of the crystalline and amorphous phases and the crystalline phases, respectively. These experimental results indicate that amorphous forming ability of Nb–TiNi alloys decreases with increasing Nb content.

Hydrogen permeability at 673 K, i.e. $\Phi_{673\,K}$, of the as-quenched amorphous $Nb_{20}Ti_{40}Ni_{40}$ alloy is 8.1×10^{-9} ($molH_2/m/s/Pa^{0.5}$), which is almost same as pure Pd [8]. Both of the as-quenched $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloy ribbons are too brittle to measure their Φ.

3.2. Structure, microstructure and hydrogen permeability of annealed $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloy ribbons

The $Nb_{30}Ti_{35}Ni_{35}$ and the $Nb_{40}Ti_{30}Ni_{30}$ alloy ribbons were annealed at elevated temperatures. These two alloys remain brittle even though they are annealed below 1073 K which is above the crystallization temperature of the amorphous phase in the as-quenched $Nb_{30}Ti_{35}Ni_{35}$ alloy. On the contrary, both of them show good bending ductility after annealing at 1173 K for 10 h.

Fig. 2 shows XRD patterns for the $Nb_{30}Ti_{35}Ni_{35}$ and the $Nb_{40}Ti_{30}Ni_{30}$ alloys after annealing at 1173 K for 10 h. The broad XRD maximum in the as-quenched $Nb_{30}Ti_{35}Ni_{35}$ alloy disappears and sharp Bragg peaks indexed on the basis of the bcc and the B2 structures are seen clearly. The XRD pattern for the annealed $Nb_{40}Ti_{30}Ni_{30}$ alloy indicates the two-phase microstructure consisting of the bcc and the B2 phases. A small amount of the Ti_2Ni phase is formed in both the annealed alloys.

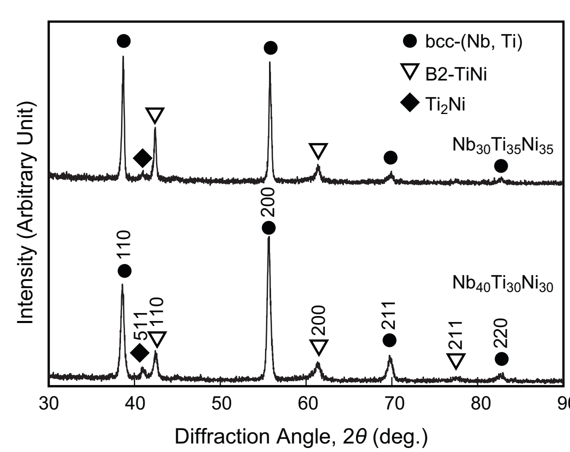

Fig. 2. XRD patterns for the $Nb_{30}Ti_{35}Ni_{35}$ and the $Nb_{40}Ti_{30}Ni_{30}$ alloys annealed at 1173 K for 10 h.

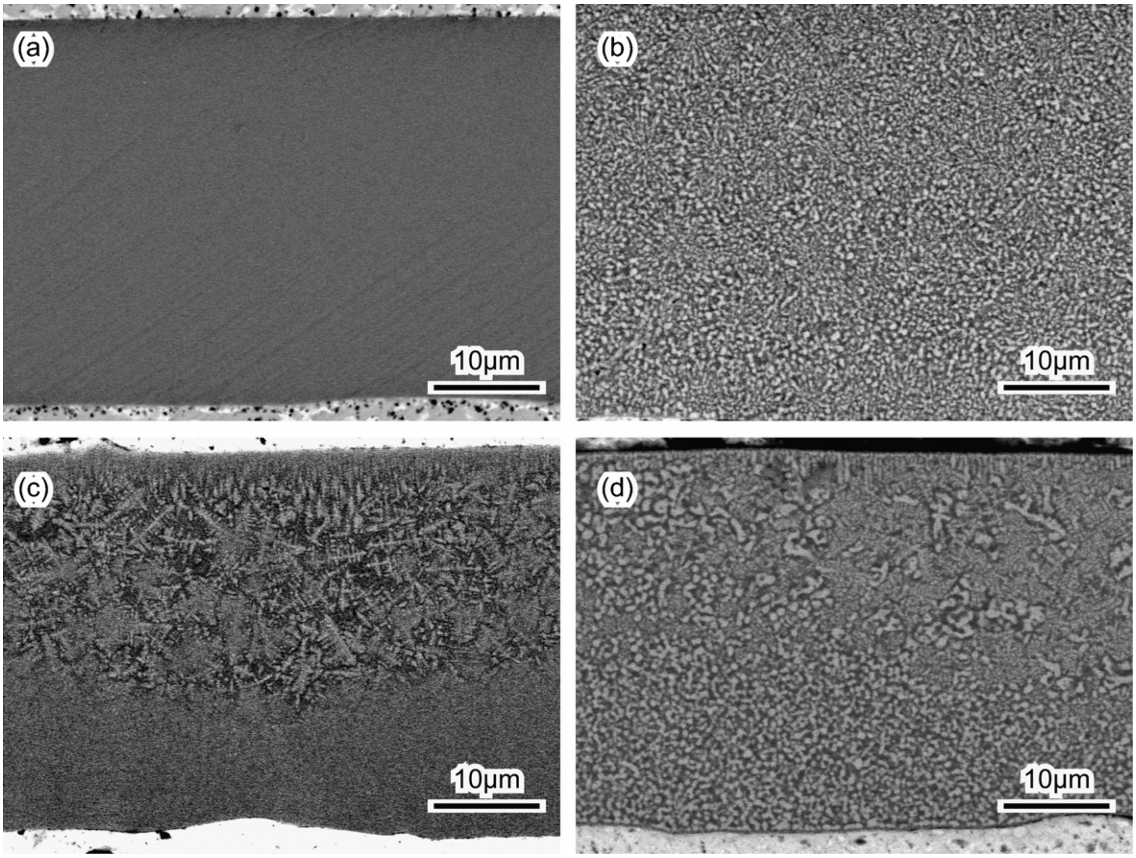

Fig. 3. Cross-sectional SEM micrographs for the (a) as-quenched and (b) annealed $Nb_{30}Ti_{35}Ni_{35}$ alloy and the (c) as-quenched and (d) annealed $Nb_{40}Ti_{30}Ni_{30}$ alloy.

Fig. 3 shows cross-sectional SEM images for the (a) as-quenched and (b) annealed $Nb_{30}Ti_{35}Ni_{35}$ alloys and for the (c) as-quenched and (d) annealed $Nb_{40}Ti_{30}Ni_{30}$ alloys. The horizontal directions in these photographs correspond to the long direction of the ribbon samples. Upper and bottom sides in the photographs are free surface and roller sides, respectively. The SEM image of the as-quenched $Nb_{30}Ti_{35}Ni_{35}$ alloy (a) shows a featureless microstructure in spite of the existence of the bcc and the B2 crystalline phases. By annealing, the granular (Nb, Ti) phase (white) is formed in the TiNi matrix (dark) (b). No microstructural difference between roller and free surface sides is observed in these alloy ribbons. This SEM image is analyzed in order to determine the volume fraction and average diameter of the (Nb, Ti) phase using a software of "ImageJ". Resulting from image analysis, the volume fraction of the (Nb, Ti) phases in the annealed $Nb_{30}Ti_{35}Ni_{35}$ sample is estimated to be 0.35 ± 0.03. If the spherical (Nb, Ti) phase is assumed to be precipitated in this alloy, the average diameter of the (Nb, Ti) phase is calculated to be 0.42–0.50 μm. On the other hand, we can see the dendritic (Nb, Ti) phase in the free surface side of the as-quenched $Nb_{40}Ti_{30}Ni_{30}$ alloy ribbon (top of Fig. 3(c)), while featureless microstructure in the roller surface side of it (bottom of Fig. 3(c)). By heat treatment, the two-phase microstructure in which the (Nb, Ti) phase is embedded in the TiNi phase is formed in roller side of the ribbon (bottom of Fig. 3(d)), while the dendritic (Nb, Ti) phase is still observed in the free side of the ribbon (top of Fig. 3(d)). The volume fraction of the (Nb, Ti) phase is determined to be 0.44 ± 0.04 and its average diameter is 0.70–0.75 μm in the annealed $Nb_{40}Ti_{30}Ni_{30}$ alloy. We have already reported that the amorphous $Nb_{20}Ti_{40}Ni_{40}$ alloy crystallized into the (Nb, Ti) + TiNi two-phase microstructure by crystallization [6–8]. This microstructure is very similar to that of the annealed crystalline $Nb_{30}Ti_{35}Ni_{35}$ alloy. The volume fraction of the (Nb, Ti) phase in the annealed $Nb_{20}Ti_{40}Ni_{40}$ alloy was 0.23 [8]. Therefore, we can conclude that the volume fraction of the (Nb, Ti) phase increases with increasing Nb content.

Hydrogen flux J permeating an alloy membrane can be expressed by the next equation using the Fick's first diffusion law:

$$J = D \cdot \frac{C_u - C_d}{L} \quad (1)$$

where D and L are the diffusion coefficient and thickness of the membrane. Hydrogen content in the upstream and the downstream sides of the membrane are expressed as C_u and C_d, respectively. We have investigated that hydrogen content of the $Nb_{19}Ti_{40}Ni_{41}$ alloy having (Nb, Ti) + TiNi two-phase structure is expressed as the next equation when the hydrogen pressure is limited between 0.1 and 0.4 MPa [9];

$$C = K \cdot P^{0.5} + \alpha \quad (2)$$

where K and α are the hydrogen solution coefficient and constant which depend on temperature, respectively. If $\alpha = 0$, then Eq. (2) is called as the Sieverts' equation. We can obtain next equation from Eqs. (1) and (2);

$$J = D \cdot K \cdot \frac{P_u^{0.5} - P_d^{0.5}}{L} = \Phi \cdot \frac{\Delta P^{0.5}}{L} \quad (3)$$

P_u and P_d are the hydrogen pressures in the upstream and the downstream sides, respectively. Here, product of D and K is defined as hydrogen permeability Φ. Fig. 4(a), for example, shows the relation between $\Delta P^{0.5} (= P_u^{0.5} - P_d^{0.5})$ and $J \times L$ for the annealed $Nb_{40}Ti_{30}Ni_{30}$ alloy at respective measurement temperatures. We can see that these experimental data are well fitted by lines passing through the origin. The gradient of these lines is defined as hydrogen permeability Φ. This fact indicates that Φ is independent of the hydrogen pressure between 0.1 and 0.35 MPa H_2. We should note that the hydrogen content of these alloys do not obey Eq.

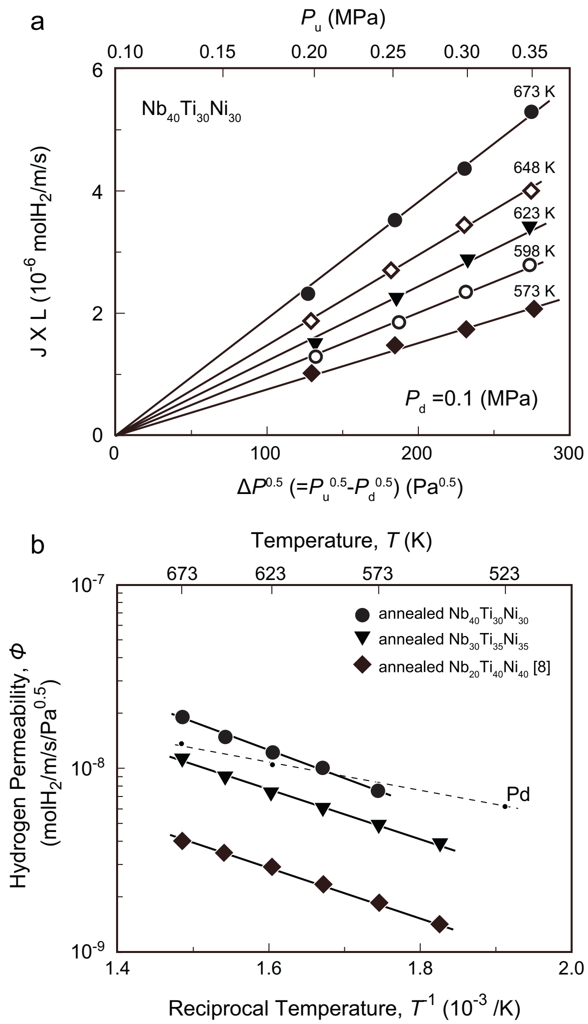

Fig. 4. (a) Relation between $\Delta P^{0.5}(= P_u^{0.5} - P_d^{0.5})$ and $J \times L$ of the annealed $Nb_{40}Ti_{30}Ni_{30}$ alloy at respective measurement temperatures and (b) temperature dependence of hydrogen permeability (Φ) for the annealed $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloys. Those of the annealed $Nb_{20}Ti_{40}Ni_{40}$ alloy [8] and pure Pd are also plotted for reference.

(2) when hydrogen pressures are below 0.1 MPa or above 0.4 MPa. On the other hand, new interpretation on hydrogen permeability which is applicable over a wide pressure range has recently been proposed by Hara et al. [10] and Zhang et al. [11]. Fig. 4(b) shows temperature dependence of Φ for the annealed $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloys in the form of the Arrhenius plot. Those of the annealed (at 1373 K for 10 h) $Nb_{20}Ti_{40}Ni_{40}$ alloy [8] and pure Pd are also plotted for reference in this Fig. The value of $\Phi_{673\,K}$ for the annealed $Nb_{30}Ti_{35}Ni_{35}$ alloy is 1.1×10^{-8} ($molH_2$/m/s/$Pa^{0.5}$), which is slightly lower than that of pure Pd. This alloy resists to hydrogen embrittlement at 548 K, but it is broken down during cooling to 523 K. The value of $\Phi_{673\,K}$ for the annealed $Nb_{40}Ti_{30}Ni_{30}$ alloy is 1.9×10^{-8} ($molH_2$/m/s/$Pa^{0.5}$), which is higher than that of pure Pd. However, hydrogen permeation measurement for this sample cannot be carried out at 548 K due to hydrogen embrittlement. The microstructure of the arc melted $Nb_{40}Ti_{30}Ni_{30}$ alloy, consisting of the primary (Nb, Ti) phase and the eutectic {TiNi + (Nb, Ti)} phase, turns into the granule (Nb, Ti) phase embedded in the TiNi phase by cold rolling and subsequent annealing. However, two different sizes of the (Nb, Ti) phase are observed, that is, primary one of 10–20 μm and precipitates of 2–5 μm formed in the eutectic phase, respectively [3]. The value of $\Phi_{673\,K}$ for the conventionally solidified $Nb_{40}Ti_{30}Ni_{30}$ alloy is 1.9×10^{-8} ($molH_2$/m/s/$Pa^{0.5}$) in the as-cast state, and it reduces to 0.6×10^{-8} ($molH_2$/m/s/$Pa^{0.5}$) by 50% rolling. Although $\Phi_{673\,K}$ value of this alloy by annealing at 1173 K for 10 h has not been reported, it is considered that $\Phi_{673\,K}$ is unchanged because it is not recovered by annealing for 10 h below 1373 K. However, it recovers to 1.7×10^{-8} ($molH_2$/m/s/$Pa^{0.5}$) after annealing at 1373 K for 168 h, which is almost equivalent value to that of the rapidly quenched and annealed alloy.

As reported in our previous paper [8], the annealed (at 1173 K for 10 h) $Nb_{20}Ti_{40}Ni_{40}$ alloy ribbon consists of the bcc-(Nb, Ti) and B2-TiNi and its $\Phi_{673\,K}$ value is 4.1×10^{-9} ($molH_2$/m/s/$Pa^{0.5}$). These experimental results indicate that hydrogen permeability and resistance to hydrogen embrittlement are improved and degraded by increasing Nb concentration in the annealed Nb–TiNi alloy ribbons, respectively.

The present work demonstrates that thin Nb–TiNi alloy ribbons can be successfully prepared by a single roller melt spinning machine, and ductility of these alloys is improved by annealing above 1173 K. Their hydrogen permeability is even or higher than that of pure Pd. Therefore, we can conclude that the rapid quenching technique and subsequent annealing process are useful and attractive method for the preparation of high performance hydrogen permeable Nb–TiNi alloy membrane.

4. Summary

Rapidly quenched $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloy ribbons with 50 mm in width and 30–40 μm in thickness were prepared by a single roller melt spinning machine. The as-quenched $Nb_{30}Ti_{35}Ni_{35}$ alloy consists of the crystalline (Nb, Ti) and the TiNi phases along with the amorphous phase. On the contrary, only the crystalline (Nb, Ti) and the TiNi phases are formed in the as-quenched $Nb_{40}Ti_{30}Ni_{30}$ alloy. Both of them are too brittle to measure hydrogen permeability. After annealing at 1173 K for 10 h, the (Nb, Ti) phase precipitates in the TiNi matrix and ductility recovers in both alloys. The volume fraction of the (Nb, Ti) phase increases with increasing Nb content. The value of $\Phi_{673\,K}$ for the $Nb_{30}Ti_{35}Ni_{35}$ and $Nb_{40}Ti_{30}Ni_{30}$ alloys are 1.1×10^{-8} and 1.9×10^{-8} ($molH_2$/m/s/$Pa^{0.5}$), respectively. Consequently, it is concluded that the rapid quenching and subsequent annealing process are useful and hopeful method to get the Nb–TiNi based hydrogen permeation alloy membrane.

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