Changes in microstructures and hydrogen permeability of $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ eutectic alloy membranes by annealing

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Abstract: Changes in microstructures and hydrogen permeability by long-time annealing (168 h) at 1073, 1173 and 1173 K for eutectic $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy are investigated. After annealing at 1073 K and 1173 K for 168 h, the fully lamellar eutectic microstructure in as-cast state has disappeared and turned to a duplex microstructure. Correspondingly, the hydrogen permeability at 673 K, decreases from 3.3×10^{-8} to $(0.82-1.5) \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$ after annealing. The annealed (a-) sample at 1273 K for 168 h is brittle and susceptible to hydrogen embrittlement that results from the appearance of the additional Hf_2Co phase. The hydrogen solubility coefficient (K) for each a- samples at 673 K is almost the same as that for the as-cast sample, while the hydrogen diffusion coefficient (D) for the a- samples are (1/4-1/2) times than that for the as-cast one. It is thus concluded that the lower permeability by annealing for eutectic $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ is mainly attributed to the significant reduction of hydrogen diffusivity after annealing.

Keywords: Hydrogen permeability; Microstructures; Nb-HfCo eutectic alloy

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1. Introduction

Pd and its alloys are presently used as the hydrogen permeation membrane for purification of hydrogen gas [1, 2]. However, since Pd is too expensive and a rare metal, much of the current research [3-7] on hydrogen permeable alloys is focused on Nb-based alloys containing less or no Pd, such as Nb-TiNi [3, 4], Nb-TiCo [5] and Nb-HfNi [6] etc. These alloys generally contain a multi-phase microstructure containing a primary BCC-Nb solid-solution phase and eutectic phases. The primary BCC-Nb phase provides the major contribution to hydrogen permeation, while the eutectic phases contribute to suppress the hydrogen embrittlement. The hydrogen permeability, which is generally used as a measure to evaluate the performance of these hydrogen permeable membranes, is related to the hydrogen diffusion flux (J). The steady-state flux through the membrane, which is defined by a variation of Fick's first law, can be rewritten as follows,

$$J = \frac{D \cdot K(\Delta P^{0.5})}{L} = \frac{\Phi(\Delta P^{0.5})}{L} = \frac{\Phi(P_u^{0.5} - P_d^{0.5})}{L} \quad (1)$$

Where D and K are the hydrogen diffusion and solubility coefficient, and L is the thickness of the membrane. P_u and P_d represent the hydrogen pressures in the upstream and downstream sides of the membrane, respectively. The product of D and K is defined as the hydrogen permeability, Φ . A large J can be obtained not only by using a high-performance hydrogen permeation alloy (large Φ) but also by operating a thin alloy membrane under a large pressure difference (small L). Obviously, appropriate processing method to achieve thin alloy membranes is important to increase J during hydrogen permeation.

For conventional as-cast alloys, thin alloy membranes are generally produced by working such as rolling, forging, pressing and so on [7-9]. Correspondingly, mechanical strain and defects are introduced in the deformed membranes which act as hydrogen trapping sites. A sequent annealing is thus needed to remove these defects, but in turn may induce microstructural changes [8]. Wang et al. [10] investigated the microstructural change and its effect on hydrogen permeability in as-cast eutectic $\text{Nb}_{19}\text{Ti}_{40}\text{Ni}_{41}$ alloy by annealing, and found that the initial fully lamellar eutectic microstructure turned into a duplex phase by annealing at 1373 K for 168 h. Correspondingly, its hydrogen permeability at 573 K, $\Phi_{573\text{ K}}$, is about one half of the as-cast state. Subsequently, Li et al. [11] studied the microstructural stability and its effect on hydrogen permeability in eutectic $\text{Nb}_{30}\text{Ti}_{35}\text{Co}_{35}$ alloys. The similar transformation of the eutectic morphology is also found in the as-cast samples after annealing, which is accompanied by a decrease in hydrogen permeability. In contrast, the directionally solidified samples show a much higher stability and much less reduction in permeability after annealing. A reverse case was observed in $\text{Nb}_{40}\text{Ti}_{18}\text{Zr}_{12}\text{Ni}_{30}$ [12]. After rolling and subsequent annealing, its eutectic phase disappeared and was replaced by a small spherical (Nb, Ti, Zr) phase embedded in the (Ti, Zr)Ni matrix. However, its hydrogen permeability decreased firstly and then increased and the final value was 1.13 times higher than that of the as-cast one. These works imply that complex microstructural change by annealing is responsible to the various hydrogen permeation behaviors. Therefore, it is important to understand

systematically the effect of annealing on microstructures and hydrogen permeability as well as the related underlying mechanisms.

Recently, a new metallic hydrogen permeation membrane, Nb-HfCo alloys, with pronounced high hydrogen permeability, was reported by the present authors [13]. Eutectic Nb₃₀Hf₃₅Co₃₅ was found to achieve a combination of high hydrogen permeability and excellent tolerance regarding hydrogen embrittlement, which is a promising hydrogen permeation membrane material. However, it is still unknown whether Φ of this alloy itself changes by the microstructural change during annealing. A further study about this problem will accelerate its potential implication in industry. If this alloy exhibits a high Φ value compared to the eutectic Nb₃₀Ti₃₅Co₃₅ [11] and Nb₁₉Ti₄₀Ni₄₁ [10] alloys after annealing, then we may use the rapid quenching technique to prepare thin Nb-HfCo amorphous membrane. However, amorphous alloys are usually thermally unstable and their desirable properties may be lost by crystallization under different annealing temperatures [14, 15]. Accordingly, it is essential to research on the crystallization behaviors and microstructure stability by heat treatments under different temperatures. Thus, annealing of as-cast Nb₃₀Hf₃₅Co₃₅ samples at three different temperatures, i.e. 1073, 1173 and 1273 K for 168 h, was performed. Microstructural changes, corresponding hydrogen permeability, and the hydrogen solubility and diffusivity of the as-cast and a- samples are characterized. Finally, we emphasize the superiority and difference of the (or a-) Nb₃₀Hf₃₅Co₃₅ alloy respect to the previous ones in the field.

2. Experimental procedure

25 g ingots of Nb₃₀Hf₃₅Co₃₅ alloys were prepared by arc melting using Nb, Hf and Co (99.9 mass% purity for all) in an Ar atmosphere. The ingots were melted several times for macroscopic homogenization. Disk samples of 12 mm in diameter and 0.7 mm in thickness were cut from the as-cast alloys by a spark erosion wire-cutting machine. Some of disks were annealed at 1073, 1173 and 1273 K for 168 h under Ar atmosphere. Both sides of the disks were ground, polished and then coated by 190 nm of Pd by a radio frequency (RF) sputtering machine to prevent oxidation and to act as catalyzer for dissociation of hydrogen molecule. Pd-coated samples were sealed with copper gaskets and placed into the hydrogen permeation measuring apparatus. Hydrogen permeability (Φ) was measured by a conventional gas-permeation technique at 523, 573, 623 and 673 K. 0.1 MPa of hydrogen gas (99.99999 mass% purity) was introduced to the upstream and downstream sides of the membrane, and then the hydrogen pressure in the upstream side was increased to 0.5 MPa by 0.05 MPa intervals. The experimental procedure has been described in more detail in our previous paper [16]. The pressure-composition-temperature (PCT) curves were measured using a Sieverts-type apparatus at 673 K in a pressure range from 0.01 to 0.65 MPa for the as-cast and a-Nb₃₀Hf₃₅Co₃₅ alloys. The amount of absorbed hydrogen was calculated from the pressure drop in a constant inner volume chamber. The crystal structures were identified by powder X-ray diffractometry (XRD) employing Cu K_α radiation with a tube voltage of 40 kV and a current of 40 mA. Microstructural observations were characterized by Scanning Electron Microscope (SEM) backscattered electron imaging (BSE).

3. Results and discussion

Fig. 1 shows SEM micrographs for the as-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloys annealed under various conditions. As-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ consists of equiaxed eutectic grains with a fully lamellar eutectic structure, Fig. 1(a). XRD patterns and EDS results identify the dark BCC-(Nb, Hf) solid solution and the gray $\text{B}_f\text{-HfCo}$ phases (cf. Ref. [13]). After annealing at 1073 K and 1173 K for 168 h, the fully lamellar eutectic microstructure in as-cast state has disappeared and turned to a duplex microstructure which consists of dark granular BCC-(Nb, Hf) regions surrounded by gray $\text{B}_f\text{-HfCo}$ regions, Figs. 1(b) and (c). Such a microstructural change during annealing is attributed to the simultaneous coarsening of the both phases. Similar coarsening phenomenons were also observed in eutectic $\text{Nb}_{19}\text{Ti}_{40}\text{Ni}_{41}$ [10] and $\text{Nb}_{30}\text{Ti}_{35}\text{Co}_{35}$ [11] after annealing. A Hf_2Co phase additionally appears in a- samples at 1273 K for 168 h, Fig. 1(d). The Hf_2Co phase is inherently brittle so that annealing temperature for as-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ should be lower than this temperature.

Fig. 2 shows the PCT curves for the as-cast and a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ samples as well as Pd measured at 673 K. The square root of hydrogen pressure is plotted against the hydrogen concentration in the form of $P^{0.5}$ vs. C (Sieverts' plot), in Fig. 2(b). The PCT curve of Pd passes through the origin, which indicates that Sieverts' law holds for Pd at 673 K. The hydrogen absorption capacity for the as-cast and a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ samples is obviously higher than that for pure Pd. A linear relation between C and $P^{0.5}$ is only found for the as-cast and a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ samples in the pressure range of 0.1-0.5 MPa (the inset in Fig. 2(b)), but the straight lines do not pass through the origin. This implies

that Sieverts' law does not hold for these alloys at 673 K. The fact that hydrogen dissolution into niobium and its alloys does not obey Sieverts' law in the low hydrogen content region has also been reported by Yukawa et al [17]. Although the straight lines in Fig. 2(b) do not pass through the origin, the hydrogen content C between 0.1 and 0.5 MPa can also be expressed as,

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

where α is a constant. Table 2 shows the values of K and α for each alloy, determined by the Sieverts' plots in Fig. 2(b).

As mentioned above, the steady-state hydrogen flux, J , through metal membrane is defined by a variation of Fick's first law,

$$J = -D \times \left(\frac{\partial C}{\partial L} \right) \quad (3)$$

where $\partial C / \partial L$ is the gradient of the hydrogen composition across the membrane. Provided C in Eq. (3) is substituted with C in Eq. (2), the hydrogen flux J can be also expressed as Eq. (1), which implies that we can still define hydrogen permeability (Φ) for the present alloys in a limited hydrogen pressure range even if Sieverts' law does not hold in Eq. (2). The slope of each straight line in the plot of $J \times L$ vs. $\Delta P^{0.5}$ corresponds to the hydrogen permeability (Φ). Such a method is usually used to determine Φ for other alloys such as Nb-Ti-Ni [3, 4], Nb-Ti-Co [5] and Nb-Hf-Ni [6] etc. Further on the basis of $\Phi = D \times K$, the value of D for each sample can be derived.

Fig. 3(a) shows a representative relation between $J \times L$ and square-root hydrogen pressure ($\Delta P^{0.5}$) for the a- Nb₃₀Hf₃₅Co₃₅ alloy at 1073 K for 168 h from 523 to 673 K. The linear relation coefficient R^2 , obtained by a linear regression method, is higher than

0.99 at every temperature. Therefore, it is reasonable to calculate the hydrogen permeability (Φ) of the sample from the slope of the straight line according to the Eq. (1). A linear relation between $J \times L$ and $\Delta P^{0.5}$ is also found in other samples, and their Φ values are thus determined similarly.

The temperature dependence of the Φ value in the form of an Arrhenius plot for the as-cast and a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ samples is shown in Fig. 3(b). The values of pure Pd are also included for comparison. The variations of Φ appear to be linear in the Arrhenius plot in all cases and the Φ values of each sample evidently increase with increasing temperature. The as-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ samples exhibit significantly higher Φ values than that of pure Pd, especially at high temperatures. After annealing at 1073 and 1173 K for 168 h, its hydrogen permeability obviously decreases. Typically, $\Phi_{673\text{K}}$ reduces from 3.3×10^{-8} to $(1.5-0.82) \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$, as also shown in Table 1. The reason and related underlying mechanisms will be described later. The a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ sample obtained by annealing at 1273 K for 168 h broke down during the hydrogen permeation experiment at all temperatures. This suggests that it is susceptible to hydrogen embrittlement that may result from the appearance of the brittle Hf_2Co phase in the duplex microstructure. Additionally, the a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ sample after annealing at 1173 K for 168 h is broken down at 523 K, while is hydrogen permeable at higher temperatures (see Table 1). The results above indicate that annealing temperature for the as-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ sample should not be higher than 1173 K.

The value of K at 673 K for the as-cast and a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ samples at 1073 K, 1173 K, and 1273 K is 28.52, 29.14, 29.75 and 30.63 $\text{mol H}_2 \text{ m}^{-3} \text{ Pa}^{-0.5}$, respectively, as shown

in Table 2. They are almost the same, while about 6 times larger than that for Pd. The minor increase of K values may be ascribed to the difference of phase construction and the volume fraction of phases after annealing. The volume fraction of BCC-(Nb, Hf) phase for the as-cast and a- samples at 1073 K, 1173 K, and 1273 K is ~35.1 vol.%, ~36.2 vol.%, ~36.8 vol.% and ~37.5 vol.%, respectively. The value of K in a BCC-Nb solid-solution phase is usually much higher than that in corresponding intermetallic phase for Nb-based multi-phase alloys [17, 18]. Increase in annealing temperature lead to increase in the volume fraction of solid-solution BCC-(Nb, Hf) phase and decrease in the volume fraction of intermetallic HfCo phase, thus raising its hydrogen solubility coefficient. Moreover, it should also be noted that the brittle Hf₂Co phase is formed in the a- alloy at 1273 K. The appearance of this new phase will increase the hydrogen solubility and thus deteriorates the resistance against hydrogen embrittlement. In contrast, the values of D at 673 K for the as-cast and a- Nb₃₀Hf₃₅Co₃₅ samples at 1073 K, and 1173 K are 11.6×10^{-10} , 5.1×10^{-10} and $2.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively. The D values for the a- samples are 0.23-0.46 times than that of the as-cast one. In a general view taking into account the values of Φ , K and D , it is concluded that the lower permeability caused by the microstructural change from a lamellar to the duplex microstructure is mainly attributed to the significant reduction of hydrogen diffusivity after annealing. The similar case was observed in Nb-Ti-Co [11], Nb-W-Mo [19] and Cr-Mo steel [20] alloys.

In a general view taking into account the lowering of Φ and/or D and the microstructural change in the a- Nb₃₀Hf₃₅Co₃₅ alloys, we find that it can be explained

quantitatively based on the composite rule using effective medium theory models [21]. These models have advantages over other generic models such as the semi-empirical Krischer model, which are not dependent on any empirical parameter. According to these models, the relationship between the microstructure and Φ (or D) of Nb-TiNi/TiCo alloys has been investigated systematically by Saeki et al. [22, 23]. In the present case, when the continuous and discontinuous distributions of BCC-(Nb, Hf) and HfCo phases in as-cast and a- samples are analogized to the parallel and mixed microstructure, respectively, hydrogen permeability (Φ_p and Φ_m) can be described as follow [8, 14]:

$$\Phi_p = \Phi_{\text{BCC-(Nb,Hf)}} \times V_{\text{BCC-(Nb,Hf)}} + \Phi_{\text{HfCo}} \times V_{\text{HfCo}} \quad (4)$$

$$\Phi_m = \frac{\Phi_{\text{HfCo}} \times V_{\text{HfCo}} + \Phi_{\text{BCC-(Nb,Hf)}} \times V_{\text{BCC-(Nb,Hf)}} (3\Phi_{\text{HfCo}} / (2\Phi_{\text{HfCo}} + \Phi_{\text{BCC-(Nb,Hf)}}))}{V_{\text{HfCo}} + V_{\text{BCC-(Nb,Hf)}} (3\Phi_{\text{HfCo}} / (2\Phi_{\text{HfCo}} + \Phi_{\text{BCC-(Nb,Hf)}}))} \quad (5)$$

where $V_{\text{BCC-(Nb,Hf)}}$, V_{HfCo} , $\Phi_{\text{BCC-(Nb,Hf)}}$ and Φ_{HfCo} represent the volume fraction and hydrogen permeability of the BCC-(Nb, Hf) and the HfCo phases, respectively. The value of $\Phi_{\text{BCC-(Nb,Hf)}}$ is larger than that of Φ_{HfCo} . The as-cast and a- microstructures can be considered to be close to the mixed and the parallel type arrangement, respectively. These equations show clearly that a low Φ value is at all times obtained from the mixed type arrangement at a given volume fraction of the BCC-(Nb, Hf) phase, compared with that in the parallel type arrangement.

Migration of H through the Nb-based alloys is via a series of jumps between interstitial sites [24]. Calculations based on theoretical models have shown that the diffusion of atomic H is usually governed by the electronic structure and the size of the interstitial sites [7, 25]. In addition, the spatial distribution of BCC-Nb in the membrane is also

important for hydrogen permeation, because this phase in the eutectic aligned perpendicular to the membrane surface can act as the pathways for hydrogen diffusion. If all eutectic grains perpendicular to the membrane surface so that no BCC-Nb grains are suspended in the membrane, the highest hydrogen permeability and diffusivity is expected, which has been testified by several researches [10, 16, 26]. In the present work, it should be noted that the as-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ sample shows a higher hydrogen diffusion compared to the a- samples, which is attributable to the eutectic grains with more contiguous BCC-(Nb, Hf) regions penetrating the membrane, as seen in the inset in Fig. 1(a). The values of D for all the a- samples are lower than that of as-cast samples. This discrepancy may be ascribed to the drastic microstructure change from initially fully lamellar eutectic (Fig. 1(a)) to discontinuous granules (Figs. 1(b)(c)(d)). The lowering of D in the $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy caused by microstructural change after annealing can also be explained by an electrical analogy, as seen in Fig. 4. When the BCC-(Nb, Hf) and HfCo phases are arranged in parallel with the hydrogen permeation direction, diffusion of H through the membrane can be analogized to the current through the parallel circuits. Similarly, the hydrogen diffusion through the membrane with the BCC-(Nb, Hf) phase embedded in the HfCo phase can be analogized to the current through the mixed circuits [27]. The diffusion barrier of hydrogen corresponds to the electric resistance in the electrical circuit. R_1 , R_2 and R_3 represent the diffusion barriers of hydrogen in the HfCo phase, BCC-(Nb, Hf) phase and their boundaries, respectively ($R_3 > R_1 > R_2$). Obviously, the discontinuous distribution of BCC-(Nb, Hf) leads to a large total sum of diffusion barrier. After annealing, the BCC-(Nb, Hf) in the eutectic

transform from a continuous thin layer to discontinuous granules (see Fig. 1), which induces a decrease of the hydrogen diffusivity. Therefore, the value of D of a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ is much lower than that of the as-cast one (see Table 2). Correspondingly, the permeability of a- sample is much lower than that of the as-cast one due to minor difference of K in these cases.

Finally, we emphasize the superiority and difference of the as-cast (or a-) $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy, respect to the previous ones in the field. Firstly, the as-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy exhibits a stable permeability and also possesses pronounced high hydrogen permeability of $3.3 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$, compared with the as-cast $\text{Nb}_{19}\text{Ti}_{40}\text{Ni}_{41}$ and $\text{Nb}_{30}\text{Ti}_{35}\text{Co}_{35}$ alloys [10, 11]. High permeability will promote this alloy to meet the US DOE performance targets [28]. However, for other alloys such as $\text{Nb}_{19}\text{Ti}_{40}\text{Ni}_{41}$ and $\text{Nb}_{30}\text{Ti}_{35}\text{Co}_{35}$, a lower permeability will limit their potential implication in industry. Secondly, the value of $\Phi_{673\text{K}}$ of the a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ ($1.5 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$) is about 7 times higher than that of reported a- $\text{Nb}_{19}\text{Ti}_{40}\text{Ni}_{41}$ alloy ($0.24 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$) [10]. And the annealing temperature (1073 K) of the a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ is much lower than that of the a- $\text{Nb}_{19}\text{Ti}_{40}\text{Ni}_{41}$ (1373 K). It should be possible to develop new amorphous membrane prepared by melt-spinning technique and rolling for $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy, due to its large permeability and lower annealing temperature. Thirdly, a new phenomenon is observed, i.e. an additional new brittle Hf_2Co phase is formed in the a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ samples after annealing at 1273 K, while no new phase is formed in the a- $\text{Nb}_{19}\text{Ti}_{40}\text{Ni}_{41}$ and a- $\text{Nb}_{30}\text{Ti}_{35}\text{Co}_{35}$ samples. This indicates that the $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy exhibits low microstructural stability and its annealing temperature

should be lower than that of above two alloys. According to the above analysis, it is worthwhile to investigate the microstructure, hydrogen solubility, hydrogen diffusivity and hydrogen permeability of rolled and a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloys, which will be reported in the near future.

4. Conclusions

Changes in microstructures and hydrogen permeability by long-time annealing (168 h) at 1073, 1173 and 1173 K for eutectic $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy are investigated by SEM, XRD, PCT and gas-permeation measurements. The initially fully lamellar eutectic microstructure of the as-cast samples turns into to a duplex one after annealing at 1073 K and 1173 K for 168 h. Correspondingly, its hydrogen permeability at 673 K, $\Phi_{673\text{ K}}$, decreases from 3.3×10^{-8} to $(0.82-1.5) \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$. A further increase of annealing temperature (at 1273 K) leads to form an additional Hf_2Co phase, which induces severe hydrogen embrittlement during hydrogen permeation. The hydrogen solubility coefficient at 673 K for each a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy is almost the same as that for the as-cast sample. Therefore, lowering of hydrogen permeability for a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy is mainly attributed to the reduction of hydrogen diffusivity. The present work demonstrates that annealing can't enhance the hydrogen permeability of the as-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ eutectic alloy membrane and its lower permeability is mainly attributed to the significant reduction of hydrogen diffusivity after annealing.

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Fig. 1 SEM micrographs of the as-cast (a) and a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloys after annealing at 1073 K (b), 1173 K (c) and 1273 K (d) for 168 h.

Fig. 2 Pressure-composition-temperature (PCT) curves of the as-cast and a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloys after annealing at 1073, 1173 and 1273 K for 168 h, and for Pd at 673 K. (a) PCT curves for each alloy. (b) The Sieverts' plot, i.e. $P^{0.5}$ vs. hydrogen composition C , between 0 and 0.6 MPa for each alloy.

Fig. 3 Representative relation between $(J \times L)$ and $\Delta P^{0.5}$ for the a- $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy after annealing at 1073 K for 168 h in the temperature range of 523-673 K (a), and temperature dependence of hydrogen permeability Φ for the as-cast $\text{Nb}_{30}\text{Hf}_{35}\text{Co}_{35}$ alloy annealed under various conditions in the form of an Arrhenius plot (b).

Fig. 4 Schematic illustration of an electrical analogy to analyze the hydrogen diffusion in a dense membrane. The diffusion barrier of hydrogen corresponds to the electric resistance in the electrical circuit. R_1 , R_2 and R_3 represent the diffusion barriers of hydrogen in the HfCo phase, BCC-(Nb, Hf) phase and their boundaries, respectively.

Table 1 Values of hydrogen permeability (Φ) for the as-cast Nb₃₀Hf₃₅Co₃₅ alloys annealed under various conditions (NG:

unmeasureable due to hydrogen embrittlement).

Annealing condition		Hydrogen permeability ($10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{0.5}$)			
Temperature (K)	Period (h)	673 K	623 K	573 K	523 K
1073	168	1.5	1.1	0.72	0.46
1173	168	0.82	0.62	0.47	NG
1273	168	NG	NG	NG	NG
as-cast	—	3.3	2.1	1.2	0.62

Table 2 Hydrogen permeability (Φ), hydrogen solubility coefficient (K), hydrogen diffusion coefficient (D) and fitting parameter (α)

for the as-cast Nb₃₀Hf₃₅Co₃₅ alloys annealed under various conditions as well as those for Pd at 673 K.

Annealing condition		Φ	K	D	α
Temperature (K)	Period (h)	[mol H ₂ m ⁻¹ s ⁻¹ Pa ^{-0.5}]	[mol H ₂ m ⁻³ Pa ^{-0.5}]	[10 ⁻¹⁰ m ² s ⁻¹]	[mol H ₂ m ⁻³]
1073K	168	1.5×10 ⁻⁸	29.14	5.1	5629
1173K	168	0.82×10 ⁻⁸	29.75	2.7	5749
1273K	168	—	30.63	—	5835
As-cast	—	3.3×10 ⁻⁸	28.52	11.6	5425
Pd	—	1.6×10 ⁻⁸	5.23	30.5	—