Changes in microstructure, solidification path and hydrogen permeability of Nb-Hf-Co alloy by adjusting Hf/Co ratio

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Abstract: The effect of Hf/Co ratio on microstructure, solidification path and hydrogen permeability of as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys is investigated. The above two series of alloys mainly consist of the primary BCC-(Nb, Hf) and the eutectic {BCC-(Nb, Hf) + $\text{B}_\text{f}\text{-HfCo}$ } phases, while $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ alloy additionally contains small fractions of the Hf_2Co phase that results from a ternary eutectic reaction. Increase of Hf/Co ratio induces higher fraction of primary BCC-(Nb, Hf) and Hf_2Co phases. Two kinds of solidification paths are found in this two series of alloys, particularly $[\text{L} \rightarrow \text{BCC}(\text{Nb}, \text{Hf})] \rightarrow [\text{L} \rightarrow \text{BCC}(\text{Nb}, \text{Hf}) + \text{B}_\text{f}\text{-HfCo}]$ and $[\text{L} \rightarrow \text{BCC}(\text{Nb}, \text{Hf})] \rightarrow [\text{L} \rightarrow \text{BCC}(\text{Nb}, \text{Hf}) + \text{B}_\text{f}\text{-HfCo}] \rightarrow [\text{L} \rightarrow \text{BCC}(\text{Nb}, \text{Hf}) + \text{B}_\text{f}\text{-HfCo} + \text{Hf}_2\text{Co}]$. The permeability increases with increasing Hf/Co ratio and increasing volume fraction of the primary BCC-(Nb, Hf) phase. $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ ($x = 2$) exhibits a high hydrogen permeability of $5.21 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$ at 673 K and excellent durability in hydrogen permeation (~ 72 h), which becomes superior to that of the $\text{Nb}_{40}\text{Hf}_{30}\text{Co}_{30}$ previously reported to be the best in the Nb-Hf-Co alloy series. The present work demonstrates that the hydrogen permeability of this alloy series can be optimized by appropriately adjusting the Hf/Co ratio for a given niobium content.

Keywords: Hydrogen permeability; Microstructures; Solidification path; Nb-Hf-Co alloy

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1. Introduction

Nb-based alloys, such as Nb-TiNi [1-6], Nb-TiCo [7-8] and Nb-HfNi [9-11] etc, are ones of the most promising materials for hydrogen permeable membrane to be substituted for currently used Pd–Ag alloys, because they possess higher hydrogen permeability than Pd-based alloys [12-15]. 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 (such as Nb+TiNi eutectic) contribute to suppress the hydrogen embrittlement [1]. Based on the above idea of combining functions of different phases, several similar alloy systems such as V-Ta-Ni-Ti [16, 17], Nb-W-Mo [18], V-Ni-Al [19] etc. have been extensively developed, which show comparable or even higher hydrogen permeability than that of Pd. Consequently, such alloys are promising to achieve a combination of high hydrogen permeability and excellent tolerance regarding hydrogen embrittlement. However, there still remain several challenges for above Nb-based alloys to meet the US DOE performance targets [20] for hydrogen permeation applications. Considering that they can nowadays certainly meet durability requirements, temperature and cost targets, meeting flux (150 cm³/cm²/min with $dP(H_2)$ of 100 psia) remains the key issue to be solved for these materials [12].

The steady-state hydrogen flux (J) through above metal 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 in Eq. (1) is defined as the hydrogen permeation coefficient, $\Phi = D \cdot K$, and generally used as a measure to evaluate the performance of the hydrogen permeable membranes. A large J can be obtained not only by operating a thin alloy membrane under a large pressure difference (small L) but also by using a high-performance hydrogen permeation alloy (large Φ). Although several special processing methods such as melt-spinning technique [5, 21-23] and rolling followed by annealing [24-26] can be used to fabricate a thinner alloy membrane with the aim to obtain larger J , composition design with the aim to improve the immanent hydrogen permeability of these alloys is also important [1, 7, 8, 10, 12, 18, 27-30]. Obviously, finding favorable composition to tailor the above multi-phase microstructure and hydrogen permeability for higher Φ value in these alloy systems is the first issue to be addressed for defining their usefulness in hydrogen permeation. Generally, the composition leading to the crystallization of the multi-phase microstructure exists in the pseudo-binary isopleth, especially on the line connecting the eutectic point and the primary Nb phase [1, 2, 7-11, 17, 31, 32]. So the volume fraction of phases in microstructure can be adjusted by different Nb content, thus improving its Φ value. To address this problem, lots of alloy composition existing in the pseudo-binary isopleth have been studied and developed, such as $\text{Nb}_x\text{Ti}_{(100-x)/2}\text{Ni}_{(100-x)/2}$ [1, 2, 33], $\text{Nb}_x\text{Ti}_{(100-x)/2}\text{Co}_{(100-x)/2}$ [7, 8] and $\text{Nb}_x\text{Hf}_{(100-x)/2}\text{Ni}_{(100-x)/2}$ [9-11] etc. However, some other compositions leading to crystallization of the above mentioned microstructures also exist in both sides of pseudo-binary isopleth [4, 7, 27, 29, 33-35]. In this case, the volume fraction of phases in microstructure can be adjusted by different A or B content (A/B ratio) for a given Nb content, thus affecting its Φ value (In a Nb-A-B ternary alloy system, A and B represent Ti or Hf and

Ni or Co, respectively). For example, K. Aoki et al [34] investigated the effect of Ti/Ni ratio on microstructure and hydrogen permeability of Nb-Ti-Ni alloy and found that the microstructure and hydrogen permeability of this alloy can be optimized by appropriately adjusting the Ti/Ni ratio for a given niobium content. Our recent work [27] confirmed the above conclusion and found a new compositional window in above alloys leading to the crystallization of the multi-phase microstructure. The Φ value strongly depends on the composition for a given niobium content, especially the Ti/Ni ratio. A similar case was observed in Nb-Hf-Ni ternary alloys [10]. This indicates that in addition to the initial Nb content, the initial A/B ratio can also tailor the microstructures, thus affecting its Φ value. Recently, a new family of metallic hydrogen permeation membranes, Nb-HfCo alloy, with pronounced high hydrogen permeability, was reported by the present authors [36]. Nb₄₀Hf₃₀Co₃₀ shows the highest permeability, particularly $4.96 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$ at 673 K, which is also the highest value among all the currently reported ones. However, the effect of Hf/Co ratio on microstructure and hydrogen permeability of above alloy is currently unclear, and the composition with higher Φ value in Nb-Hf-Co alloys is not yet fully explored. It is most likely that this alloy with Hf/Co ratios lower or higher than unity can be also qualified for hydrogen permeation applications.

The purpose of the present work is to investigate the effect of Hf/Co ratio on microstructure, solidification path and hydrogen permeability of as-cast Nb₄₀Hf_{30+x}Co_{30-x} and Nb₃₅Hf_{32.5+x}Co_{32.5-x} (x=-2, 0, 2, 4) alloys. The former alloys are based on the multi-phase Nb₄₀Hf₃₀Co₃₀ alloy far from the eutectic valley of $L \rightarrow \text{BCC}-(\text{Nb}, \text{Hf}) + \text{B}_f\text{-HfCo}$, with the aim to develop new alloy composition with high performance by appropriate adjusting Hf/Co ratio.

The latter alloys are based on multi-phase $\text{Nb}_{35}\text{Hf}_{32.5}\text{Co}_{32.5}$ alloy near the eutectic valley, so that the microstructural changes induced by adjusting Hf/Co ratio in this alloy system may be observed clearly. Solidification experiments and subsequent microstructural characterization are combined with numerical calculation of solidification paths. The correlation of microstructures, numerically calculated solidification paths and hydrogen permeability sheds light on exploring hydrogen permeable alloys with high performance. The solubility and diffusivity of hydrogen in the two series of alloys are characterized for revealing the detailed response of hydrogen permeability to the Hf/Co ratio. **Finally, we emphasize the superiority and difference of the present alloy system respect to the previous ones in the field.**

2. Experimental and numerical procedures

25 g ingots of Nb-Hf-Co 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. The serial numbers #1-#8 of the representative alloys are listed in table 1. Disk samples of 12 mm in diameter and 0.6 mm in thickness were cut from these ingots by using an electrical discharge machine. Crystal structures were identified by a powder X-ray diffractometer (XRD, Cu $K\alpha$). Microstructural examinations were carried out using a Scanning Electron Microscope (SEM). Chemical compositions were determined using an Energy Dispersive X-ray Spectrometer (EDS) attached to the SEM. The volume fraction of the constituent phases was analyzed using the public domain NIH Image program. 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 by two copper seal gaskets and placed in the

hydrogen permeation apparatus, as shown in Fig. 1. Both sides of the disks were evacuated to below 3×10^{-3} Pa, and then heated to 673 K and kept for 20 minutes. 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 hydrogen flux through the disks was measured by a hydrogen flow meter. The measurements were repeated at 623 K, 573 K and 523 K. The membranes of some alloys were also chosen for a test of durability. The pressure–composition–temperature (PCT) is also measured for some representative alloys by using a Sieverts-type apparatus at 673 K and in the pressure range from 0 to 0.55 MPa in order to investigate the hydrogen solubility in the sample. Experimental processes are described in detail in Refs. [28, 37, 38].

In addition, numerical calculations of solidification paths were conducted using the CALPHAD method for phase equilibria coupled with a microsegregation model proposed by the present authors' group [27, 39, 40, 41]. This microsegregation model not only includes a unified expression of Scheil model and lever-rule model limit solute redistribution effect of any solid back diffusion but also includes the factors of any dendritic geometry morphology during the solidification. Through the Thermo-Calc TQ6.0 interface for Intel Visual Fortran, the corresponding algorithms for predicting the solidification paths of Nb-Hf-Co ternary alloys are proposed. The numerical calculations aim at investigating the detailed relationship between initial compositions, cooling rates, and type and volume fraction of phases. The data used in the present calculations are listed in Table 2. The main changes of the parameters in this work are the functional relationship between the hydrogen diffusion coefficient and the temperature compared with those of Nb-Ti-Ni alloys [27]. A cooling rate of 0.1 K/s is

exclusively considered, neglecting off-equilibrium effects for simplicity. More detail derivation process and integral algorithm for calculation can be seen in our earlier work [27, 41].

3. Results and discussion

3.1 The crystal structures and microstructures

The chemical compositions and volume fraction of constituting phases in the as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys as determined by XRD, SEM and EDS are tabulated in Table 1. The XRD patterns of the two series of alloys are shown in Figs. 2 and 3. The above two series of alloys mainly consist of the primary BCC-(Nb, Hf) and the eutectic {BCC-(Nb, Hf) + $\text{B}_f\text{-HfCo}$ } phases, while $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ alloy additionally contains small fractions of the Hf_2Co phase. For $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ ($x=-2, 0, 2, 4$) alloys, the intensity of the main diffraction peak of the BCC-(Nb, Hf) increases with increasing x value except for $x=4$. The same case was observed in $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ alloys. This indicates that more and more BCC-(Nb, Hf) phase is present in these alloys with the increase of Hf/Co ratio.

SEM micrographs of the as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys are shown in Fig. 4. Primary BCC-(Nb, Hf) dendrites embedded in eutectic {BCC-(Nb, Hf) + $\text{B}_f\text{-HfCo}$ } are observed in this two series of alloys, whereas a small amount of Hf_2Co phase additionally appears in $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ alloy, Fig. 4(d). The microstructural observations correspond to the XRD results. The above multi-phase microstructure is appropriate for hydrogen permeation based on the new concept to design hydrogen permeable alloys. The inset in Fig. 4(d) reveals the appearance of Hf_2Co that results from the ternary eutectic

reaction of $L \rightarrow \text{BCC}-(\text{Nb}, \text{Hf}) + \text{B}_\Gamma\text{-HfCo} + \text{Hf}_2\text{Co}$ at a late stage of solidification. For the above two series of alloys, increase of Hf/Co ratio induces higher volume fractions of the primary phase and less eutectic, as shown in Fig. 4 and Table 1. This can be related to the fact that the two series of alloys gradually far away from the eutectic valley of $L \rightarrow \text{BCC}-(\text{Nb}, \text{Hf}) + \text{B}_\Gamma\text{-HfCo}$ with the increasing of Hf/Co ratio (described later). A further increase of Hf/Co ratio may lead to an even higher permeability, but such alloys would be close to the eutectic point ($\text{Nb}_9\text{Hf}_{57}\text{Co}_{34}$) and a small amount of Hf_2Co phase additionally appears in alloy. The above results show that alloys contain the primary BCC-(Nb, Hf) phase and the eutectic $\{\text{BCC}-(\text{Nb}, \text{Hf}) + \text{B}_\Gamma\text{-HfCo}\}$ in a certain range of Hf/Co ratio, and alloys with Hf/Co ratios lower or higher than unity may be also qualified for hydrogen permeation applications.

It should be noted that the above XRD patterns and as-cast microstructures represent off-equilibrium conditions, as cooling rates after arc melting are usually higher than 200 K/s. Although such microstructures are popular to design the hydrogen permeable alloys, a question is whether the above relationships between compositions and microstructures are independent of the cooling rate. Recently, several new processing methods with extremely low cooling rates such as directional solidification have been adopted to produce hydrogen permeation membranes with improved performance [6]. Therefore, the solidification behaviors for Nb-Hf-Co alloy under near equilibrium conditions should be studied, which will be investigated by numerical calculations in the following.

3.2 Numerically calculated solidification paths

Fig. 5 shows the predicted solidification paths of as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys in the BCC-(Nb, Hf) phase region for a cooling rate

of 0.1 K/s. The calculated volume fractions of solid as a function of temperature for the above two series of alloys are given in Figs. 5(b) and (c), respectively. It can be seen that this two series of alloys only experience two transformations of $[L \rightarrow \text{BCC}-(\text{Nb}, \text{Hf})] \rightarrow [L \rightarrow \text{BCC}-(\text{Nb}, \text{Hf}) + \text{B}_\Gamma\text{-HfCo}]$ besides $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ alloy, which corresponds to the as-cast microstructure in Fig. 4. $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ alloy as an exception experiences three different solidification stages successively, i.e., the formation of primary BCC-(Nb, Hf) from liquid $[L \rightarrow \text{BCC}-(\text{Nb}, \text{Hf})]$, binary eutectic $[L \rightarrow \text{BCC}-(\text{Nb}, \text{Hf}) + \text{B}_\Gamma\text{-HfCo}]$ and finally the ternary eutectic transformation $[L \rightarrow \text{BCC}-(\text{Nb}, \text{Hf}) + \text{B}_\Gamma\text{-HfCo} + \text{Hf}_2\text{Co}]$. For $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ ($x=-2, 0, 2, 4$) alloys, the volume fraction of primary BCC-(Nb, Hf) phase is ~9 vol.%, ~20 vol.%, ~25 vol.% and ~31 vol.%, respectively and the volume fraction of binary eutectic is ~91 vol.%, ~80 vol.%, ~75 vol.% and ~67 vol.%, respectively, as seen in Fig. 5(b). For $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys, the volume fraction of primary phase is ~4 vol.%, ~10 vol.%, ~12 vol.% and ~20 vol.% and the volume fraction of binary eutectic is ~96 vol.%, ~90 vol.%, ~87 vol.% and ~80 vol.%, respectively, as seen in Fig. 5(c). With the increase of Hf/Co ratio for each series of alloy, the volume fraction of primary BCC-(Nb, Hf) increases, whereas the volume fraction of binary eutectic $[\text{BCC}-(\text{Nb}, \text{Hf}) + \text{B}_\Gamma\text{-HfCo}]$ decreases. $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ (#3) possesses the highest fraction of primary BCC-(Nb, Hf), 25.7 Vol.%, in the above multi-phase alloys. It is worth noting that the calculated results of the volume fraction of phases have minor differences with the experimental values (see Table 1). The maximum differences between calculated and experimental values of this two series of alloys are 3% and 1.7%, respectively. This discrepancy may be ascribed to the difference of cooling rates and the present microsegregation model neglecting several factors such as ignoring nucleating processes, no

pore formation and so on [27, 39-41].

In addition, the calculated solidification paths for Nb₄₀Hf₃₂Co₂₈ alloy under the cooling rate of 300 K/s (off-equilibrium condition) are presented in Fig. 5(b), where it experiences two kinds of solidification processes: [L→BCC-(Nb, Hf)] and [L→BCC-(Nb, Hf) + B₁-HfCo]. It can be seen that cooling rates have less influence on its solidification process, i.e., the solidification path of Nb₄₀Hf₃₂Co₂₈ alloy still experiences the above two process even if the cooling rate is very large. With the decrease of cooling rate R_f , the volume fraction of primary BCC-(Nb, Hf) phase decreases whereas the volume fraction of binary eutectic increases. This can be attributed to more and more residual liquid entering the latter binary eutectic reaction with the decrease in R_f . A similar law of solidification appears in other alloys. Overall, both of the predicted solidification paths correspond to their experimental counterparts in Fig. 4, respectively.

Based on the above results of arc melted and numerical calculation together, we find that Nb-Hf-Co alloys contain the primary BCC-(Nb, Hf) phase and the eutectic [BCC-(Nb, Hf) + B₁-HfCo] phases in a relatively wide range of cooling rates. Alloys with a proper Hf/Co ratio only go through the former two transformations and merely consist of the multi-phase microstructure. In addition to the initial Nb content, the Hf/Co ratio is also appropriate for potentially balancing their multi-phase microstructure. The above results obtained not only give a relatively wide range of compositions for designing of hydrogen permeable Nb-Hf-Co alloys, but also break through the conventional limits that the composition leading to the crystallization of the multi-phase microstructure for hydrogen permeable alloys merely exist in the pseudo-binary isopleth [1, 2, 7-11, 17, 31, 32].

3.3 Hydrogen permeability

Fig. 6 shows a representative relation between $J \times L$ and square-root hydrogen pressure ($\Delta P^{0.5}$) for the as-cast $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ alloy 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. A similar relation between $J \times L$ and $\Delta P^{0.5}$ appears in other alloys. Although the above relation gives a better fit, this does not indicate these alloys follow the Sieverts' law [5, 30, 42, 43]. Further information about the pressure dependence of hydrogen solubility in alloys is needed [5].

Fig. 7 shows the PCT curves for the as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys measured at 673 K. A representative case for the cast $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ is shown in Fig. 7(a), especially, the square root of hydrogen pressure is plotted against the hydrogen concentration in the form of $P^{0.5}$ vs. C (Sieverts' plot), the inset in Fig. 7(a). The PCT curves plotted in the form of $P^{0.5}$ vs. C for both alloys show straight lines between 0.1 and 0.5 MPa, so that the hydrogen content C in each alloy can be expressed as,

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

Where α is a fitting constant. Table 3 shows the values of K and α for each alloy, determined by the Sieverts' plots in Fig. 7(b). Although Sieverts' law does not hold for the present alloys, the hydrogen permeability (Φ) in the present hydrogen pressure range can still be defined by the gradient of the lines in the plot of $J \times L$ vs. $\Delta P^{0.5}$, as shown in Eq. (1). Such a method is usually used to determine Φ for other alloys such as Nb-Ti-Ni [1-6, 22, 28, 34], Nb-Ti-Co [7, 8], Nb-Hf-Ni [9-11] and Nb-Zr-Ni [23, 44] etc. Further on the basis of $\Phi = D \times K$, the value of D for each alloy can be derived, as seen in Table 3.

Fig. 8 shows Arrhenius plots of Φ for the cast as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and

Nb₃₅Hf_{32.5+x}Co_{32.5-x} (x=-2, 0, 2, 4) alloys as well as for Pd. The variations of Φ appear to be linear in the Arrhenius plot in all cases. All values of Φ evidently increase with increasing temperature. The value of hydrogen permeability for this two series of alloys is higher than that of pure Pd, especially at high temperatures. The hydrogen permeability of the Nb₄₀Hf₃₂Co₂₈ alloy at 673 K is $5.21 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$ at 673 K, which indicates that it becomes superior to that of the Nb₄₀Hf₃₀Co₃₀ previously reported to be the best in the Nb-Hf-Co alloy series [36]. The Nb₄₀Hf₃₆Co₂₄ (x = 4) is prone to embrittlement and broke during hydrogen permeation at 523 and 573 K, so that the Φ value could not be measured. At higher temperatures, this alloy exhibits higher hydrogen permeability, but inherently suffers from severe hydrogen embrittlement in a long-time test of hydrogen permeation (described later), so that it cannot practically be used as hydrogen permeation membrane. No cracks were observed after the hydrogen permeability experiment for other alloys, which suggests that they are not susceptible to hydrogen embrittlement. It can also be seen that the Φ values for each series of alloys increase with increasing Hf/Co ratio and increasing volume fraction of the primary BCC-(Nb, Hf) phase, see Tables 1 and 3. Therefore, appropriately adjusting the Hf/Co ratio can also tailor the multi-phase microstructures, thus optimizing the Φ value besides the initial Nb content.

Based on the results in Tables 1, 3 and Figs. 4, 7 and 8, a relationship of microstructures, hydrogen permeability, hydrogen solubility and hydrogen diffusivity can be built for the as-cast Nb₄₀Hf_{30+x}Co_{30-x} and Nb₃₅Hf_{32.5+x}Co_{32.5-x} (x=-2, 0, 2, 4) alloys, respectively. The hydrogen permeability of both alloys increasing with Hf/Co ratio is found to be induced by the simultaneous increase of the hydrogen solubility and diffusivity, see Table 3. The

hydrogen solubility in metals is governed mainly by the size and the electronic structure of the interstitial sites associated with the change of the interstitial binding energy [45, 46]. For the BCC-Nb, the occupation of tetrahedral sites (6 nearest neighbors) by H in Group 5 bcc lattices is favored as compared to the octahedral ones (4 nearest neighbors). Due to the larger atomic radius of Hf (159 pm) as compared to Co (125.2 pm), increasing with Hf/Co ratio will slightly increase the size of the tetrahedral interstitial sites. This may potentially increase the tolerance to expansion of the lattice for accommodating the H atom and thus the hydrogen solubility. From the view of electronic effect, the hydrogen charge and the interstitial binding energy have tightly coupled relationships. For Nb-based alloys, the stability of the site is reduced when hydrogen gains less charge.. When the neighboring niobium atoms are replaced with a similar or higher electronegativity than that of hydrogen (such as Pd), less charge is shared between the lattice and hydrogen, thereby decreasing the binding energy, which has been testified by several Aboud et al [47]. For the present alloys, the Hf (1.3) and Co (1.38) in Nb lattice have a lower electronegativity than that of hydrogen [45]. Especially, the electronegativity of Hf is much lower than that of Co. It is expected that a large Hf/Co ratio may increase the charge shared between the lattice and hydrogen and thus increase the binding energy and the solubility. In addition, it also should be noted that Nb₄₀Hf₃₄Co₂₆ alloy contains a certain amount of Hf₂Co phase, which is known to absorb hydrogen [46]. Its hydrogenation contributes partially to the high hydrogen solubility for this alloy. Maybe it is the main reason why this alloy is prone to embrittlement and broke during hydrogen permeation at 523 and 573 K in Fig. 8.

Migration of H through the Nb-based alloys is via a series of jumps between interstitial sites,

which is also related to the hydrogen content in metals [48, 49]. At dilute contents, hydrogen atoms are essentially found in the sites with the strongest binding energies. In contrast, the most favorable sites are occupied by some population of hydrogen atoms at higher contents, which allows more hydrogen atoms to stay and hop among less favored sites. In this case, the population moves far more rapidly than atoms trapped in the most favored sites, so they dominate the overall diffusion coefficient [48]. Therefore, the diffusivity of hydrogen increases markedly as the hydrogen content increases. This has been testified by a variety of experiments and first-principle calculations [50-52]. For the present $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys, increasing Hf/Co ratio induces an increase of hydrogen contents (see Fig. 7 and Table 3), which potentially leads to the increase of the hydrogen diffusivity.

3.4 The durability with respect to long-time hydrogen permeation

For hydrogen permeable membranes, the durability with respect to long-term hydrogen permeation also should be taken into account besides the high hydrogen permeability. Fig. 9 shows the hydrogen permeation flux with the time for the as-cast $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ and $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ alloy at 673 K. It can be seen that the $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ exhibits excellent durability in hydrogen permeation and the flux decreases slightly in 72 h after initial transient and reaching a maximum value. The final membrane remains totally free from cracks or pores (see the inset in Fig. 9), which was confirmed by a room temperature permeation test with Ar. This indicates that this alloy exhibits a relatively stable flux and excellent resistance to failure during long-time hydrogen permeation. In contrast, $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ are subjected to hydrogen embrittlement after hydrogen permeation of ~22 h. Membrane cracking is observed near the

edge and the middle of the membrane (see the inset in Fig. 9), which indicates that the higher hydrogen pressure on the retentate side of the membrane resulted in a higher hydrogen concentration in the membrane causes it to bow out in that direction. This is not detectable in a short-time test of hydrogen permeation, because this alloy also exhibits a stable permeability during the early 20 hours.

In a general view taking into account the microstructure, solidification path, hydrogen permeability and the durability of the as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys, we find that $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ is a promising candidate to fabricate high-performance membranes for hydrogen separation, especially compared with the Nb-Ti-Ni and Nb-Ti-Co alloys [1-8]. This alloy consists of the multi-phase microstructure (with the highest volume fraction of primary BCC-(Nb, Hf) phase and without any intermetallic Hf_2Co phase), exhibits a high hydrogen permeability of $5.21 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$ at 673 K (which is the highest value among all the currently reported ones) and excellent durability in hydrogen permeation ($\sim 72 \text{ h}$). High permeability will promote this alloy to meet the US DOE performance targets [20]. However, for other alloys such as $\text{Nb}_{40}\text{Ti}_{30}\text{Ni}_{30}$ and $\text{Nb}_{40}\text{Ti}_{30}\text{Co}_{30}$, a lower permeability will limit their potential implication in industry. Therefore, it is worthwhile to investigate the microstructure and hydrogen permeability of this alloy membrane prepared by several special methods such as melt-spinning technique, rolling followed by annealing and directional solidification which will be reported in the near future.

Finally, we emphasize the superiority and difference of this new family of metallic hydrogen permeation membranes, Nb-Hf-Co alloys, respect to the previous ones in the field [1-9, 11, 17,

22-24, 27, 28, 33, 44]. These alloys exhibit a stable permeability and also possess pronounced high hydrogen permeability. The eutectic in microstructure not only contributes much to hydrogen permeation but also plays an important role in resisting hydrogen embrittlement. This allows this alloy membrane reaching a combination of high permeability and large resistance to embrittlement by appropriately lowering the fraction of primary BCC-(Nb, Hf) and thus increasing that of the eutectic. However, for other alloys such as Nb-Hf-Ni [11], Nb-Zr-Ni [44] and V-Ti-Ni [17] etc, a high permeability leads to a low fraction of eutectic in microstructure which sacrifices the ability of embrittlement resistance. For example, Nb₄₀Zr₃₀Ni₃₀ alloy exhibit a high permeability of $2.9 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-0.5}$ at 673 K, and the permeability of this alloy mainly depends on the volume fraction of primary bcc-Nb (~40 Vol. %), as seen in Table 4. The contribution to hydrogen permeation from the eutectic is low [44]. Therefore, a high fraction of primary BCC-Nb is required for high permeability of this alloy, but this may result in a low tolerance regarding hydrogen embrittlement due to a low fraction of the eutectic. It is not easy to balance both properties. This kind of dilemma also appears in other alloys as Nb₄₀Hf₃₀Ni₃₀ [11], V₄₀Ti₃₀Ni₃₀ [17] etc. In comparison, although containing a low fraction of primary BCC-Nb (~20 Vol. %), Nb₄₀Hf₃₀Co₃₀ exhibits a higher permeability among these alloys. Simultaneously, the high fraction of eutectic (~80 Vol. %) ensures its high tolerance to hydrogen embrittlement [36]. Similar laws are also were observed in other Nb-Hf-Co alloys such as Nb₄₀Hf₃₂Co₂₈. Therefore, this alloy series not only clearly reaches an excellent balance among microstructure, hydrogen permeability and embrittlement resistance, but also achieves a sound combination of high hydrogen permeability, excellent resistance against hydrogen embrittlement and excellent durability in

hydrogen permeation.

4. Conclusions

The effect of Hf/Co ratio on microstructure, solidification path and hydrogen permeability of as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys is investigated by SEM, XRD, PCT and gas-permeation measurements. It has shown that increasing with Hf/Co ratio in these two series of alloys increases hydrogen solubility and diffusivity and thus hydrogen permeability, but greater hydrogen solubility brings the penalty of poorer resistance against hydrogen embrittlement. Increase of Hf/Co ratio also induces higher fraction of primary BCC-(Nb, Hf) and brittle intermetallic Hf_2Co phase. $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ alloy with an initial Hf/Co ratio of $c_{\text{Hf}}/c_{\text{Co}}=8:7$ clearly reaches an excellent balance among microstructure, hydrogen permeability and embrittlement resistance. This alloy consists of the multi-phase microstructure (with the highest fraction of primary BCC-(Nb, Hf) phase and without any intermetallic Hf_2Co phase), exhibits a high hydrogen permeability of $5.21 \times 10^{-8} \text{ mol H}_2 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1/2}$ at 673 K (which is the highest value among all the currently reported ones) and excellent durability in hydrogen permeation ($\sim 72 \text{ h}$), which is a promising candidate to fabricate high-performance membranes for hydrogen separation.

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Fig. 1 Schematic of planar membrane testing module. The membrane discs are 12 mm in diameter.

Fig. 2 XRD patterns of the as-cast $Nb_{40}Hf_{30+x}Co_{30-x}$ alloys ($x=-2, 0, 2, 4$).

Fig. 3 XRD patterns of the as-cast $Nb_{35}Hf_{32.5+x}Co_{32.5-x}$ alloys ($x=-2, 0, 2, 4$).

Fig. 4 SEM images of the as-cast alloys of (a) $\text{Nb}_{40}\text{Hf}_{28}\text{Co}_{32}$, (b) $\text{Nb}_{40}\text{Hf}_{30}\text{Co}_{30}$, (c) $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$, (d) $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$, (e) $\text{Nb}_{35}\text{Hf}_{30.5}\text{Co}_{34.5}$, (f) $\text{Nb}_{35}\text{Hf}_{32.5}\text{Co}_{32.5}$, (g) $\text{Nb}_{35}\text{Hf}_{34.5}\text{Co}_{30.5}$ and (h) $\text{Nb}_{35}\text{Hf}_{36.5}\text{Co}_{28.5}$.

Fig. 5 Calculated solidification paths for the as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys in the primary BCC-(Nb, Hf) phase region: (a) solidification paths for each alloy, (b)-(c) solid volume fractions as a function of temperature (T) for each alloy. The short dash line represents the solidification paths for $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ alloy under the cooling rate of 300 K/s.

Fig. 6 Representative relation between $(J \times L)$ and $\Delta P^{0.5}$ for the as-cast $\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$ alloy in the temperature range of 523-673K.

Fig. 7 The pressure-composition-temperature (PCT) curves for the as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys measured at 673 K. (a) A representative case for the cast $\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$ alloy (the inset: a Sieverts' plot, i.e., $P^{0.5}$ vs. hydrogen composition C , between 0.1 and 0.5 MPa). (b) The Sieverts' plot for each alloy between 0.1 and 0.5 MPa.

Fig. 8 Temperature dependence of hydrogen permeability Φ for the as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys in the form of an Arrhenius plot.

Fig. 9 Variations of hydrogen permeability flux with time in 72 h for the as-cast Nb₄₀Hf₃₄Co₂₆ and Nb₄₀Hf₃₂Co₂₈ alloys at 673 K. Inset: the samples sandwiched between two copper seal gaskets after the hydrogen permeation test.

Table 1 Summary of constituting phases, the compositions (mol %) and volume fraction (%) of the primary and binary eutectic phases in the as-cast $\text{Nb}_{40}\text{Hf}_{30+x}\text{Co}_{30-x}$ and $\text{Nb}_{35}\text{Hf}_{32.5+x}\text{Co}_{32.5-x}$ ($x=-2, 0, 2, 4$) alloys.

Number	Samples	x value	Chemical Composition of the constituting phases (mol %)						Volume fraction of the constituting phases (%)	
			Primary BCC-(Nb, Hf) phase			{BCC-(Nb,Hf) +NiTi} phase			Primary BCC phase	Binary eutectic
			Nb	Hf	Co	Nb	Hf	Co		
#1	$\text{Nb}_{40}\text{Hf}_{28}\text{Co}_{32}$	-2	83.4	12.2	4.4	30	34.2	35.8	5.2	94.8
#2	$\text{Nb}_{40}\text{Hf}_{30}\text{Co}_{30}$	0	83.3	12.6	4.1	29.8	34.8	35.4	23.4	76.6
#3	$\text{Nb}_{40}\text{Hf}_{32}\text{Co}_{28}$	2	83.0	13.3	3.7	29.7	35.1	35.2	25.0	75.0
#4	$\text{Nb}_{40}\text{Hf}_{34}\text{Co}_{26}$	4	82.7	13.9	3.4	29.6	35.4	35.0	28.6	70.1
#5	$\text{Nb}_{35}\text{Hf}_{30.5}\text{Co}_{34.5}$	-2	81.8	13.4	4.8	29.4	34.8	35.8	2.3	97.7
#6	$\text{Nb}_{35}\text{Hf}_{32.5}\text{Co}_{32.5}$	0	81.4	13.9	4.7	29.3	35.1	35.6	10.1	89.9
#7	$\text{Nb}_{35}\text{Hf}_{34.5}\text{Co}_{30.5}$	2	81.1	14.6	4.3	29.4	35.3	35.3	12.9	87.1
#8	$\text{Nb}_{35}\text{Hf}_{36.5}\text{Co}_{28.5}$	4	80.2	15.8	4.0	29.3	35.6	35.1	19.1	80.9

Table 2 The physical and thermodynamic data used in the present calculations of solidification paths

Parameters	Values	Literature
Solidification shrinkage	0.043	[12]
The distance of secondary dendrite (μm)	0.1	Calculated
Nb–Hf–Co	$D_{\text{Co}}^a (\text{mm}^2 \text{s}^{-1})$	$18 \exp(-15000/T)$ [7, 8, 32]
	$D_{\text{Hf}}^a (\text{mm}^2 \text{s}^{-1})$	$28 \exp(-12000/T)$ [7, 8, 32]
Solidification/cooling rates $R_f (\text{s}^{-1})$	0.1 or 300	Calculated
Step length of α (Δf_s)	0.0025	Initial value
Step length of binary eutectic ΔT ($^{\circ}\text{C}$)	0.25	Initial value

Table 3 Hydrogen permeability (Φ), hydrogen solubility coefficient (K), hydrogen diffusion coefficient (D) and fitting parameter (α) at 673 K for the as-cast Nb₄₀Hf_{30+x}Co_{30-x} and Nb₃₅Hf_{32.5+x}Co_{32.5-x} (x=-2, 0, 2, 4) alloys.

Number	Samples	x value	Φ [mol H ₂ m ⁻¹ s ⁻¹ Pa ^{-0.5}]	K [mol H ₂ m ⁻³ Pa ^{-0.5}]	D [10 ⁻¹⁰ m ² s ⁻¹]	α [mol H ₂ m ⁻³]
#1	Nb ₄₀ Hf ₂₈ Co ₃₂	-2	3.91×10 ⁻⁸	29.64	13.19	5629
#2	Nb ₄₀ Hf ₃₀ Co ₃₀	0	4.96×10 ⁻⁸	31.75	15.62	5749
#3	Nb ₄₀ Hf ₃₂ Co ₂₈	2	5.21×10 ⁻⁸	32.33	16.11	6213
#4	Nb ₄₀ Hf ₃₄ Co ₂₆	4	5.52×10 ⁻⁸	33.12	16.66	6425
#5	Nb ₃₅ Hf _{30.5} Co _{34.5}	-2	3.58×10 ⁻⁸	29.07	12.31	2417
#6	Nb ₃₅ Hf _{32.5} Co _{32.5}	0	4.02×10 ⁻⁸	30.13	13.34	3283
#7	Nb ₃₅ Hf _{34.5} Co _{30.5}	2	4.31×10 ⁻⁸	30.87	13.92	3795
#8	Nb ₃₅ Hf _{36.5} Co _{28.5}	4	4.65×10 ⁻⁸	31.23	14.88	4561

Table 4 Hydrogen permeability along with the volume fractions of primary phase and eutectic and the tolerance to hydrogen embrittlement for some representative alloys, obtained from the research group of K. Aoki.

Alloys	Volume fraction (Vol.%)		Hydrogen permeability (Φ) at 673 K ($10^{-8}\text{mol H}_2\text{ m}^{-1}\text{ s}^{-1}\text{ Pa}^{-0.5}$)	Tolerance to hydrogen embrittlement
	Primary BCC-Nb phase	Binary eutectic		
Nb ₄₀ Ti ₃₀ Ni ₃₀ ^[1]	29	71	1.8	High
V ₄₀ Ti ₃₀ Ni ₃₀ ^[17]	40	60	1.1	Low
Nb ₄₀ Ti ₃₀ Co ₃₀ ^[8]	25	75	1.99	High
Nb ₄₀ Hf ₃₀ Ni ₃₀ ^[11]	40	60	4.3	Low
Nb ₄₀ Zr ₃₀ Ni ₃₀ ^[44]	40	60	4.64	Low
Nb ₄₀ Hf ₃₀ Co ₃₀ ^[36]	23	77	4.96	High