Effect of partial Ni substitution in V₈₅Ni₁₅ by Ti on microstructure, mechanical properties and hydrogen permeability of V-based BCC alloy membranes

Peng Jiang¹,²,⁵, Bolin Sun¹, Haichuan Wang³, Guosheng Peng¹, Yangzhou Ma¹, Guangsheng Song¹,⁵ and Michael Dolan⁴

¹ School of Materials Science and Engineering, Anhui University of Technology, Maanshan 243002, People’s Republic of China
² School of Mechanical Engineering, Changzhou University, Changzhou 213164, People’s Republic of China
³ School of Metallurgical Engineering, Anhui University of Technology, Maanshan 243002, People’s Republic of China
⁴ CSIRO, Energy, Queensland Centre for Advanced Technologies, 1 Technology Court, Pullenvale, QLD 4069, Australia
⁵ Authors to whom any correspondence should be addressed.

E-mail: penn.jiang@gmail.com and song_ahut@163.com

Keywords: vanadium-nickel-titanium, alloy elements, alloy membranes, microstructures, hydrogen permeability, mechanical properties

Abstract
Vanadium-based alloy membranes with body-centred-cubic (BCC) structure are considered as one of the leading alternatives to Pd-based alloys for hydrogen separation applications due to their lower cost and higher permeability. As permeability and mechanical properties depend on what microstructure can be produced mainly by alloy composition under same processing conditions, the effect of alloy composition on microstructure, mechanical properties and hydrogen permeability has been investigated for the V₈₅Ni₁₅ and V₈₅Ni₁₀Ti₅ (at%) alloys prepared by a same process route. All Ni atoms dissolve into the V-matrix to form a single highly supersaturated solid solution with dendritic segregation of Ni-solute atoms in the binary alloy. A part of Ni replacement with 5 at% Ti leads to the formation of small interdendritic phases NiTi and NiTi₂ in addition to major phase of V-based solid solution. The mechanical property testing shows that the ultimate strength of the ternary alloy is higher than that of the binary alloy, but the elongation and rollability are lower due to a combination of solid solution hardening and particle strengthening effect. The addition of Ti can greatly increase permeability about 4 times greater than the binary alloy at a permeation testing of 400 °C. But the presence of small amounts of interdendritic compounds provides a barrier to hydrogen migration, resulting in a relatively lower hydrogen diffusion coefficient. In theory, the diffusivity and solubility of hydrogen atom in the presence of alloying element Ti is higher than that in the presence of alloying element Ni in vanadium. This is demonstrated using first principles calculation which further explains the mechanism of hydrogen permeation.

1. Introduction
As a non-renewable energy, the utilization of fossil fuel energy produces a lot of pollution gases, which affects the air quality and people’s health. Hydrogen energy is considered to be one of the most important new energy sources in the future due to its renewability and environmental friendliness. Hydrogen will be required much in the near future, especial ultra-high purity hydrogen, which mainly used in semiconductor and fuel cell industries [1]. The production and purification of H₂ is an important link of its application in industrial production [2–5]. Membrane separation of H₂ is considered as one of the most promising separation technologies because of its low cost and energy consumption, and high purity of separated H₂ [6–8]. The commercial application of Pd-Ag alloy membranes in the field of H₂ separation was realized in 1960s, but its large-scale application in membrane separation was limited due to the scarcity and price of Pd. For non-palladium based alloy membranes, the permeability of VB group metals (V, Nb and Ta, etc) with BCC structure
is 20–100 times higher than that of FCC structure metals (Pd, Cu and Ni, etc) [9]. However, H transport through pure V, Nb and Ta metals leads to lattice expansion and hydride formation due to high H solubility in V, Nb and Ta metals, resulting in hydrogen embrittlement. Allying is one of the most effective methods to solve hydrogen embrittlement [10–15].

V-based solid solutions (Vss) with BCC structure can be formed with a wide range of alloy elements [16]. The addition of Nickel to Vanadium has been reported to increase resistance to embrittlement and maintain a higher permeability than commercially available Pd-Ag alloy membranes [17]. This finding makes V-Ni alloys highly attractive for membrane applications. Of these alloys, a composition of V85Ni15 (at%) has been proposed as a promising candidate for hydrogen separation membranes. Partial substitution of Ni by Ti can result in a multi-phase microstructure. A new alloy V85Ni10Ti5 (at %) has been reported to be ~4 times greater than V85Ni15 in hydrogen permeability at 400 °C [16]. This ternary alloy consisted of a primary BCC V-rich solid solution and small amount of secondary phase particles as evidenced by SEM. Unfortunately, the identification of secondary phase has not been determined since then. In the present work, we used EBSD Kikuchi patterns and micro-XRD to determine the types of all secondary-phase compounds in the V-matrix interdendritic region, and also established a relationship of the multi-phase microstructure with mechanical properties for the development of high-strength alloy membranes. In order to investigate the rollability of thinner sheet alloy membrane fabrication, cold rolling was carried out on these two alloys to allow a higher hydrogen flux. In addition, based on the permeability and solubility data obtained, and combined with the first principle calculation, we gain an insight into the understanding of the effect of Ti which is opposite to Ni on the solubility and diffusivity of hydrogen in vanadium. This is very helpful to design a new composition in the V-Ni-Ti ternary system for the development of both high-permeability and high embrittlement-resistant alloy membranes.

2. Experimental procedure

2.1. Alloy preparation

The V85Ni15 and V85Ni10Ti5 (at%, nominal composition) samples were made from high purity (99.9%) Vanadium, Nickel and Titanium metals. Vanadium, Nickel and Titanium pellets were mixed and melted on a water-cooled copper hearth using a vacuum/argon arc melter. The melting chamber was evacuated and then filled to ensure the ingots not to be oxidized. In order to ensure compositional homogeneity, the arc-melted (AM) ingots (total weight 60 g for each) were melted several times.

2.2. Hardness and tensile testing, and rolling

The samples for testing properties and observing microstructures were cut using electrical discharge machining (EDM) from the arc-melted ingots. Vickers hardness of both samples were measured using a digital micro-hardness tester with loads of 500 g and a dwell time of 10 s. The final micro-hardness was the average value of 10 measurements performed on the samples surface. The samples surfaces for measurement were ground and then polished using diamond pastes, followed by etching in solution containing HF and HNO3. Tensile specimens were sectioned from the arc-melted ingots with gauge length of 10 mm, width of 2 mm and thickness of 1.5 mm. Tensile tests were carried out on a tensile machine at the room temperature and constant speed of 0.01 mm s−1.

Rolling process was carried out on a 120-mm diameter rolling mill with a roller speed of 0.1 ms−1 at the room temperature. The initial thickness of the samples is 1.5 mm. Ultimate reduction rate of the first pass rolling (rup) was used to evaluate the rollability of V85Ni15 and V85Ni10Ti5 alloys. The maximum reduction of the first pass rolling was measured using the method referring to [18]. The ultimate reduction rate of the first pass rolling (rup) is defined as follows.

\[
  r_{up} = \frac{t_0 - t}{t_0}
\]  

where \( t_0 \) and \( t \) are the thickness of the AM sample and the rolled sample with the maximum reduction of the first pass rolling, respectively.

2.3. Microstructural analysis

The microstructures of the alloy samples were observed in back-scattered electron (BSE) mode using a Quanta 400 field emission gun scanning electron micro-scope (FEG-SEM) equipped with x-ray Energy Dispersive Spectroscopy (EDS). Secondary electron (SE) imaging mode in the SEM was also employed for fracture surface morphology observation. A JEOL 8500F electron microprobe was employed for quantitative composition microanalysis of different areas both in V85Ni15 and V85Ni10Ti5 alloys. The intensity measurements were conducted at 12 kV accelerating voltage and a beam current of 30 nA.
X-ray diffraction (XRD) patterns were obtained by a Bruker D8 Advance x-ray Diffractometer employing CuKα radiation (40 kV, 40 mA) and a graphite (002) monochromator. The samples were scanned over the 2-theta range 30° to 100° with a step size of 0.02° and a count time of 4 s per step. Bruker XRD search match program EVA was used to analyze the collected XRD data. Crystalline phases were identified from the powder diffraction database (ICDD-JCPDS). For lattice parameter measurements, the Quartz (SiO2) was used as an external standard for the XRD instrument alignment. The whole diffraction patterns corresponding to the V-phase solid solution were fitted using the Bruker TOPAS software to obtain the lattice parameters.

Minor phases in V85Ni10Ti5 alloy which levels are below the detection limit of bulk XRD were identified by Micro-XRD. The Micro-XRD patterns were obtained using a Bruker General Area Detection Diffraction (GADDS) x-ray micro-diffractometer equipped with a HiStar area detector, CuKα radiation (40 kV, 40 mA), and cross-coupled Goebel monochromating mirrors. A pinhole collimator was employed to collimate the x-ray beam to a 300 μm spot with a count time of 300 s. Position-sensitive proportional counter (PSPC) was used to collect two-dimensional intensity patterns which were converted to conventional XRD patterns.

The presence of minor phases in V85Ni10Ti5 alloy was confirmed by electron back-scatter diffraction (EBSD) technique. A JEOL 7001F FEG-SEM was used to collect Kikuchi patterns under specimen inclination of 70° and operating at 20 kV. Oxford Instruments Channel 5 HKL software was employed to index the acquired EBSD patterns for phase determination.

2.4. Permeation and solubility testing
A constant pressure method reported elsewhere [16] was used to measure hydrogen permeability of the samples. Both sides of the samples for the testing were chemically cleaned and radio frequency (RF) sputtered with a Pd layer of 500 nm to promote H2 dissociation. The samples were sealed in a custom—designed apparatus using circular copper gaskets (internal diameter of 16 mm). The feed-side was supplied with a mixture of 90% H2 + 10% CO2 at a pressure of 4.0 bar (a) and 200 ml min⁻¹ during hydrogen permeation testing. The permeate side was supplied with argon stream at 200 ml min⁻¹. The hydrogen concentration in the Ar stream was determined using a gas chromatograph, and hydrogen flux across the membrane was calculated from this resulting concentration. Detection of CO2 in the permeate stream was confirmed the integrity of the membrane. Permeability was calculated as the gradient of hydrogen flux against (P₁⁰.⁵ − P₂⁰.⁵), where P₁ and P₂ are the feed-side pressure and permeate-side pressure, respectively.

The hydrogen uptake of two alloys with varying hydrogen pressure at 400 °C and up to 12 bar (a) was measured by the Sieverts’ technology to determine solubility. Only the data of the increasing pressure cycle is showed due to little difference between the increasing and decreasing pressure cycles.

3. Results and discussion
3.1. Microstructure
The BSE-SEM images of the microstructures of arc-melted V85Ni15 and V85Ni10Ti5 alloys were showed in figure 1. Coarse grains were observed and no secondary phase was present in the arc-melted V85Ni15 alloy (as shown in figure 1(a)). Combined with the XRD results (figure 2), it is clear that the arc-melted V85Ni15 alloy is a single-phase Vanadium-based solid solution (Vss). It should be noted that dendritic segregation of Ni-solute atoms in Vss of the arc-melted V85Ni15 alloy has been observed, suggesting compositional inhomogeneity of elemental Ni distribution. It can be seen from the V-Ni phase diagram in figure 3 [19], the maximum solubility
of Ni in the vanadium solid solution is 24 at% at peritectic temperature of 1280 °C and shows a pronounced temperature dependence decreasing to 10 at% at peritectoid temperature of 900 °C and around 2 at% at 200 °C. For a given composition of 15 at% Ni located between 10 and 24 at%, the resulting equilibrium microstructure should be a two-phase mixture of Vss and NiV3 compound below the peritectoid temperature. However, the arc-melting process belongs to non-equilibrium rapid solidification, and thus prevents the kinetically slow precipitation of NiV3 compound due to rapid cooling, forming a highly supersaturated solid solution with dendritic segregation of Ni-solute atoms.

Substitution of Ni by 5 at% Ti can result in a multi-phase microstructure. As shown in figure 1(b), primary Vss phase in the as-cast V85Ni10Ti5 alloy has a dendritic microstructural feature with small amounts of secondary phases formed in the interdendritic regions. Pores at the grain boundaries and between dendrites were formed by irregular shrinkage during solidification of the alloy, but these are discontinuous and do not result in leakage of gases across the alloy membrane. The presence of minor secondary phases in the interdendritic regions was not detected by the conventional XRD instrumentation which provides bulky information about the structure of crystalline materials (see figure 2). However, the micro-XRD patterns detected from three different spots by the position-sensitive proportional counter reveals the presence of NiTi2
compound in the cast V\textsubscript{85}Ni\textsubscript{10}Ti\textsubscript{5} alloy (as shown in figure 4). Actually, there are two types of intermetallic compounds as shown in the higher magnification SEM microstructure (figure 5(a)). It can be seen in more details that the interdendritic region mainly consisted of white-phase and dark-phase compounds in addition to primary V-rich BCC solid solution. The EDS was used in semi-quantitative mode to determine chemical composition of these phases observed in the SEM microstructure, as shown in figure 6. The energy peaks correspond to the various elements in the three phases, and their peak intensity indicate that the white-phase compound contains more Ni and Ti, whereas the dark-phase particles is a Ti-rich intermetallic compound. The EDS results are correlated with the crystallographic structure of each of three phases measured by electron
backscatter diffraction. The experimental EBSD patterns obtained from the V-matrix, white-phase and dark-phase compounds were reliably indexed as Vanadium solid solution, NiTi and NiTi2, respectively, as shown in figures 5(b)–(d).

The electron probe microanalysis was carried quantitatively on both V85Ni15 and V85Ni10Ti5 alloys and the compositional data together with phase structure information are listed in table 1. It shows that the addition of Ti reduces the Ni content in the Vss, while more than half of Ti is retained in the Vss. The presence of this part of Ti in the V solid solution resulted in the expansion of the Vss lattice in comparison with the V85Ni15 lattice constant (table 1). The Ti-induced lattice expansion can be explained by large atomic size difference between the solutes Ni (0.1246 nm)/Ti (0.1462 nm) and solvent V (0.1316 nm) [20].

3.2. Mechanical properties

3.2.1. Vickers hardness
Table 2 compares the hardness from bulk (500 g load) and Vss (100 g load) in the V85Ni15 and V85Ni10Ti5 alloys, bulk hardness is equal to Vss hardness of single-phase V85Ni15 alloy. The bulk and Vss hardness of V85Ni15 alloy are lower than that of V85Ni10Ti5 alloy, and Vss hardness of V85Ni10Ti5 alloy is lower than that of the bulk. Atomic size difference between Ti and V is twice larger than that between Ni and V, Ti addition generates more distortion of the Vss lattice, resulting in a higher Vss hardness of V85Ni10Ti5 alloy than that of V85Ni15 alloy. The bulk hardness of V85Ni10Ti5 alloy is higher than Vss hardness due to hard and brittle NiTi2 phases. The difference of the bulk and Vss hardness of V85Ni10Ti5 alloy is small, which suggests that the Vss is a major factor controlling the change in hardness.

3.2.2. Tensile properties
The ultimate strength and elongation of V85Ni15 and V85Ni10Ti5 alloys obtained are shown in table 3. From table 3, it can be seen that the ultimate strength of V85Ni10Ti5 alloy is higher than that of V85Ni15 alloy, but the elongation is lower. It should be noticed that the elongations of both alloys are lower than 15%, which refer to supersaturated solid solution of Vss due to rapid cooling. The fracture surfaces of the specimens are shown in figure 7. As can be seen, a number of uneven size dimples appear on the fracture of V85Ni15 alloy (figure 7(a)) and local areas with no dimple are relatively smooth, while the fracture of V85Ni10Ti5 alloy (figure 7(b)) is rough and a number of extremely shallow dimples were observed, which is consistent with poor plastic (low elongation). High hardness Vss and hard-brittle NiTi2 in V85Ni10Ti5 alloy are predominant factor controlling the tensile properties.

3.3. Rollability
Table 4 shows the comparison of ultimate reduction rate of the first pass rolling (rup) for V85Ni15 and V85Ni10Ti5 alloys at room temperature. It can be noted that the rollability of single-phase V85Ni15 alloy is higher than that of multiphase V85Ni10Ti5 alloy, and the rup increases about 21%. The Vss and NiTi2 phases in the V85Ni10Ti5 alloy make the alloy has high hardness and low plastic. The interface between the Vss and NiTi2 phase in V85Ni10Ti5 alloy is difficult to coordinate for deformation during rolling, and therefore the stress concentration occurs easily at the interface after dislocations movement is obstructed, resulting in forming of the cracks.
Table 1. Chemical and structural characteristics of the arc-melted V$_{85}$Ni$_{15}$ and V$_{85}$Ni$_{10}$Ti$_{5}$ alloys.

| Nominal composition (atom%) | Measured Vss composition (atom%) | Vss Space group | Vss Lattice parameters (Å) | Phases present |
|-----------------------------|----------------------------------|-----------------|-----------------------------|----------------|
| V$_{85}$Ni$_{15}$           | V$_{85.0}$Ni$_{15.0}$            | Im3m (229)      | a: 3.0051 ± 0.018           | V$_{ss}$       |
| V$_{85}$Ni$_{10}$Ti$_{5}$   | V$_{92.1}$Ni$_{5.1}$Ti$_{2.8}$   | Im3m (229)      | a: 3.0091 ± 0.023           | V$_{ss}$, NiTi, NiTi$_2$ |
3.4. Hydrogen permeability, hydrogen absorption and diffusion coefficients

The hydrogen permeability data of the V85Ni15 and V85Ni10Ti5 alloys between 300 and 400 °C are listed in Table 5. The V85Ni10Ti5 alloy exhibited higher permeability than V85Ni15 alloy in the temperature range. From the view of alloying element effect, with a permeability of \( \sim 2 \times 10^{-7} \text{ mol m}^{-1}\text{s}^{-1}\text{Pa}^{-0.5} \) of pure V at 400 °C [21], the addition of 15 at% Ni into V reduces the permeability to \( 2.60 \times 10^{-8} \) [16], while the substitution of partial Ni by 5 at% Ti increases this value to \( 9.30 \times 10^{-8} \). The role of Ti in increasing the permeability of V is clearly demonstrated by contrast with the role of Ni.

The hydrogen permeability of multiphase V-Ni-Ti alloys with a higher proportion of intermetallic compounds in compositions have been examined previously by other groups [14], and the microstructure of the alloys consist of discrete BCC phases within the Ni-Ti compounds which greatly affected the hydrogen permeation. Large amounts of Ni-Ti compounds are the barriers to H migration. In contrast, our V85Ni10Ti5 alloy contains a large amount of BCC matrix as a major phase (see figure 1(b)) for hydrogen diffusion and thus the hydrogen permeability of this alloy is vastly greater than that reported in [14]. That is to say the BCC V-rich phase is a predominant factor controlling the hydrogen permeability.

### Table 2. Microhardness of bulk and Vss for V85Ni15 and V85Ni10Ti5 alloys.

| Alloy       | Vickers hardness |
|-------------|-----------------|
| V85Ni15     | 319 ± 4         |
| V85Ni10Ti5  | 407 ± 6         |

### Table 3. The tensile properties of V85Ni15 and V85Ni10Ti5 alloys.

| Alloy       | Ultimate strength/MPa | Elongation/% |
|-------------|------------------------|--------------|
| V85Ni15     | 167                    | 11.7         |
| V85Ni10Ti5  | 185                    | 8.1          |

### Table 4. Ultimate reduction rate of the first pass rolling (\( r_{up} \)) for V85Ni15 and V85Ni10Ti5 alloys at room temperature.

| Alloy       | \( r_{up} \)     |
|-------------|------------------|
| V85Ni15     | 45.83%           |
| V85Ni10Ti5  | 37.76%           |

Figure 7. SEM fracture surface analysis of the tensile samples for (a) V85Ni15 and (b) V85Ni10Ti5 alloys.
The relationship of hydrogen solubility (expressed as \( \frac{H}{M} \)) with pressure for pure V, V\(_{85}\)Ni\(_{15}\) and V\(_{85}\)Ni\(_{10}\)Ti\(_5\) alloys at 400 °C was established as displayed in Figure 8. It is clearly shown that alloying V with Ni significantly reduced the hydrogen solubility, while Ti increased the hydrogen solubility in the alloy. The diffusion coefficients for H through pure V, V\(_{85}\)Ni\(_{15}\) and V\(_{85}\)Ni\(_{10}\)Ti\(_5\) alloys at 400 °C were calculated by combining the permeability and solubility data, and listed in Table 6 for comparison. Pure V displayed the highest hydrogen diffusion coefficient (\( 1.20 \times 10^{-8} \) at 400 °C). The addition of 15at% Ni reduces this value to \( 0.96 \times 10^{-8} \). The addition of the third element Ti further reduces the diffusion coefficient to \( 0.67 \times 10^{-8} \).

The intrinsic permeability of the alloy involves both hydrogen solubility and diffusivity. Since \( P = SD \), where \( P \), \( S \) and \( D \) are permeability, solubility coefficient and diffusion coefficient, respectively, high permeability can be reached by increasing either solubility or diffusion. In order to better understand the effect of alloying elements with different atomic size on solubility and diffusion of hydrogen in the V-matrix solid solution, the obtained data about the solution energy (\( E_{\text{sol}} \)) and diffusion energy barrier (\( E_a \)) of hydrogen in pure V, V-Ni and V-Ti using the first-principle calculation [22] were used as a measure of the ease of solubility and diffusion (see Table 7). The more negative \( E_{\text{sol}} \) means more H dissolution into the V-matrix solid solution, and is favorable to reach a higher H solubility. The solution energy of H in pure V was calculated to be \( -0.218 \) eV, whereas the presence of Ni in V increased the hydrogen solution energy to a value of \( -0.107 \) eV, which is about 2 times greater than that of H in pure V, making the hydrogen dissolution more difficult. For the V-Ti system alloy, the hydrogen solution energy (\( -0.294 \) eV) is lower than that of H in pure V. The more negative value indicates that

| Table 5. Permeability of V\(_{85}\)Ni\(_{15}\) and V\(_{85}\)Ni\(_{10}\)Ti\(_5\) alloys between 300 and 400 °C. |
|-----------------------------------------------|
| Temperature/°C | \( V \) [21] | \( V_{85}\)Ni\(_{15}\) | \( V_{85}\)Ni\(_{10}\)Ti\(_5\) |
|----------------|--------------|----------------|----------------|
| 300            | —            | \( 2.09 \times 10^{-8} \) | —              |
| 350            | —            | \( 2.44 \times 10^{-8} \) | \( 8.38 \times 10^{-8} \) |
| 400            | \( \sim 2 \times 10^{-7} \) | \( 2.60 \times 10^{-8} \) | \( 9.30 \times 10^{-8} \) |

Figure 8. Hydrogen solubility (expressed as \( \frac{H}{M} \)) of pure V, V\(_{85}\)Ni\(_{15}\) and V\(_{85}\)Ni\(_{10}\)Ti\(_5\) alloys [16].

| Table 6. Calculated diffusion coefficients of H though pure V, V\(_{85}\)Ni\(_{15}\) and V\(_{85}\)Ni\(_{10}\)Ti\(_5\) alloys [16]. |
|---------------------------------------------------------------|
| Nominal composition (at%) | \( D_H \) (m \( s^{-2} \)) 400 °C, 4.0 bar |
|--------------------------|------------------------------------------|
| \( V \)                  | \( (1.20 \pm 0.10) \times 10^{-8} \)     |
| \( V_{85}\)Ni\(_{15}\)    | \( (0.96 \pm 0.10) \times 10^{-8} \)     |
| \( V_{85}\)Ni\(_{10}\)Ti\(_5\) | \( (0.67 \pm 0.10) \times 10^{-8} \)     |
the presence of Ti in V increases more hydrogen absorption than pure V. We had a composition of Ti greater than 30 at% at which the hydrogen solubility of the V-Ti alloy exceeded pure V. However, considering that the primary BCC phase in the V85Ni10Ti5 alloy is the V-Ni-Ti solid solution (V92.1Ni5.1Ti2.8), the co-presence of small amounts of Ti content (2.8 at%) and highly reduced Ni content (5.1 at%) undoubtedly results in a larger increase in hydrogen absorption than the V85Ni15, but is not enough to surpass pure V. Overall, the hydrogen solubility behavior of the V85Ni10Ti5 alloy can be better understood based on the fact that alloying elements Ti and Ni have different levels of solution energy of hydrogen in V.

According to the calculated diffusion energy barrier data, the Eₐ value of H in V-Ni alloy is higher than that of H in pure V, which suggests that the diffusion rate of hydrogen through the V-Ni (Ni-induced V lattice contraction) is slower than through pure V. This theoretical calculation is consistent with the experimental results obtained from pure V and V85Ni15 alloy. Compared to pure V and V-Ni, the V-Ti alloy has a relatively lower Eₐ value of hydrogen. This means the presence of Ti in V increases hydrogen transport through the V-Ti solid solution with larger lattice constant than pure V. The dissolution of Ti into the host V85Ni15 BCC alloy would therefore be expected to obtain a higher diffusion coefficient of hydrogen through the major V-Ni-Ti solid solution (V92.1Ni5.1Ti2.8) phase in the V85Ni10Ti5 alloy than through the V85Ni15 alloy. In fact, our result is conflict with the expectation. This should be attributed to the formation of non-BCC hydrogen diffusion phases such as NiTi and NiTi₂ compounds in the multi-phase microstructure. These compounds act as barriers to inhibit hydrogen transport, resulting in the reduction of hydrogen diffusion coefficient through the bulk alloy. Further work needs to entirely make the BCC single-phase alloy of the V92.1Ni5.1Ti2.8 composition in order to verify the first-principle calculation of the V-Ni-Ti ternary BCC structure.

The solubility and diffusion coefficient of hydrogen are both necessary to increase in order to increase the hydrogen permeability through a given alloy membrane. However, excessive hydrogen solubility will lead to hydrogen embrittlement and make the degradation of mechanical properties [23]. As increasing diffusivity does not induce a mechanical penalty, therefore, it is desirable to develop an alloy with large D and low H/M. Our results showed that although partial substitution of Ni with 5 at% Ti increased permeability mainly due to increasing the hydrogen solubility in the alloy, the diffusion coefficient value is higher than that of Pd (∼0.55 × 10⁻⁸ m² s⁻¹ at 400 °C [24]). In order to better develop the promising vanadium alloys for H₂ selective membrane application, further work to maximizing hydrogen diffusivity needs to construct a multi-component model against the experimental results using the first-principle calculation. This type modelling would help us to understand how two or more alloying elements together exert a synergistic effect on solubility and diffusion behavior of hydrogen in the multi-component BCC alloys.

4. Conclusion

The effect of alloying elements Ni and Ti on microstructure, mechanical properties and hydrogen permeability has been investigated for both V₈₅Ni₁₅ and V₈₅Ni₁₀Ti₅ alloys prepared by the same process route. The conclusions can be drawn as follows:

1. All Ni atoms dissolve into the V-matrix to form a single highly supersaturated BCC solid solution with dendritic segregation of Ni-solute atoms in V₈₅Ni₁₅ alloy. The addition of Ti into the base V₈₅Ni₁₅ alloy results in the formation of multi-phase microstructure consisting of primary BCC V-matrix solid solution and small amounts of intermetallic compounds. These compounds are visualised and identified as NiTi and NiTi₂ using EBSD technique providing simultaneous information of crystal structure and chemical composition for excellent phase identification.

2. The mechanical property testing shows that the ultimate strength of the V₈₅Ni₁₀Ti₅ alloy is higher than that of the V₈₅Ni₁₅ alloy, but the elongation and rollability are lower due to a combination of solid solution hardening and particle strengthening effect. The ultimate reduction rate of the first pass rolling (τₑₙ) for both V₈₅Ni₁₅ and V₈₅Ni₁₀Ti₅ alloys at room temperature are above 55%, showing good formability to allow for the fabrication of thinner membranes for high-efficiency hydrogen permeation.

### Table 7. Calculated lattice constant and hydrogen transport parameters of pure V, V-Ni and V-Ti alloys using first-principles method [22].

| Alloy   | Lattice constant (Å) | Solution energy (eV) | Diffusion energy barrier (Eₐ at 673K (eV)) | Diffusion coefficient at 673 K (× 10⁻⁸ m s⁻¹) |
|---------|---------------------|----------------------|------------------------------------------|-----------------------------------------------|
| V       | 2.990               | ~0.218               | 0.165                                    | 1.25                                          |
| V-Ni    | 2.977               | ~0.107               | 0.198                                    | 0.78                                          |
| V-Ti    | 3.009               | ~0.294               | 0.127                                    | 2.10                                          |
(3) The major V-Ni-Ti solid solution (V_{82.1}Ni_{5.1}Ti_{2.8}) phase in the V_{83}Ni_{10}Ti_{5} alloy can greatly increase hydrogen permeability and solubility, but doesn’t provide larger hydrogen diffusion coefficient than the V_{85}Ni_{15} single-phase alloy, even though the first-principle calculation demonstrates that alloying element Ti has both lower solution energy and diffusion energy barrier of hydrogen in V than alloying element Ni. The main reason should be attributed to the formation of non-BCC hydrogen diffusion phases NiTi and NiTi_{2} compounds in the multi-phase microstructure. These compounds act as barriers to inhibit hydrogen transport through the bulk alloy.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Grant Nos. 51705038 and 51875002), China Postdoctoral Science Foundation (Grant No. 2019M652158) and Natural Science Foundation of Jiangsu Province of China (Grant No. BK20150268).

ORCID iDs

Peng Jiang © https://orcid.org/0000-0003-4317-1005

References

[1] Lubitz W and Tumas W 2007 Hydrogen: an overview Chem. Rev. 107 3900–3
[2] Yan E, Huang H, Sun S, Zou Y, Chu H and Sun L 2018 Development of Nb-Ti-Co alloy for high-performance hydrogen separating membrane J. Membr. Sci. 565 411–24
[3] Jiang P, Liang D, Kellam M, Song G, Yuan T, Wu W and Li X 2017 Effect of rolling and annealing on microstructures and mechanical properties of V-Ti-Ni alloy for hydrogen separation J. Alloys Compd. 728 63–70
[4] Liu F et al 2018 Structures and mechanical properties of Nb-Mo-Co(Ru) solid solutions for hydrogen permeation J. Alloys Compd. 756 26–32
[5] Robina A, Bechthold P, Juan A, Pistonesi C and Pronsato M E 2018 Hydrogen storage in Zr0.7Ti6.1(Ni0.65Co0.35–0.5V3) laves phase, with x = 0.1, 0.25, 0.375, 0.5, 0. A theoretical approach Int. J. Hydrogen Energy 43 16085–91
[6] Phair J W and Donelson R 2006 Developments and design of novel (non-palladium-based) metal membranes for hydrogen separation Ind. Eng. Chem. Res. 45 5657–74
[7] Ockwig N W and Nenoff T M 2007 Membranes for hydrogen separation Chem. Rev. 107 4078–110
[8] Breidt R, Jordal K and Bolland O 2004 High-temperature membranes in power generation with CO2 capture Chem. Eng. Process. 43 1129–58
[9] Dolan M D 2010 Non-Pd BCC alloy membranes for industrial hydrogen separation J. Membr. Sci. 362 12–28
[10] Jiang P, Yuan T and Yu Y 2017 Effect of processing conditions on microstructure and property of multiphase V-Ti-Ni alloys for hydrogen purifying Acta Metall. Sin. 53 433–9 https://www.ams.org.cn/EN/Y2017/V53/4/433
[11] Song G, Dolan M D, Kellam M E, Liang D and Zambelli S 2011 V-Ni-Ti multi-phase alloy membranes for hydrogen purification J. Alloys Compd. 509 9322–8
[12] Magnone E, Jeona S I, Park J H and Fleury E 2011 Relationship between microstructure and hydrogen permeation properties in the multiphase Ni_{91}Ti_{11}B_{8}Ni_{99} alloy membranes J. Membr. Sci. 384 136–41
[13] Li X Z, Liu D, Chen R, Yan E, Liang X, Rettenmayr M, Su Y, Guo J and Fu H 2015 Changes in microstructure, ductility and hydrogen permeability of Nb-(Ti, Hf)Ni alloy membranes by the substitution of Ti by Hf J. Membr. Sci. 484 47–56
[14] Hashi K, Ishikawa K, Matsuda T and Aoki A 2005 Hydrogen permeation characteristics of (V, Ta)-Ti-Ni alloys J. Alloys Compd. 404–406 273–8
[15] Luo W, Ishikawa K and Aoki K 2008 Hydrogen permeable Ta–Ti–Ni duplex phase alloys with high resistance to hydrogen embrittlement J. Alloys Compd. 460 353–6
[16] Dolan M D, Song G, Liang D, Kellam M E, Chandra D and Lamb J H 2011 Hydrogen transport through V85Ni10M5 alloy membranes J. Membr. Sci. 373 14–9
[17] Nishimura C, Komaki M, Hwang S and Amano M 2002 V-Ni-Alloy membranes for hydrogen purification J. Alloys Compd. 330–332 902–6
[18] Yu Y and Jiang P 2014 Effect of heat treatment on precipitate free zones and rollability of V_{83}Ti_{10}Ni_{5}, alloys Intermetallics 53 56–61
[19] Smith J F, Carlson O N and Nash P G 1989 Phase Diagrams of Binary Vanadium Alloys ed J F Smith (ASM International)
[20] Senkov O N and Miracle D B 2001 Effect of the atomic size distribution on glass forming ability of amorphous metallic alloys Mater. Res. Bull. 36 2183–2198.
[21] Steward S A 1983 Review of hydrogen isotope permeability through metals US National Laboratory Report UCRL-53441 Lawrence Livermore National Laboratory Livermore, CA, USA
[22] Lu Y, Gou M, Bai R, Zhang Y and Chen Z 2017 First-principles study of hydrogen behavior in Vanadium-based binary alloy membranes for hydrogen separation Int. J. Hydrogen Energy 42 22925–32
[23] Kim K H, Park H C, Lee J, Cho E and Lee S M 2013 Vanadium alloy membranes for high hydrogen permeability and suppressed hydrogen embrittlement Script. Mater. 68 905–8
[24] Amano M, Nishimura C and Komaki M 1990 Effects of high concentration CO and CO2 on hydrogen permeation through the palladium membrane Mater. Trans., JIM 31 404–8