Influence of Gas for Thermal Treatment on Hydrogen Permeation in V−Ni Alloy Membranes

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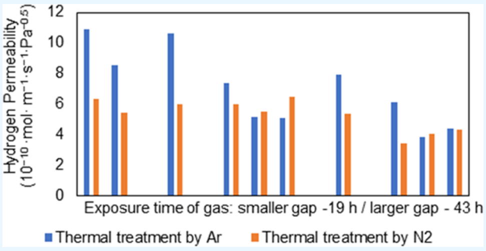

ABSTRACT: Hydrogen separation is an important step for the utilization of hydrogen energy. Metallic alloys, such as vanadium−nickel, are potential hydrogen separation materials. Due to the strong propensity of vanadium to form oxides and hydrides, vanadium alloy has a lower hydrogen permeability, and it is difficult to maintain the permeability over time. Therefore, special preparation processes such as Pd coating have been suggested for hydrogen separation vanadium-based membranes. However, aside from the prohibitive price of palladium, the interdiffusion of palladium and vanadium makes the coated membrane inviable to be used at a high temperature. Thermal treatment with inert gas was investigated in this study to assess the applicability of the vanadium alloy without palladium coating for hydrogen separation and clarify the mechanism behind the thermal treatment. Argon is inert with vanadium and displayed permeability recovery after 43 h thermal treatment, but the permeability declined under certain conditions. In contrast, nitrogen is known to interact with vanadium and the hydrogen permeability was maintained at a level lower than the test with argon. Given that nitrogen can compete with hydrogen for the active sites on vanadium, nitrogen might hinder hydrogen adsorption and hydride formation, whereas argon reduced the partial pressure of hydrogen during the thermal treatment, enhancing the driving force of hydrogen desorption. In the X-ray diffraction spectrum, vanadium hydrides and oxides were confirmed after hydrogen permeation and thermal treatment. In the X-ray photoelectron spectroscopy data, oxygen was a dominant element due to vanadium oxides and adsorbed nitrogen was also observed. According to binding energy shifts of nitrogen, nitrogen used for thermal treatment might substitute or compete for active sites with adsorbed nitrogen and hydrogen, existing in vanadium lattice. Although thermal treatment can be used to recover hydrogen permeability, the alloy cannot be recovered as hydrogen-free. However, results demonstrate the potential of thermal treatment to complement an uncoated vanadium alloy for a hydrogen separation membrane.

1. INTRODUCTION

Hydrogen is an important alternative energy source and must be separated from mixed gas from various sources to be used in applications. One of the promising technologies to separate hydrogen is a metal alloy membrane. Palladium-based alloys have demonstrated desirable performance, but the prohibitive price of palladium limits the applicability of the technology. Vanadium-based materials have drawn attention from researchers due to the affinity of vanadium with hydrogen[1] as well as the high solubility and diffusivity of hydrogen in vanadium.[2] However, its affinity with hydrogen hinders the application of vanadium-based materials for hydrogen separation.

The high solubility of hydrogen in vanadium causes hydrogen embrittlement due to the expansion, decohesion, and phase transition of vanadium-based materials.[3] Hydrogen bearing vanadium materials become brittle when the hydrogen concentration in metal exceeds 0.22 [hydrogen/metal (H/M)].[4] Thus, to reduce the solubility of hydrogen, substituting vanadium with other metals has been adopted to maintain the stability and performance of vanadium-based materials.[5,6] Nevertheless, in most studies, especially without a palladium coating, the pressure of hydrogen was set to pressure not greater than 10 kPa.[7,8] Dolan et. al. showed that, other than alloying, temperature control can also prevent mechanical failure of vanadium-based alloys caused by the miscibility gap between vanadium hydride phases during the operation of a palladium-coated vanadium tubular membrane.[3] Moreover, vanadium stores hydrogen by forming hydrides rather than passing it through the alloy due to high solubility. This inclination will yield low hydrogen permeability without a palladium coating.

Another drawback of vanadium-based alloys stems from the affinity of vanadium with oxygen. Vanadium oxides will form instantly at the surface of vanadium when vanadium meets oxygen. Vanadium oxides could have a significant influence on hydrogen permeation in a vanadium membrane.[9] In general, a palladium coating was applied or vacuum was utilized to

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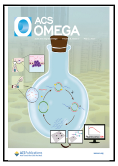

reduce the contact between the alloy and other gases to address the oxidation of vanadium.[10] However, palladium coatings have an issue of intermetallic diffusion with vanadium at high temperatures and the catalytic behavior of palladium decreases with the performance of the alloy.[11] Application of vacuum or in situ cleaning of the surface is not suitable for a scalable technology.

Therefore, a different approach is required to use uncoated vanadium alloy for hydrogen separation. Some researchers introduced the thermal treatment to enhance the permeability of palladium-based metallic membranes by removing components adsorbed onto a surface[12] or reducing the dislocations, voids, and boundaries that can act as hydrogen traps and rendering more homogeneous grains in the alloy.[13,14] Thermal treatment can be further investigated with the vanadium alloy as a potential alternative to palladium coating. In particular, thermal treatment can reduce hydrides that formed in the vanadium lattice during hydrogen permeation. Because of the high hydrogen solubility of vanadium, excessive hydrides in the vanadium lattice will block active sites of hydrogen and reduce the catalytic capacity of vanadium to dissociate hydrogen, which are detrimental to a long-term operation. Differential scanning calorimetry results with vanadium hydrides showed that at 500 °C, α-phase vanadium hydrides were dissociated into hydrogen and hydrogen-free vanadium.[6] Therefore, thermal treatment can reduce the amount of hydrides that formed in the vanadium lattice during hydrogen permeation, regenerating the active sites to dissociate hydrogen. Vanadium oxides, which are detrimental to hydrogen permeation, cannot be removed by thermal treatment at 500 °C. However, it is important to demonstrate that hydrogen permeation through uncoated vanadium alloy would be maintained in the presence of oxide layers for a long time with thermal treatment.

For commercialization of vanadium-based alloy as a hydrogen separation membrane, high price and intermetallic diffusion of palladium coating should be avoided. Without a palladium coating, long-term operation should overcome setbacks from vanadium hydrides and oxides as well as hydrogen embrittlement. Previous studies have been heavily focused on palladium coating. Uncoated membranes were used only for short-term test with very low hydrogen pressure (less than 30 kPa). A new approach to improve performance and lifespan of the vanadium-based membrane is required.

To use a vanadium-based alloy without a palladium coating, thermal treatment was examined as a method to maintain, or recover, the hydrogen permeability of a vanadium alloy membrane without a palladium coating. During thermal treatment, gas other than hydrogen, such as nitrogen, was filled into the system which bears the membrane. The type of gas used in the thermal treatment is crucial in determining the efficiency of the thermal treatment in a palladium-based membrane.[14] This study aims to find out the influence of gas on the efficiency of thermal treatment, as well as on maintaining the hydrogen permeability with thermal treatment. The mechanism behind the interaction between the alloy, hydrogen, and gas used for the thermal treatment is instrumental in understanding the permeability change due to the hydrogen permeation.

Argon or nitrogen was filled into a membrane cell during the thermal treatment to maintain the hydrogen permeability of the vanadium-based alloy membrane. Argon and nitrogen do not have a reaction with vanadium in the range of 350−500 °C, where this study was conducted. While argon is inert with vanadium, nitrogen can adsorb and stay in the vanadium lattice[15] or form triple bonds with vanadium [vanadium nitrides, (VN)] under a high temperature over 600 °C.[16] Hence, when argon is introduced for the thermal treatment, argon will only reduce the partial pressure of hydrogen but would not interact with the alloy. In contrast, nitrogen might interact with the vanadium−hydrogen system and affect hydrogen permeation. To investigate the influence of gas and determine a more suitable condition for the thermal treatment, argon and nitrogen were tested at different pressures and thermal treatment times. Among the vanadium-based alloys, the vanadium−nickel alloy (15 atom % Ni) was adopted because it does not cause hydrogen embrittlement and miscibility gap under the conditions of this study,[2] reducing the chance of mechanical failure with the temperature and pressure swings. Moreover, high hydrogen solubility of vanadium induces hydrogen embrittlement. Hence, alloying with smaller metals such as nickel and cobalt has been used to reduce the high solubility of vanadium. Two main qualifications to be an effective alloy component are as follows: (1) Occupying the interstitial sites where hydrogen can occupy and (2) the component should be small enough not to expand the lattice of vanadium, which makes a longer diffusion path of hydrogen. Nickel is widely adopted alloy component with vanadium to reduce these drawbacks. Therefore, V−Ni15% alloy is used in this study as a primary hydrogen separation membrane.

2. EXPERIMENTAL SECTION

2.1. Membrane Preparation. Vanadium (99.9%) and nickel (99.99%) were arc-melted and mixed at 85 and 15 at% ratios, respectively, and then annealed for 12 h at 1350 °C under argon to generate a bcc vanadium structure and reduce dislocations and sigma phases to avoid variation in hydrogen permeation due to the microstructure.[8,17] X-ray diffraction (XRD) (SmartLab; Rigaku, Japan) was used to confirm the structure of the alloy. The alloy was wire-cut into 2 × 2 cm^2 and ground and polished to 220−270 μm in thickness. The alloys were rinsed with ethanol and sealed before the experiment. Palladium coating was not applied for the vanadium membranes in this study.

2.2. Hydrogen Permeability Measurement. The membrane system used for the study is custom-made, and the schematic diagram is shown in Figure 1. The alloy was installed in the membrane cell on top of a stainless-steel grill for physical support. (The picture of the membrane cell is provided in the Supporting Materials.) A donut-shaped copper gasket whose thickness of 0.6 mm was installed on the alloy for

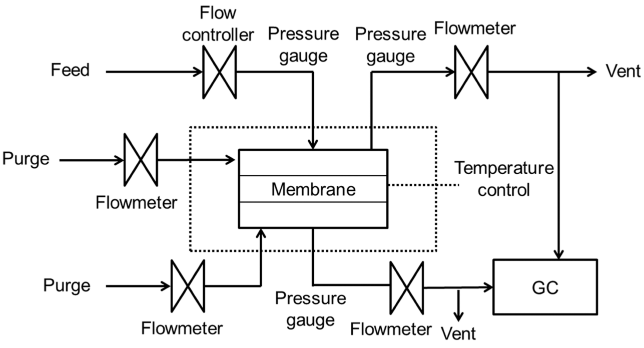

Figure 1. Schematic diagram of the membrane system.

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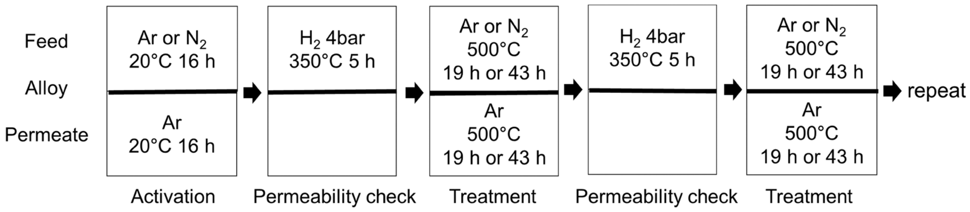

Figure 2. Simplified scheme of the hydrogen permeation and thermal treatments. (Resized for clarity, the original figure is listed at the end of the manuscript).

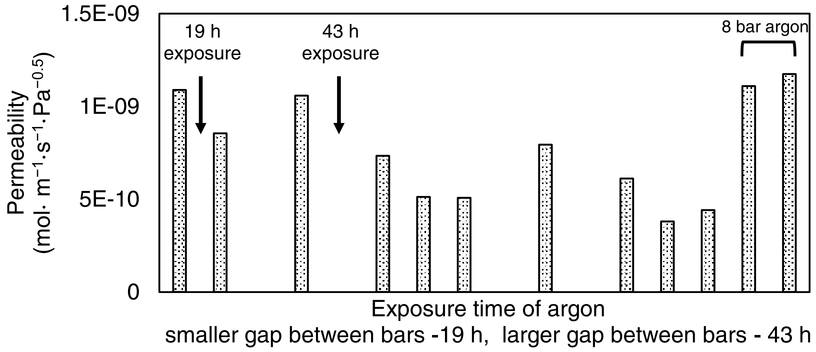

Figure 3. Permeability after the thermal treatments with 4 bar argon (8 bar argon was used before measuring the last two permeability values). Thermal treatments were conducted before every measurement other than the first permeability. (Resized for clarity, the original figure is listed at the end of the manuscript).

sealing. After the membrane was mounted, argon or nitrogen was filled into the membrane cell through purge lines. The type of gas used accorded with the gas used for thermal treatment. Prior to hydrogen permeation, the cell was sealed for 16 h at 20 °C, monitoring the pressures of the gas filled at the feed and permeate sides to check fissures in the membrane. The gas was ventilated 30 min after the designated temperature was reached. Hydrogen permeability was measured at 350 °C with pure hydrogen gas (purity of 99.999%) at 4 bar and no sweep gas or vacuum was applied. To avoid hydrogen embrittlement, the temperature was kept over 350 °C after hydrogen was introduced until the entire test set was over. The effective surface area of the membrane was 0.385 cm^3. Thermal mass flow controllers and meters (Flow Prestige; Bronkhorst, The Netherlands) were used to control the pressure and flow of the feed and measure the hydrogen flux at the permeate side, respectively. The mass flowmeter installed at the permeate side recorded the amount of hydrogen at the point of measurement. Hydrogen gas was introduced to the feed side of the membrane and the amount of hydrogen passed through the membrane was measured in volume/time at the permeate side using the mass flowmeter. The unit of measured values was converted into the unit of flux to obtain the permeability. The permeability (mol·m^{-1}·s^{-1}·Pa$^{-0.5}$) was calculated from the measured flux, membrane thickness, and pressure difference using the formula $\Phi = J\frac{l}{\sqrt{P_f}-\sqrt{P_p}}$, where J is the measured flux (mol·m^{-1}·s^{-1}), l is the membrane thickness (m), and P_f and P_p are the pressures at the feed and permeate sides (Pa), respectively. The permeate side of the membrane was purged with argon and maintained at atmospheric pressure before measuring the hydrogen permeability to maintain the pressure difference.

2.3. Thermal Treatments. Thermal treatments under various circumstances were conducted to determine the optimal condition to obtain the hydrogen permeability of the vanadium−nickel alloy. The alloy was exposed to argon or nitrogen (both gases have a purity of 99.999%) at 500 °C to remove hydrides that formed in the vanadium lattice and renew the alloy after 5 h of hydrogen permeation. Helium (purity of 99.999%) was also used for the thermal treatment to compare the effects of the thermal treatments with argon and nitrogen on hydrogen permeability. The time for gas exposure varied from a few hours to a few days. The typical exposure times were 19 and 43 h. The pressure of the gas was set at 4 and 8 bar at the feed side and 3 and 7 bar at the permeate side. The pressure difference was designed to monitor possible cracks in the alloy during the operation of the membrane. The gas was fixed as argon at the permeate side and varied at the feed side to estimate the influence of gas on the alloy. Given that the alloy facing the feed side was facing 4 bar hydrogen, hydride formation affecting hydrogen permeation significantly was suspected to be on the feed side. Therefore, the gas on the feed side was set as a variable in this study.

After the thermal treatment, 5 h hydrogen permeation was repeated to assess the change in hydrogen permeability induced by the thermal treatment and to expose the alloy to hydrogen. The hydrogen permeability values before and after the thermal treatment were compared to investigate the impact of thermal treatment on hydrogen permeability. The process was repeated in a series for a long-term application. A simplified scheme of the thermal treatments is presented in Figure 2. XRD and X-ray photoelectron spectroscopy (XPS) (AXIS SUPRA; KRATOS, U.K.) were used to analyze the structure of the membranes after the hydrogen permeation and thermal treatments.

3. RESULTS AND DISCUSSION

Permeability value of the V−Ni alloy prepared in this study was compared to other studies using V−Ni with and without coating because the number of studies using the V−Ni alloy without palladium coating is very limited. Hydrogen

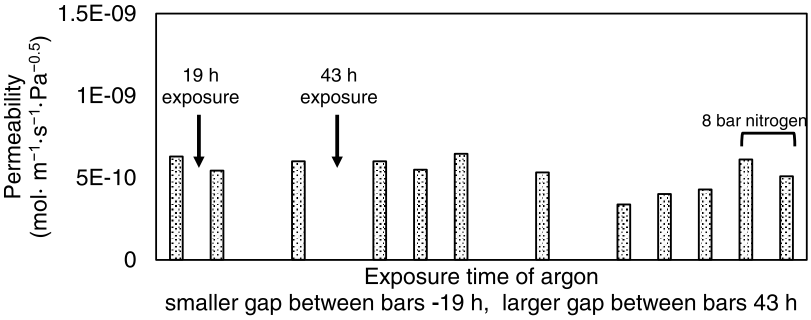

Figure 4. Permeability after the thermal treatments with 4 bar nitrogen (8 bar nitrogen was used before measuring the last two permeability values). Thermal treatments were conducted before every measurement other than the first permeability. (Resized for clarity, the original figure is listed at the end of the manuscript).

permeability of this study measured at 350 °C was in the range of 6−10 × 10^{-10} $mol^{-1}\cdot m^{-1}\cdot s^{-1}\cdot Pa^{-0.5}$. The value was varied depending on the gas used to activate the alloy before measuring hydrogen permeability. Argon activation resulted in a higher hydrogen permeability. An activation process includes leakage check and temperature elevation to 350 °C. Other studies reported the similar magnitude of hydrogen permeability (2 × 10^{-10} $mol^{-1}\cdot m^{-1}\cdot s^{-1}\cdot Pa^{-0.5}$) without palladium coating, while with a palladium coating, the permeability of V−Ni was at least 100 times higher than the alloy without the coating.[8] The difference in the permeability stems from the fabrication method (without annealing) and feed hydrogen pressure (6.5−8 kPa).

The permeability change was determined as the change bigger than the standard deviation of nitrogen thermal treatment under identical conditions. The detail is addressed in Section 3.2 near Figure 7.

3.1. Determination of Thermal Treatment Conditions.

Initial experiments to determine the conditions of the thermal treatment were conducted. The hydrogen permeability of the membrane was decreased by consecutive hydrogen permeation. When the temperature of the thermal treatment was under 500 °C (350−450 °C), the permeability was not recovered. Thermal treatment at atmospheric pressure (purged and then ventilated) was not able to maintain the permeability. Therefore, the temperature of the thermal treatment was set at 500 °C and the initial pressure of argon or nitrogen was set at 4 bar to balance with the feed pressure of the hydrogen permeation.

As shown in Figure 3, the thermal treatment with argon is not able to maintain the initial hydrogen permeability. Compared to the 19 h thermal treatment, the 43 h thermal treatment showed clear permeability recovery when the previous permeability was low. However, after the permeability recovery, the subsequent permeability declined, indicating that the permeability was not maintained at a high level under this condition. Better permeability recovery after a longer time of thermal treatment indicates that the permeability recovery or renewal of the alloy during the thermal treatment did not instantly occur following the pressure−composition−temperature (PCT) curve of vanadium hydrides. In comparison with low-pressure hydrogen permeation (less than 30 kPa) with the vanadium−nickel alloy without the palladium coating, 4 bar hydrogen permeation had an H/M value of 0.15, which is at least 10 times higher.[2] Hence, the removal of vanadium hydrides is crucial for the renewal of the active sites for hydrogen in the alloy. In contrast, the pure vanadium tubular membrane (which has an even higher H/M value than the vanadium−nickel alloy) with a palladium coating demonstrated that temperature management allowed the membrane to work without hydrogen embrittlement,[3] indicating instant response to temperature following the PCT curve. Therefore, another factor was impacting the change in hydrogen permeability. Vanadium oxide layers that can trap hydrogen[9] might affect the hydride removal relevant to the permeability recovery. By considering that the palladium-coated alloy is oxide free, catalytic dissociation of hydrogen can be active in the remaining spots in vanadium as well as in palladium. However, without palladium, the vanadium oxide layers trapped hydrogen, occupying the active sites when the high-pressure hydrogen permeation continues.

The pressure of argon also affected the permeability recovery. With 8 bar argon and 19 h exposure at the end of the experiment, the permeability values were recovered close to the initial value. Because of the difference in hydrogen permeability by the pressure of argon, the structural change in the vanadium−nickel alloy due to temperature was not considered as a crucial contributor. The changes in permeability were attributed to the interaction between the alloy and argon. Longer exposure time might allow more hydrogen desorption from both hydrides and oxide layers, and higher argon pressure reduced the partial pressure of hydrogen in the system.

However, the exact cause of the overall declining trend in hydrogen permeability after the thermal treatment with argon under certain conditions is inexplicable as of this writing. Unlike palladium-based or palladium-coated materials where thermal treatment focused on cleaning surface contamination to reset the active sites, hydride- and oxide-related vanadium-based materials might undergo a more complex transformation during the hydrogen permeation and thermal treatment.

In the case of the thermal treatment with nitrogen, the permeability values seemed to be maintained throughout the experiments (Figure 4). A similar pattern of permeability recovery as in the argon experiment was observed but not as dramatic as with argon. The overall declining trend of the permeability and the dominant permeability recovery when 8 bar nitrogen was used for the thermal treatment were observed. However, important differences were the initial hydrogen permeability and the permeability change after 43 h of exposure. Before measuring the initial value, the membrane was kept with either argon or nitrogen to check the integrity of the membrane. Throughout this study, the initial value of the hydrogen permeability with nitrogen was half the permeability with argon. In Figure 4, 43 h of thermal treatment with nitrogen does not lead to permeability recovery but maintains

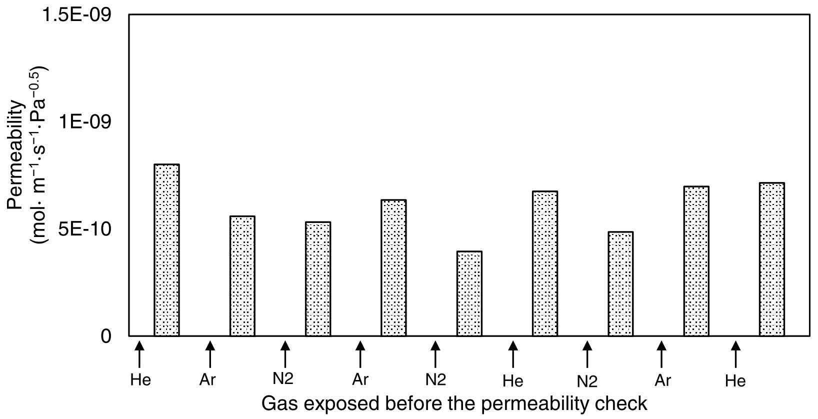

Figure 5. Permeability after the thermal treatment with different gases. The pressure of each gas used for the thermal treatment was 8 bar and the thermal treatment was conducted for 43 h. (Resized for clarity, the original figure is listed at the end of the manuscript).

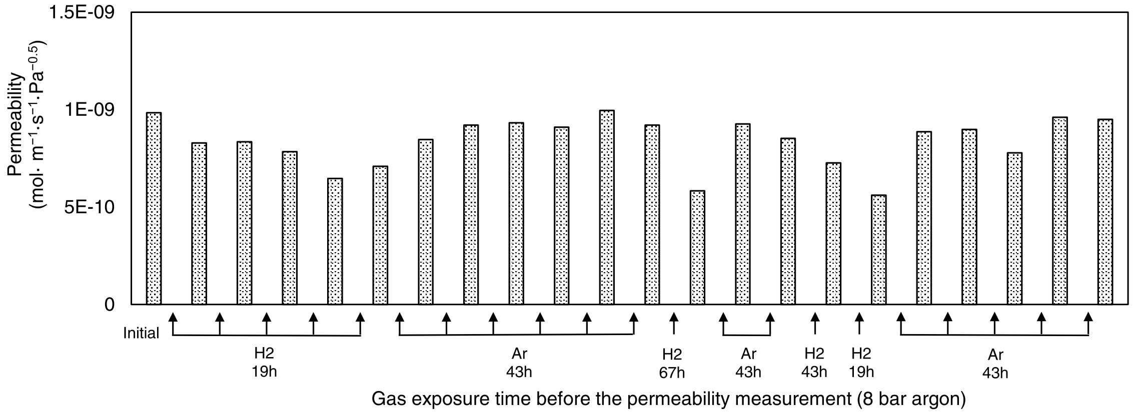

Figure 6. Permeability after repeated hydrogen permeation and thermal treatments with 8 bar argon. (Resized for clarity, the original figure is listed at the end of the manuscript).

the permeability value. In the second exposure of 43 h to nitrogen (seventh and eighth permeability values), the permeability was clearly reduced. These trends might be relevant to the interaction between the alloy and the exposed gas.

Nitrogen atoms can adsorb onto the vanadium lattice and tend to stay on the surface.[15] Thus, nitrogen might compete with hydrogen for the sites in the lattice through competitive sorption. With palladium composite membranes, inhibiting the effect of nitrogen on hydrogen permeation was reported due to blocking of active sites.[18] In contrast, argon atoms do not occupy the same spots, only acting as an inert gas reducing the partial pressure of hydrogen in the system to accelerate the desorption of hydrogen. Therefore, the effect of nitrogen was more focused on hindering the generation of hydrides, inducing a low initial value but inefficient to recover the hydrogen permeability, leading to a stable permeability trend compared to the result in the argon test. Similarly, longer exposure to nitrogen allowed more nitrogen sorption, which is detrimental to hydrogen permeation. However, when the pressure of nitrogen increased to 8 bar, partial pressure dilution might play a greater role than competitive sorption, recovering the permeability. Nevertheless, the permeability was not maintained unlike in Figure 3, highlighting the inhibiting role. Given the different patterns between the tests using argon and nitrogen, hydride removal under the circumstance of oxide layers to regenerate the active sites for hydrogen permeation might be instrumental in maintaining the hydrogen permeability of the vanadium−nickel alloy without the palladium coating but might not be the only factor. Moreover, the impact of the alloy surface on the feed side was deemed crucial to the hydrogen permeability. Since the gas used in the thermal treatment differed only on the feed side (the gas on the permeate side was fixed as argon), the difference in data in Figures 3 and 4 shows that the changes on the feed side surface of the alloy played an important role.

3.2. Influence of Gas for Thermal Treatment. To clarify the influence of gases, different gases were used for the thermal treatment in a single test (Figure 5). To avoid repeated exposure and compare the effects of nitrogen and argon, helium was introduced. The thermal treatment was conducted for 43 h with a gas pressure of 8 bar. The order of three gases was chosen to avoid repetition and three thermal treatments were performed for each gas. The gas in the *X*-axis was the gas used for the thermal treatment before measuring the permeability of the corresponding *Y*-axis. As in the difference in Figures 3 and 4, the permeability values after exposure to nitrogen were lower than those after exposure to argon or helium. Argon showed permeability recovery after nitrogen reduced the permeability. Helium was expected to have a similar effect as argon. Theoretically, helium can pass through vanadium, but low solubility makes the passage highly unlikely.[19] Since the solubility of helium is low, competitive sorption as with nitrogen might be negligible. Thus, helium only fostered the diluted partial pressure of hydrogen during the thermal treatment. As a result, argon and helium facilitated

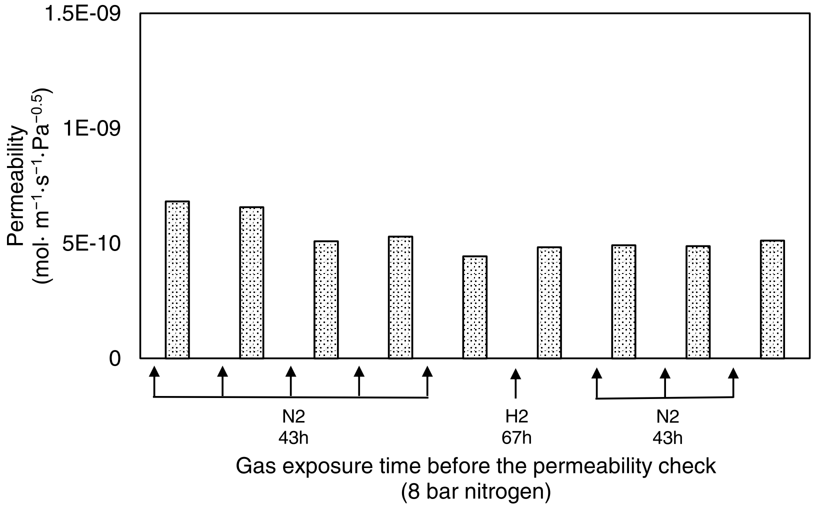

Figure 7. Permeability after repeated hydrogen permeation and thermal treatments with 8 bar nitrogen. (Resized for clarity, the original figure is listed at the end of the manuscript).

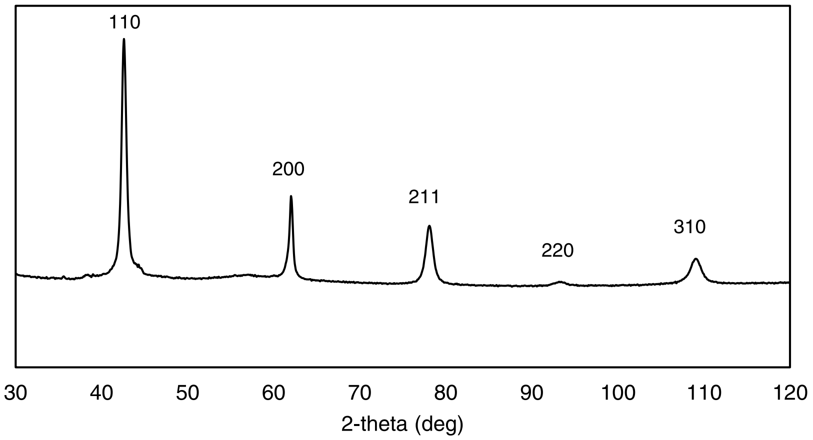

Figure 8. XRD spectrum of the fresh vanadium−nickel alloy. (Resized for clarity, the original figure is listed at the end of the manuscript).

the permeability rise, whereas nitrogen decreased the permeability. In short, argon was better in permeability recovery from low permeability, whereas nitrogen reduced the permeability initially but was better in maintaining the permeability.

To evaluate the feasibility of the thermal treatments with argon and nitrogen for a long time, the hydrogen permeation followed by the thermal treatment was repeated for several days. The thermal treatment with argon was conducted focusing on permeability recovery (Figure 6). Hydrogen permeation preceded the thermal treatment to induce a permeability drop. "H2 19 h" in the *X*-axis means that 4 bar hydrogen was exposed for 19 h before the typical 5 h permeation. About 67 h of continuous hydrogen permeation reduced the permeability to 60% of the initial value. Unlike in the 4 bar and 19 h thermal treatment, the permeability drops were not observed over time after the thermal treatment with 8 bar argon. The hydrogen permeability values were about 90% of the initial permeability. Repeated tests demonstrated that repeated recovery of hydrogen permeability is possible using the thermal treatment with argon.

When nitrogen was used for the thermal treatment, lower permeability values than the argon tests were obtained regardless of hydrogen permeation or thermal treatment with nitrogen (Figure 7). A slight decline in permeability over time was observed, but the permeability values were maintained as in Figure 5. However, overall permeability values were generally lower than the permeability values in Figure 6.

The study centers on qualitative assessment of thermal treatment capability to maintain hydrogen permeability of uncoated vanadium alloy over time. Nevertheless, the standard deviation of nitrogen experiments in Figure 7 was used as a criterion for the change in permeability since nitrogen thermal treatment was assumed as a stable permeability trend. Data in Figure 7 was obtained from a single condition of 43 h of 8 bar nitrogen thermal treatment. The standard deviation was 5.81×10^{-11}. This value was much smaller than the other permeability changes, which has the order of 10^{-10}, from the argon thermal treatment tests. Therefore, the variation during the argon thermal treatment can be deemed significant.

Longer time and higher argon pressure during the thermal treatments facilitated more sustainable hydrogen permeation through the vanadium−nickel alloy. However, when nitrogen was used for the thermal treatment, the correlations between the time and pressure of the thermal treatment with hydrogen permeability were less obvious. Moreover, the permeability values were generally lower in the nitrogen experiments, possibly due to the competitive sorption of nitrogen in the active sites of the vanadium alloy. In conclusion, without the palladium coating, vanadium hydrides and oxide layers might complicate the hydrogen permeation through the vanadium−nickel alloy and the interaction between the vanadium−nickel alloy, and the gas used in the thermal treatment was influential on the hydrogen permeability after the thermal treatment.

3.3. Alloy Analysis. The alloys before and after the experiments were analyzed using XRD and XPS to gather information about the structural changes throughout the hydrogen permeation and thermal treatment. The XRD spectrum of the fresh vanadium−nickel alloy showed bcc vanadium peaks, which can be identified by a previously reported XRD spectrum in another research.[20] Vanadium XRD pattern was also identical to the vanadium pattern from the COD database (entry number 96-900-8558). (110) was the most dominant phase, followed by (200) and (211) (Figure 8). The peaks of sigma-phase V−Ni were not displayed significantly due to the annealing of the alloy.

In contrast, after the hydrogen permeation and thermal treatments, small peaks were detected from the XRD spectrum of the alloys. Vanadium oxides and hydrides were identified on the surface of the alloy (Figure 9). The peaks of the vanadium hydrides were assumed to be from the VH or V_2H spectrum.[21] Vanadium oxides were known to be dominated on the surface of the alloy. Hence, given the penetration depth of XRD, which is up to a few micrometers, oxides were not expected to be identified. On the contrary, vanadium oxides, such as V3O5, V6O11, and V9O17, were identified from the COD database (entry numbers 96-210-6480, 96-810-3817, 96-153-0103, respectively). Since the 2θ values of peaks are very similar to each other, the peaks were labeled as V_xO_y. Vanadium oxide was only detected after the test, indicating that oxidation of the alloys was stimulated due to the high temperature and the inherent oxygen in the vanadium lattice. Peaks of the vanadium nitrides[22] were not observed because the nitrides from the references are the compounds with triple bonds, which requires very high temperatures to generate. $V_{16}N_{1.5}$ were reported to be formed at 600 °C,[23] but the peaks of the compound were not identified in the spectra of this study as well.

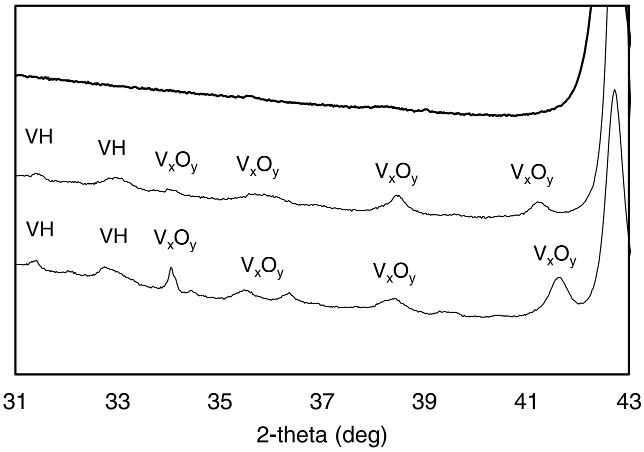

Figure 9. XRD spectra of the fresh vanadium−nickel alloy (top), the alloy after the thermal treatment with argon (middle), and the alloy after the thermal treatment with nitrogen (bottom). (Resized for clarity, the original figure is listed at the end of the manuscript).

Given that many different types of vanadium hydrides and oxides might be formed during the hydrogen permeation, some peaks in Figure 9 cannot be identified thoroughly due to similar peak positions of the components with a similar chemical structure. Since the XRD spectrum only represents a crystalline structure, the presence of amorphous V−H or V−O type of compounds should not be excluded. Nevertheless, crystalline vanadium nitrides were not formed under the thermal treatment conditions. If nitrogen interacted with vanadium during the thermal treatment, it should be in a form of physical adsorption. In conclusion, vanadium hydrides or vanadium oxides were formed during the hydrogen permeation and thermal treatment cannot reset the uncoated vanadium−nickel alloy completely anew.

When 4 or 8 bar argon or nitrogen was introduced during the thermal treatment, it is difficult to define the partial pressure of hydrogen but the hydrogen concentration in the system cannot be zero because of the presence of desorbed hydrogen. Therefore, the remaining hydrogen and hydrides can affect the ternary V−Ni−H system as well as the hydrogen permeation through the V−Ni alloy. Furthermore, the vanadium oxide layers potentially trap the hydrogen atoms,[9] leading to the accumulation of hydrogen inside the alloy unlike the palladium-coated alloy. As a result, when the hydrogen permeation was repeated after the thermal treatments, the hydrogen permeability values varied even though the pressure of gases and the temperature were identical. Given the high affinity between vanadium and hydrogen, the accumulation of hydrides must be significant in a long-term hydrogen permeation in the V−Ni alloy. The XRD results also complement the permeability data in Section 3.1 which represented the possibility of trapped hydrogen in the alloy. Especially for the application of high-pressure hydrogen, a method to maintain the hydrogen permeability over time should be instrumental for uncoated vanadium-based materials. Constant application of purge followed by inert gas or vacuum application would be desirable to clean up the alloy. However, these sequences are not practical or scalable.

In the XPS data from the alloys both before and after the experiments, oxygen was a predominant component, suggesting that the oxide layers formed on the surface of the alloy. The vanadium peaks were dominated by vanadium oxides. As a result, the vanadium hydrides which are salient to this study cannot be properly identified. Vanadium XPS data were briefly discussed in the Supporting Materials. In contrast, the nitrogen peaks provided better information of the changes during the experiments (Table 1).

The overall atomic composition of nitrogen slightly decreased after the hydrogen permeation and the thermal treatments with both argon and nitrogen. It can be presumed that the decline might display the substitution of nitrogen on

Table 1. XPS Data of the Atomic Composition and Binding Energy of Nitrogen in the Alloy before and after the Experiments[a]

samples	atomic composition of nitrogen (binding energy)		
fresh alloy	3.55% (399.45 eV)	0.29% (400.74 eV)	
after Figure 2	1.87% (399.60 eV)	1.05% (401.35 eV)	0.29% (406.73 eV)
after Figure 3	0.61% (399.52 eV)	2.12% (401.43 eV)	

[a] The composition in % is the averaged value of three different analyses.

the vanadium surface with hydrogen during the hydrogen permeation because hydrogen and nitrogen share the same catalytic mechanism of dissociation.[15] Since nitrogen composition has not increased, the formation of vanadium nitrides, whose binding energy is lower than 397 eV, was highly unlikely, as discussed in the XRD data. Higher binding energy was detected after the experiments and the proportion of higher binding energy nitrogen was higher in the experiments with nitrogen. Binding energy of nitrogen at 399 and 401 eV represents the adsorbed nitrogen on the vanadium oxides as N2-V.[24] Binding energy at 399 eV is from normal N1S ionization, whereas the state of nitrogen with the binding energy at 401 eV was unclear. The authors presumed that the nitrogen composition with the binding energy of 401 eV was the nitrogen adsorbed at the different adsorption sites on the vanadium oxides.

After the thermal treatment with argon, nitrogen with a binding energy of 406.73 eV was detected. A higher binding energy of nitrogen suggests a higher oxidation number.[25] Nitrogen's binding energy higher than 406 eV represents nitrate. Gas phase N2 also has a binding energy of 406 eV,[24] but it is highly unlikely that gaseous nitrogen was detected during XPS analysis using vacuum. Moreover, nitrogen gas was used during thermal treatment for the test of Figure 4, not the test of Figure 3 which the binding energy of 406 eV was detected. Presumably, nitrogen might form nitrate with the inherent oxygen in the vanadium structure due to the catalytic capability of vanadium. However, the experimental evidence to support the formation of nitrate was not sufficient in this study.

Although the thermal treatment with nitrogen did not generate crystalline vanadium nitrides, nitrogen underwent the change of binding energy on the surface of the alloy. Since XPS can only detect the surface of the sample up to 10 nm, the XPS data represent superficial changes, not in the bulk vanadium lattice deep below the oxide layers. Hence, the data might display the binding energy of the adsorbed nitrogen on the surface of the alloy during the experiments. With the data showing a change in nitrogen composition in the alloy used for the thermal treatment with argon, it can be suggested that not only the high-pressure nitrogen injection during the thermal treatment but also the hydrogen permeation at high temperatures affected the nitrogen atoms on the surface of the alloy. When nitrogen was used for the thermal treatment (bottom spectrum of Figure 10), more nitrogen with a binding energy at 401 eV was detected than any other samples. Since hydrogen permeation occurred at 350 °C and thermal treatment was conducted at 500 °C, the result indicates that high nitrogen fugacity at 500 °C might affect the binding energy distribution of the sample after Figure 4 test.

The value of the binding energy did not guarantee any specific compound but the overall shift to the higher binding energy suggests that adsorbed nitrogen on the surface was shaken up (N2-V adsorption, 401 eV) or oxidized (nitrate, 406 eV) to some extent during the experiment by the interaction with oxygen or vanadium on the surface of the alloy. It is unclear with the XPS data whether nitrogen adsorbed on the surface underwent catalytic dissociation on the vanadium surface. The behavior of nitrogen at the atomic level during the thermal treatment would be interesting for future research. Since air contains 78% of nitrogen, nitrogen is also a crucial element when air is utilized for activation or thermal treatment of vanadium-containing materials.

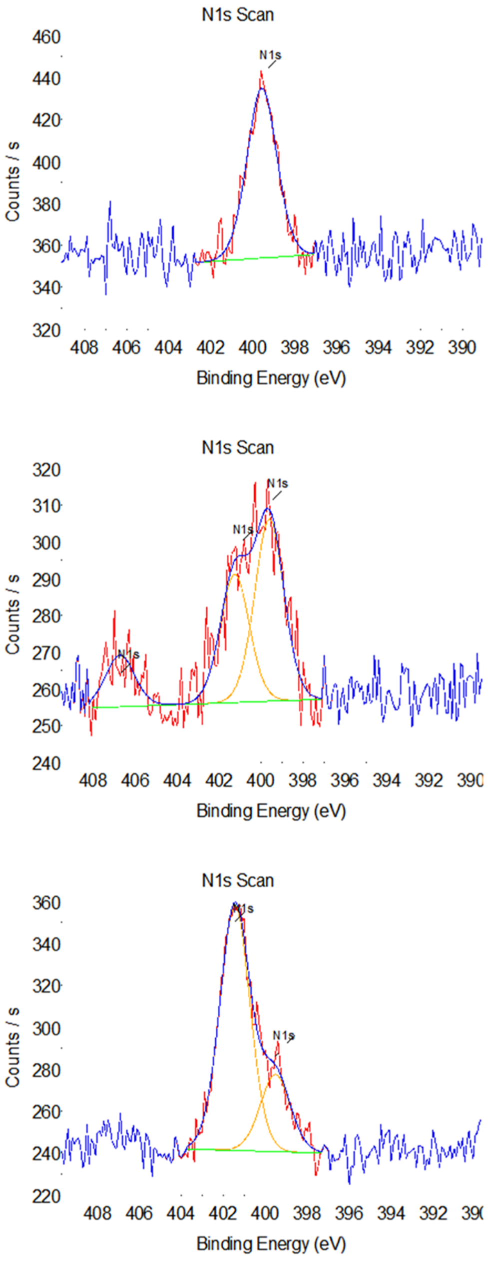

Figure 10. XPS spectra of nitrogen of fresh alloy (top), after Figure 3 test (middle), and after Figure 4 test (bottom).

By comparing the XPS and XRD data, it can be inferred that the hydrides formed below the oxide layer. XPS can cover up to 10 nm compared to a depth of XRD penetration up to a few micrometers. The absence of oxides is better for hydrogen permeation.[9] Nevertheless, hydrogen permeation was possible beneath the thin oxide layers. However, without the palladium coating, hydride formation and trapping of hydrogen by the oxides generated before and during the hydrogen permeation might have reduced the spots for the dissociation of hydrogen molecules and the alloy was acting more like a hydrogen storage material. Furthermore, nitrogen interacted with the alloy during the thermal treatment, even though the result can be assessed only qualitatively.

The microstructural changes in the alloy after the experiments cannot be excluded as well. Processing methods and various surface structures of the vanadium alloy also affects hydrogen permeation by affecting vanadium–hydrogen interaction.[8,10,20] Nevertheless, the different patterns of hydrogen permeability when different gases were applied during the thermal treatment inferred structural changes in the alloy induced by temperature and hydrogen permeation cannot be a sole contributor to this phenomenon. However, thorough structural analysis was beyond the scope of this study. Further research on structural changes of the vanadium−nickel alloy after long-term hydrogen permeation will provide valuable insights to understand the changes in the properties of the material.

4. CONCLUSIONS

This study demonstrated that nonreactive gases such as argon or nitrogen can affect the stability and performance of the uncoated vanadium−nickel alloy for hydrogen separation. Completely inert argon and less reactive nitrogen were used in the thermal treatment to compare the effects of the gases on the hydrogen permeability of the vanadium−nickel alloy without a palladium coating. Argon reduced the fugacity of hydrogen during the thermal treatment to remove hydrides, which occupied the active catalytic sites, inducing the recovery of the hydrogen permeability after the thermal treatment. Nitrogen can compete with hydrogen by adsorbing onto the vanadium alloy, hindering both the permeation and adsorption of hydrogen. When nitrogen was used for the thermal treatment, the hydrogen permeability was lower than that in the argon test but steady. The difference might be incurred from the availability of active catalytic sites for hydrogen dissociation and complex interaction of the vanadium−hydrogen−nitrogen system during the thermal treatment.

The XRD and XPS data showed qualitative evidence of the hydride and oxide formation on the surface of the alloy and complement the permeability data to investigate the role of nitrogen. The oxide layers on the vanadium surface interrupted not only the hydrogen permeation but also the surface analysis using XPS. The thermal treatment was not able to eliminate the hydrides and oxides that formed during the tests. Binding energy of adsorbed nitrogen was shifted due to oxidation during hydrogen permeation and thermal treatment. Furthermore, the interaction of nitrogen, hydrogen, and the alloy was confirmed with XPS data. In future works, quantification of the phase change in the vanadium−nickel alloy will show the influence of gas during the thermal treatment. Detailed microstructural assessment during the thermal treatment with neutron scattering or X-ray absorption fine structure (XAFS) will provide further information to corroborate the influence of the gases.

The thermal treatment in this study can maintain the hydrogen permeability to some extent, but the process was not practical because the time of the thermal treatment and the pressure of argon or nitrogen were longer and higher than the time and pressure of hydrogen permeation. However, differences between the results of the argon and nitrogen thermal treatments provided potential clues on the utilization of the vanadium−nickel alloy without a palladium coating for hydrogen separation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c00871.

Photo of the membrane cell; hydrogen permeability data; vanadium XPS data; and XPS raw data and spectra (PDF)

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Notes

The authors declare no competing financial interest.

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