A Comparison of the Performance and Stability of Pd/BCC Metal Composite Membranes for Hydrogen Purification

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Abstract

Composite membranes were fabricated by sputtering 100 nm of Pd on to both sides of dense BCC metal foils (V, Ta, Nb). Under pure H₂ gas testing at 500 °C the maximum permeability of all three metals exceeds previously reported values and closely approach theoretical limits. However, the stability of each membrane varied significantly due to unique failure mechanisms. Pd/V membranes failed quickly (<20 hours) due to a combination of Pd-V interdiffusion and high susceptibility to oxidation as shown through microscopy and compositional analysis. The Pd/Ta membranes were the most resilient to oxygen, but their mechanical integrity was relatively poor and they failed within 48 hours due to Pd-Ta interdiffusion. In contrast, Pd/Nb membranes exhibited high permeability throughout the 168 hours of testing, with no Pd-Nb interdiffusion observed. The decline in permeability observed during testing was attributed to partial Pd delamination as a result of membrane deformation. These results provide pathways for further development of these membranes.

Keywords: Hydrogen separation; BCC metal membrane; vanadium; niobium; tantalum;

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1. Introduction

Over 95% of usable H_2 is produced from fossil fuels such as natural gas or coal through steam reforming [1]. These processes produce a mixture of gases including H_2 , CO, CO_2 , and H_2O , requiring an extensive series of separation processes to produce high purity hydrogen. Current technologies such as cryogenic separation and pressure swing adsorption are both energy and capital intensive [2]. Hydrogen selective membranes could offer a cost effective and practical alternative to these technologies [3].

Palladium is an excellent H_2 permeable material because of its relatively high atomic hydrogen solubility in its face centered cubic (FCC) lattice structure, and its ability to efficiently dissociate H_2 into atomic hydrogen. These unique attributes are why membranes comprised of palladium and its alloys membranes dominate academic and industrial research [4,5]. While these properties make Pd an attractive H_2 separation material, its extremely high and volatile cost constrains widespread deployment of these technologies. Furthermore, to make cost effective and high permeance Pd membranes, films of Pd less than 20 microns in thickness are required, which are prone to defects and pinholes leading to lower purity hydrogen [6].

The group-V transition metals (V, Nb, and Ta) have theoretically higher atomic hydrogen permeability than Pd [7], a feature that has been demonstrated experimentally in a number of systems [8,9,10,11]. The high permeability of these metals is attributed to their more open BCC lattice structure that allows for greater hydrogen solubility and more rapid diffusion. Additionally, the costs of these metals are more than an order of magnitude lower than that of pure Pd. Because of the high H_2 permeability and low cost of these BCC metals, thicker layers and cold rolled foils can be used which are mechanical robust and offer infinite selectivity.

The challenge with these metals comes from the fact, that unlike Pd, they have little or no ability to catalytically dissociate H_2 into atomic hydrogen, the state in which it can be transported through the BCC lattice [12]. To overcome this limitation films of various H_2 dissociation catalysts can be added to the feed and permeate surfaces of these BCC transition metals to facilitate hydrogen dissociation and recombination [13,14]. Thin films of Pd of varying thickness have been investigated for these purposes using different methods of deposition [9,10,11]. Commonly used techniques for application of Pd include physical vapor deposition methods such as sputtering [15] or solution approaches such as electro- or electroless plating [4]. The group V metals tend to form a native oxide, which impedes hydrogen transport, so special precautions such as chemical or ion etching must be taken before deposition of a catalyst layer [9,16].

There are two failure modes for Pd/BCC composite membranes that are commonly reported. At temperatures below 350°C hydrogen embrittlement can occur, causing these membranes to break [17,18]. Hydrogen embrittlement at low temperature is thought to be due to the increase solubility of hydrogen in each of the BCC metals at low temperature. To mitigate these effects alloys have been prepared that reduce the solubility of hydrogen in the membrane material and limit embrittlement [14,19,20]. Above 350°C membrane failure mechanisms are due to a loss of catalytic activity through mechanisms such as Pd interdiffusion with the BCC metal [16,21] or Pd agglomeration and fragmentation [11,22,23,24,25]. While this work has furthered the possibility of using group V transition metal-based membranes in an industrial setting, most reports have focused on a single metal, and making direct comparisons among the three metals somewhat difficult. Further complicating comparisons is the significant variability in both the thickness of the Pd catalyst layer and its method of deposition, as well as the conditions used

during permeation testing. Furthermore, while the work of Buxbaum [9,10], Rothenberger [11], Peachey [16] and other have all achieved high permeability using these metals, the reported values have fallen short of the theoretical permeability of these materials as calculated by Steward in 1986 [7].

Herein we report direct side-by-side comparisons of Pd coated V, Ta, and Nb membranes all exposed to the same conditions with identical catalyst layers. Electron microscopy and compositional analysis performed before and after membrane testing are used to investigate the mechanisms involved in degradation. It is shown that each material closely approached the theoretical limits of permeability, but displayed very different stability behavior.

2. Experimental

2.1 Membrane fabrication

BCC composite membranes were fabricated from free standing foils of cold rolled vanadium (50 micron thickness, 99.9% purity), tantalum (100 micron thickness, 99.9% purity), and niobium (100 micron thickness, 99.98% purity) purchased from ESPI metals. The difference in thickness was due to the mechanical strength of the materials. As discussed below, the Ta and Nb-based membranes undergo mechanical deformation during H₂ permeation testing. Membranes fabricated from 50 μm foils would often break, an issue that was resolved by using 100 μm foils. In contrast, the V membranes undergo no visible deformation and are mechanically quite robust so 50 μm foils were used to maximize permeance. 100 nm Pd catalytic layers were deposited using an AJA Orion sputtering system. This layer thickness was chosen to provide efficient catalytic activity but not pose any significant transport resistance. Native oxides were first removed from the BCC surface via a pre-deposition *in situ* Ar sputter treatment. This was

accomplished by applying 100 W RF power to the substrate susceptor, which produced a plasma with an approximate 490 V DC bias. The 100 nm thick Pd catalytic layer was subsequently deposited without breaking high vacuum via DC sputtering by applying a 0.1 A current to a 2 in. diameter Pd target, which an applied voltage of 300 V. The distance between the Pd target and the rotating BCC metal substrate was fixed at 8 cm and the resulting deposition rate was 7 nm/min as determined by profilometry. Samples were then removed from the sputter system, turned over, and the process was repeated to form symmetric composite membranes.

2.2 *H₂ permeation measurements*

The fabricated membranes were sealed in commercial VCR fittings leaving an exposed area of 0.93 cm². Membranes were heated to 500 °C at 2 °C/min under ultra high purity He to avoid H₂ embrittlement. The membranes were then tested at 500 °C by delivering pure H₂ gas (99.9%) to the feed side of the membrane. The temperature of 500 °C for testing was selected for two reasons. First, this temperature is high enough to minimize issues related to hydrogen embrittlement. Second, it is known that interdiffusion between BCC metals and Pd becomes significant at $T > 400\text{ }^{\circ}\text{C}$ [26], and this temperature combined with the use of relatively thin Pd layers allowed membrane failure to be documented within reasonable time scales. The feed pressure was kept between 5 and 10 psig via a back pressure regulator located in the retentate line. Permeate flow was collected at ambient pressure and measured using a digital bubble flow meter. Membrane selectivity was periodically checked by applying a pure He feed gas at 10 psig. For all membranes discussed no leaks were detected, and thus the selectivity was found to be infinite.

2.3 *Microscopy and compositional analysis*

All membranes were characterized before and after permeation testing using a JEOL JSM-7000F field emission scanning electron microscopy (FESEM) to assess changes in surface morphology. Elemental composition was measured via EDAX electron dispersive X-ray spectroscopy (EDS). Compositions were measured at accelerating voltages of 10 and 15 kV, which have different penetrating depths and help to infer differences between the near surface and bulk compositions.

3. Results

3.1 *Permeability Measurements*

After heating to 500 °C in helium the membranes were exposed to pure H₂ and the permeate flow rate was recorded as a function of time until its value dropped below the detectable threshold of 0.1 sccm. **Fig. 1** plots the experimental permeability determined from these experiments versus time for each Pd/BCC membrane as well as the theoretical permeabilities of each BCC metal calculated by Steward [7]. The experimentally determined permeability for a cold rolled 25 micron thick Pd₇₅Ag₂₅ alloy foil at 500 °C is also included for comparison. The experimentally achieved PdAg permeability is consistent with previous literature and validates our experimental design [27]. All three Pd/BCC composites displayed qualitatively similar behavior. Initially the flux increased and shortly after the start of testing (<2 hours) the permeability of all three membranes approached their theoretical limit and then began to decline at varying rates. The experimentally achieved values for both permeability and permance are summarized in **Table 1**. All samples closely approached the theoretical limit (89 – 99%).

The H₂ permeabilities for Pd/group V transition metal composite membranes at 500 °C are significantly greater than those previously reported. Literature H₂ permeability values for Pd/V

membranes range from 11% [9] to 41% [28] of theoretical expectations at temperatures in the range of 350– 500 °C. For Pd/Nb membranes the reported H₂ permeabilities in the same temperature range is 30% [23] to 70% [9] of theoretical for flat substrates and 74% of theoretical for tubular substrates [10]. Likewise, Pd/Ta membranes have been shown to have permeabilities 4% [16] to 66% [11] of theoretical for flat substrates, and 62% of theoretical for tubular substrates [10]. There are a couple reasons for the improved values obtained in this study. First, the presence of BCC-oxides can provide significant hydrogen transport resistance as well, but our method of *in situ* high vacuum oxide removal and subsequent Pd deposition avoids this problem. Second, the thickness of the Pd catalyst layers is quite thin (100 nm), which provides sufficient catalytic ability to dissociate H₂ while not introducing a significant barrier to atomic hydrogen transport.

Figure 1. Experimental permeability vs. time at 500°C for Pd/BCC membranes compared with theoretical permeabilities of each BCC metal and experimentally achieved permeability for a 25 micron Pd₇₅Ag₂₅ cold rolled foil.

The maximum H₂ permeance values for each of the Pd/BCC membranes and for the PdAg foil are also listed in **Table 1**. Impressively, each of the Pd/BCC permeance values exceeds that of the 25 µm PdAg foil, despite the fact that the V foil is two times as thick, and the Ta and Nb foils are four times as thick as the PdAg alloy. The thickness of the PdAg membrane would need to be reduced to 8-9 µm in order to match the impressive permeance achieved in both the Pd/Nb and Pd/V systems. For PdAg films of these thicknesses it becomes cost effective to use an electroless plating method on a ceramic support rather than a cold rolled foil. This type of fabrication method, especially at thicknesses below 10 µm, is prone to defects and pinhole leaks

that decrease H₂ selectivity. Because of this it would be difficult to obtain the combination of high permeance and infinite selectivity observed with the Pd/BCC foils with a PdAg membrane.

Table 1 – Comparison of theoretical [7,27] and experimentally achieved H₂ permeability at 500°C for the membranes evaluated in this work. . Additionally, maximum experimentally achieved H₂ permeance of Pd/BCC composite membranes at 500 °C .

Pd/BCC composite membrane	Achieved permeability (mol-m/m²-s-Pa^{0.5})	Percent of theoretical permeability	Pd/BCC maximum permeance (mol/m²-s-Pa^{0.5})
Pd/V (50 μm V)	1.65x10 ⁻⁷	89.4%	3.31x10 ⁻³
Pd/Nb (100 μm Nb)	2.90x10 ⁻⁷	97.1%	2.90x10 ⁻³
Pd/Ta (100 μm Ta)	1.29x10 ⁻⁷	98.5%	1.29x10 ⁻³
Pd₇₅Ag₂₅ (25 μm)	2.69x10 ⁻⁸	97.5%	1.10x10 ⁻³

As shown in Fig. 1 the three BCC metals exhibited very different stability behavior, reflecting their unique failure mechanisms. Pd/V showed the most rapid decline in performance with undetectable H₂ flow being recorded after only 20 hours. Pd/Ta exhibited somewhat improved stability, displaying permeability to around 48 hours. Pd/Nb had a surprising result in that, while there was a significant decline from its maximum value, the Pd/Nb composite membrane still exhibited relatively high permeability throughout the 168 hours of H₂ permeation testing at 500°C. Next the mechanism of failure for each membrane was investigated via FESEM imaging and EDS compositional analysis before and after permeation testing.

3.2 *Stability of the Pd/V membranes*

Fig. 2 compares the surface of Pd/V before and after H₂ permeation testing. It can be seen that the membrane surface before and after testing is largely unchanged and has the appearance of a cold rolled foil. In addition, no physical deformation of the membrane was observed after testing. **Fig. 3** provides a summary of the composition data obtained from Pd/V membranes

before and after H₂ permeation testing. EDS spectra were taken at 10 and 15 kV to examine the composition at different electron penetration depths. This is illustrated by measurements taken from a membrane prior to testing. The Pd:V ratio measured before testing was 2.05 and 0.52 for accelerating voltages of 10 and 15 kV, respectively. This suggests that at 10 kV the electron beam samples the 100 nm Pd and approximately 175 nm of the underlying V foil. At 15 kV the sample is measured ~4 times deeper into V, or approximately 700 nm into the V foil. After H₂ permeation testing the Pd:V ratio at 10 kV drops substantially to ~0.8, with very similar values observed on both the feed and permeate sides. In contrast, the measured Pd:V ratio at 15 kV was

Figure 2. FESEM images of Pd/V feed side (a) before and (b) after 24 hours of H₂ permeation testing at 500°C. Feed and permeate sides have similar appearance.

Figure 3. Summary of Pd:V and O:V elemental ratios (weight %) as determined by EDS at two accelerating voltages from a Pd/V membrane before and after H₂ permeation testing at 500°C for 24 hours.

essentially unchanged after testing. This indicates that Pd has not been lost from the sample, but that it has migrated into the bulk V foil via diffusion and/or alloying. This finding is consistent with previous reports of Pd-V interdiffusion. Edlund *et al.*[21] observed intermetallic diffusion using cross sectional microscopy analysis of a 25 μm Pd coated 25 μm V composite membrane. In that work the H₂ flux was observed to approach zero within 25 hours of testing, very similar to what was observed here despite using much thicker Pd layers. This work also indicated that V diffuses more readily into Pd than the reverse process. The estimated diffusion coefficient (D) for V into Pd was $8 \times 10^{-11} \text{ cm}^2/\text{s}$ as compared to $D = 1 \times 10^{-11} \text{ cm}^2/\text{s}$ for Pd diffusing into V. Additionally, Edlund and coworkers [21] hypothesized that the alloying of Pd-V could make

complexes that reduce the permeability of hydrogen. Buxbaum *et al.* also reported interdiffusion as the primary cause of Pd/V membrane degradation using 2 mm thick V disks electrolessly coated with 1-2 μm of Pd [9].

The other significant change observed after permeation was the appearance of significant quantities of oxygen. Two potential contamination sources were considered. Oxygen could originate due to impurities in the foil or from the industrial grade H_2 that was used for permeation testing. We have accumulated a good deal of experience with V foils through our work developing composite membranes employing Mo_2C as the catalyst layer [12,13]. Though high permeability has been achieved, at times results have been inconsistent and the quality of the foils has been questioned. Moreover, as-received foils with nominally identical purity can vary substantially in visual appearance from shiny to dull grey, and it is suspected that oxygen impurities are responsible for such variability. **Table 2** shows the melting points of V, Nb, Ta and their associated oxides [29]. These BCC metals are somewhat unique in that their oxides melt at much lower temperatures. In particular, it is noted that the melting point of V_2O_5 is very low, and if present, it is expected to be very mobile at the membrane testing temperature of 500 $^\circ\text{C}$. Further evidence suggesting that oxygen originates in the foils is provided by EDS analysis. Though the differences are not great, in every sample tested the O:V ratio was greater when measured at 15 kV as opposed to 10 kV. If oxygen was predominantly supplied from gas-phase impurities one would expect its concentration to be higher in the near surface region. The presence of oxygen in the foil may also explain why the maximum permeability obtained with V relative to its theoretical potential was lower than the Ta and Nb-based composites (~89 vs. ~98%). However, gas-phase impurities cannot be completely ruled out as a source of oxygen.

As discussed below, significant oxygen was also detected on Nb-based membranes after H₂ permeation testing, but in this case the oxygen was concentrated at the surface.

Table 2. Melting points of the BCC elements and their associate oxides [29].

Material	V	V ₂ O ₅	Nb	Nb ₂ O ₅	Ta	Ta ₂ O ₅
Melting Point (°C)	1917	690	2468	1520	2946	1872

3.3 Stability of the Pd/Ta membranes

Fig. 4 compares the Pd/Ta surface before and after testing. The appearance of the untested Pd/Ta surface is that of a cold rolled foil, as expected (**Fig. 4a**). After 72 hours of H₂ permeation testing the membrane was removed from the system and found to be intact, but that the membrane was bowed towards the feed side, as shown schematically in **Fig. 4b**. This is interesting in that the Ta deformed *against* the imposed pressure gradient. Hydrogen absorption in metals causes volume expansion of the metal host lattice. In our permeation setup where the thin films are clamped it creates a biaxial stress state: lateral film expansion is suppressed, creating large compressive in-plane stresses that can increase by several GPa with increasing hydrogen content [30]. This bowing influenced the morphology of the Pd/Ta membrane after permeation testing, as observed in micrographs of the permeate and feed side shown in **Figs. 4c** and **4d**, respectively. In both cases the surface is significantly rougher after testing, and there are areas of partial Pd delamination, as confirmed by EDS, although Pd still covers most of the membrane surface. The degree of roughening/delamination is more pronounced on the feed side of the Pd/Ta membrane. This asymmetry is consistent with the observed deformation described above, which places the feed surface under tensile stress and the permeate surface under

compressive stress. These results suggest that the former is more detrimental to the integrity of the Pd film.

Figure 4. FESEM images of the Pd/Ta membrane surface (a) before testing; (b) a schematic diagram of deformation observed after testing; (c) the morphology of feed side after H₂ permeation; (d) the morphology of permeate side after H₂ permeation.

The EDS determined ratios of Pd:Ta and O:Ta before and after testing are summarized in **Fig. 5**. The data presented are from the feed side, but nominally identical results were obtained from the permeate side. This would suggest that the morphological differences discussed above are due to mechanical stress and not chemical in origin. In stark contrast to V, negligible oxygen is observed in these membranes, indicating that little oxide diffusion or gettering occurs in the Pd/Ta system. However, like Pd/V, the issue of Pd interdiffusion and alloying remains. The Pd:Ta ratio in the near surface region (10 kV) decreased significantly after testing, while at 15

kV the Pd:Ta ratio remained relatively constant, indicating that Pd interdiffusion and alloying is also significant in this material system.

Figure 5. Summary of Pd:Ta and O:Ta elemental ratios (weight %) as determined by EDS at two accelerating voltages from a Pd/Ta membrane before and after H₂ permeation testing at 500°C for 72 hours. The data presented are from the feed side, but nominally identical results were obtained from the permeate side.

The results described above are consistent with most previous accounts of Ta behavior in literature. Peachey *et al.* observed Pd-Ta interdiffusion via Rutherford backscattering spectroscopy when testing at temperatures between 300 and 400°C using 12 μm Ta foils sputter coated with 1 μm of Pd on each side [16]. Peachey and coworkers continued to see permeation over the course of two days, but noted that longer term use would become problematic due to the rate of Pd-Ta interdiffusion. Additionally, Buxbaum *et al.* reported interdiffusion in Pd/Ta

membrane systems [9]. In this case Buxbaum used 2 mm thick Ta planar disks with electrolessly deposited Pd films of 1 to 2 μm thickness. They found that these membranes did not degrade significantly over the course of 67 hours of testing at temperatures in the range of 350 -415 $^{\circ}\text{C}$ [9]. These authors suggested that Ta was the most promising of the three group V transition metals because of its relatively low hydrogen solubility, which lower the risk of hydrogen embrittlement. Unlike the results of Peachey and Buxbaum, Rothenberger *et al.* reported that the primary mechanism for Pd loss in Pd/Ta membranes over 49 hours at 500 $^{\circ}\text{C}$ was delamination of the Pd catalyst layer and not interdiffusion [11]. This was found using 1 mm Ta disks that had been sputter cleaned and coated with 1.2 μm of Pd. Under the conditions examined here it appears that both mechanisms contribute to loss of permeability.

It should be noted that of the three BCC metals Pd/Ta seemed to be the most prone to breaking upon heat up and pressure changes. Ta foils of thickness 50 microns or less frequently during the initial heat up to 500 $^{\circ}\text{C}$ under UHP He. Furthermore, despite its lower solubility it was observed that 50 μm Ta foils that survived heating were highly prone to H_2 embrittlement, and would turn into a dusty white powder when exposed to hydrogen pressures above 20 psig. The use of thicker 100 μm Ta foils resolved this issue for the conditions explored in this work.

3.4 Stability of the Pd/Nb membranes

Of the three Pd/BCC composites Pd/Nb showed the most promising result in that after an initial decrease in permeability, failure did not occur, and permeation began to stabilize with significant H_2 flowrates observed throughout the duration of testing (1 week). As expected the changes in morphology and composition after testing were significantly distinct from either V or Ta. The FESEM image shown in **Fig. 6a** indicates that like the other Pd/BCC membranes Pd/Nb has the appearance of a smooth, cold rolled metal foil prior to permeation testing. In contrast to Ta, it

Figure 6. FESEM images of the Pd/Nb membrane surface (a) before testing; (b) a schematic diagram of deformation observed after testing; (c) the morphology of feed side after H₂ permeation; (d) the morphology of permeate side after H₂ permeation.

was observed that the Pd/Nb membrane deformed towards the permeate side during testing as illustrated schematically in **Fig. 6b**. Significant Pd delamination was observed after permeation testing as shown in **Figs. 6c** and **6d** for the feed and permeate surfaces, respectively. On both sides there were large areas of Nb exposed that were originally covered by a uniform layer of Pd. This creates surface roughness that is visually apparent when the sample is removed from the testing apparatus. Consistent with the Ta results, the surface under tensile stress (permeate side) experienced more delamination than the surface experiencing compressive stress (feed side).

Though difficult to quantify precisely, it was clear that less than half of the Pd remained on the permeate side while the majority of the surface of the feed side remained covered by Pd. Such buckling behavior has been recently reported for niobium hydrogen films, and this phenomenon has been associated with the formation of the hydride phase [31].

Similar delamination behavior was reported in previous experiments of Pd-coated Nb membranes. Busnyuk *et al.* observed that Pd sputtered films of thickness 25, 250 and 1000 nm on 100 μm Nb foil will delaminate, but are unlikely to interdiffuse at 600°C [22]. These results are in partial contrast to Sasaki *et al.*, who reported both cracking and Pd-Nb interdiffusion in a 200 nm Pd sputter coated 0.5mm 95mol%Nb-5mol%W foil [23]. Sasaki *et al.* assessed this via heating Pd coated Nb in an inert environment to 500°C while *in situ* monitoring Pd deformation via TEM and Pd-Nb interdiffusion via cross sectional EDS. Moreover, Sasaki and coworkers saw hydrogen permeability initially start at around 66% of theoretical pure Nb, but fall to nearly zero within one day. Alimova *et al.* also observed Pd-Nb interdiffusion, but only at 600°C, whereas at 500°C no interdiffusion was observed [24]. This was found using a membrane consisting of 100 μm Nb foil sputter coated with 2 μm Pd.

The compositional results for Pd/Nb before and after testing are summarized in **Figure 7**. In this case scans were taken feed side, where it was easier to obtain data from regions with and without Pd present. The first observation is that in the Pd-coated regions the Pd:Nb ratio is essentially unchanged before and after H₂ permeation testing at both the 10 and 15 kV accelerating voltages. This indicates that Pd alloying or diffusion into Nb is not occurring over the time scales tested, which is consistent with previous literature [22,24]. As expected no Pd is detected in regions where delamination occurred. This suggests that the observed decline in

permeability is due to the reduced surface area available for catalytic dissociation/ recombination of H_2 .

Figure 7. Summary of Pd:Nb and O:Nb elemental ratios (wt. %) determined by EDS for a Pd/Nb membrane before and after H_2 permeation at 500°C for 168 hours. Data after permeation testing was obtained from regions with and without Pd present (Fig. 6).

The second interesting feature of Pd/Nb was that significant O accumulation was detected after permeation testing. Moreover **Fig. 7** shows that the measured O:Nb ratios are significantly greater at lower accelerating voltages, indicating that the oxygen content is localized on the surface of the membrane. This is in contrast to V, where the opposite behavior was observed, suggesting that in the Nb case O is due to impurities in the feed stream. It is also observed that

the oxygen content is greater in regions where Pd is present, further supporting the idea that oxygen originates from impurities in the gas-phase, and that the mechanism for introduction is catalytic dissociation. This is consistent with gravimetric measurements of a Pd/Nb membranes at elevated temperature in an oxygen environment, which showed that thin Pd films enhanced the rate of oxygen gettering [22].

4. Discussion

The results presented here combined with the previous literature provide a more complete understanding of the behavior of Pd/BCC metal membranes. It is apparent that there is no one Pd/BCC membrane system that is ideal for H₂ separations, but rather each individual Pd/BCC system has strengths and weaknesses that may be exploited dependent upon the particular application. The Pd/V system displayed the most impressive mechanical properties of the three Pd/BCC systems in that there were no difficulties experienced in heating up and cooling down a 50 μm foil, and that this foil could withstand pressure gradients of over 100 psi without any evidence of deformation. The use of thinner foils allowed for Pd/V to have the highest permeance of the three Pd/BCC membranes, achieving a maximum of $3.31 \times 10^{-3} \text{ mol/m}^2\text{-s-Pa}^{0.5}$. The drawback of course is that Pd/V was the least stable chemically. Vanadium was prone to oxidation, likely due to impurities in the foil, as well as Pd-V interdiffusion. These issues would need to be resolved in order to move forward to practical applications. Insertion of a diffusion barrier between the Pd and V foil is a proven strategy to prevent alloy formation [21], but this typically involves a tradeoff between reduced permeability and improved stability. The issue of oxidation susceptibility is an intrinsic issue that may require improved control during the production of V foils.

The advantage of Ta is that it appears exceptionally resilient to oxidation, which may prove advantageous for application in an oxidizing environment such as purification of a water gas shift stream. However, like the Pd/V system it was also prone to interdiffusion and alloying, suggesting the need for a diffusion barrier for application at elevated temperature. Pd/Ta also showed issues with delamination; however, thicker films of Pd may mitigate this problem. Rothenberger *et al.* showed that electroless Pd coatings of 1 μm could withstand high temperatures of up to 900°C without delamination or surface fouling, however this resulted in a significant decrease in permeability to around 7% of theoretical [11]. Additionally, Pd/Ta was observed to have the poorest mechanical properties of the group V transition metals, easily prone to breakage during heat-up or due to hydrogen embrittlement.

Of the composites examined in this work the Pd/Nb system was perhaps the most promising. Not only did it achieve a permeability of $2.9 \times 10^{-7} \text{ mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}^{0.5}$ and a permeance of $2.9 \times 10^{-3} \text{ mol}/\text{m}^2\cdot\text{s}\cdot\text{Pa}^{0.5}$ for a 100 μm foil, but it also showed no signs of Pd-Nb interdiffusion and retained relatively high permeability was observed over the course of 168 hours. The primary loss mechanism appeared to be delamination of the Pd due to mechanical stress induced by deformation. In principle this issue may be resolved through the use of mechanical support or alternative geometries such as cylinders. Oxygen was observed to accumulate on the Pd surface, presumably from gas-phase impurities, which may be problematic in oxidizing environments such as steam reforming. However, further testing needs to be conducted to better understand the impact of impurities on permeability. Nevertheless for this reason a Pd/Nb system may be more applicable for producing high purity, high throughput H_2 rather than membrane reforming. With an infinite selectivity and high permeance, the Pd/Nb system could work very well creating the ultra high purity hydrogen required in a variety of applications such as semiconductor processing

or polymer electrolyte membrane fuel cells. Lastly, there is significant ongoing work to develop BCC-based alloys that display improved properties over the elemental metals discussed here [14,32]. It is suggested that experimental approach described here would be an effective tool to screen the potential of new alloys for use as H₂ separation membranes.

5. Conclusions

Composite membranes consisting of 100 nm of Pd on both sides of dense BCC metal foils (V, Ta, Nb) were permeated with pure H₂ gas at 500 °C. These membranes displayed experimental permeability values which approached the theoretical limit calculated by Steward, with Pd/V, Pd/Nb, and Pd/Ta achieving 89%, 98% and 99% of the theoretical permeability for the respective metals. V membranes failed rapidly due to a combination of Pd dissolution and oxidation as shown through microscopy and compositional analysis. It is suggested that oxygen impurities in the V foil migrate to the surface during permeation testing. Ta membranes displayed little evidence of oxidation but greater care was required to prevent membrane failure due to mechanical stress and/or H₂ embrittlement. These membranes failed within 48 hours, which was attributed to dissolution of Pd. Pd/Nb membranes exhibited high H₂ flux/permeability during 168 hours of H₂ permeation testing. It was observed that Pd did not alloy with Nb but experienced partial delamination, which reduced flux through the loss of active area for H₂ dissociation/recombination. An increase in surface oxide content was also observed after H₂ permeation, suggesting gettering gas-phase impurities, and this may also have contributed to the decrease in permeability with time. The permeance of these membranes was shown to be up to 3x greater than the industry standard 25 micron Pd₇₅Ag₂₅ alloy membrane despite their thicknesses of 50 – 100 microns. Strategies are suggested that **may** assist the further

development of these systems, such as the use of tubular supports to reduced catalyst delamination, and the use of diffusion barriers to reduce catalyst-BCC interdiffusion.

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Graphical Abstract

Figure 1

Figure 2

Figure 3

Figure 4

(b) Schematic of membrane deformation

Figure 5

Figure 6

Figure 7