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ALTERNATIVE MATERIALS TO PD MEMBRANES FOR HYDROGEN PURIFICATION

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ABSTRACT

Development of advanced hydrogen separation membranes in support of hydrogen production processes such as coal gasification and as front end gas purifiers for fuel cell based system is paramount to the successful implementation of a national hydrogen economy. Current generation metallic hydrogen separation membranes are based on Pd-alloys. Although the technology has proven successful, at issue is the high cost of palladium. Evaluation of non-noble metal based dense metallic separation membranes is currently receiving national and international attention. The focal point of the reported work was to evaluate two different classes of materials for potential replacement of conventional Pd-alloy purification/diffuser membranes. Crystalline V-Ni-Ti and Amorphous Fe- and Co-based metallic glass alloys have been evaluated using gaseous hydrogen permeation testing techniques.

INTRODUCTION

Hydrogen separation and purification has been identified as a bottleneck in the development of advanced hydrogen fuel technologies. Many techniques for hydrogen separation are in use or are currently being investigated, such as cryogenic separation, pressure swing adsorption, catalytic purification and selective diffusion. As a result of its high hydrogen permeability, good mechanical characteristics and highly catalytic surface, which dissociates hydrogen rapidly, palladium is still the membrane material of choice for many applications. Unfortunately, palladium and its alloys are extremely expensive, roughly twice the cost of gold, making them impractical for large-scale or distributed applications. Therefore, an economically feasible, palladium-based, commercial scale system would require a significantly reduced amount of palladium, which can be accomplished by techniques such as thin palladium membranes supported on porous substrates or highly permeable bulk substrates. The high cost of palladium has turned the attention of researchers to palladium-free membrane technologies, such as cermets and ceramics for high-pressure, high-temperature applications.

The current generation of gas purification/separation membranes is based on Pd/Pd-alloy used either independently or in conjunction with porous ceramic supports. Palladium/Palladium alloys have been known to possess the ability to dissolve a considerable volume of hydrogen and to demonstrate increasing permeability with increasing pressure differential and temperature. However, the major drawbacks to their industrial use are high cost for Pd, relatively low flux, and that during cycling above and below a critical temperature an irreversible change takes place in the palladium lattice structure which can result in significant damage to the membrane. Palladium coated ceramic membranes offer the potential for extended temperature range operations but suffer from the fatal flaw of "pinhole" short circuit paths. Any "pinholes" in the Pd-catalytic film on the surface of the ceramic substrate will potentially allow contaminant/intermediate species to pass directly through the membrane thus effectively reducing the purification factor of the membrane. Recent efforts in the hydrogen purification/separation membrane community have focused on the development and evaluation of non-palladium based membranes that offer a lower cost, high flux, and highly durable membranes to replace Pd-based systems. Group 5A metals such as V, Nb, and Ta are currently being evaluated by numerous researchers and show promising results with respect to hydrogen permeability¹⁻³. However, these metals suffer from severe hydrogen embrittlement and thus are unacceptable for membranes.

Japanese researchers have begun to evaluate alloying additions—Al, Ni, Co, and Mo—to vanadium in hopes decreasing the susceptibility to hydrogen embrittlement^{4,5}.

Crystalline Non-Noble Metal Membranes

The most interesting recent result has been the evaluation of Ni-Ti-Nb alloys for hydrogen permeation⁶. Ni-Ti has long been known as a shape memory alloy but it also possesses good hydrogen solubility and mechanical properties. The major drawback is that hydrogen diffusivity in Ni-Ti is considerably slower than either Pd/Pd-alloy, V, Nb, or Ta. In attempt to enhance the diffusivity, additions of Nb have been made to Ni-Ti alloys and permeation and mechanical stability have been evaluated. The limited study of ternary Nb-Ti-Ni alloy has shown permeation on an order equal to pure Pd and reasonable mechanical stability in hydrogen. Recent work on V-Ti-Ni and Ta-Ti-Ni alloys by the same authors has shown similar results. The permeabilities of the V- and Ta-alloys were not quite as high as either Pd or the previous studied Nb-alloys^{7,8}. This was attributed to the inherent greater permeability of bulk Nb in comparison to V and Ta.

Amorphous Non-Noble Metal Membranes

The development of metallic glasses in bulk form has led to a resurgence of interest into the potential utilization of these materials for a variety of applications. Prior to this development, metallic glasses were produced exclusively in very thin sections by rapid solidification processing in most cases. The subsequent consolidation into something “bulk” frequently led to devitrification and a loss in the desirable properties characteristic of the glass. In fact, the unique properties of metallic glasses — strengths of 1-2 GPa, toughnesses of 30-70 MPa m^{-1/2}, good environmental resistance and unique magnetic properties in some cases — have only been exploited in a few applications where thin sections are desirable (e.g., transformer sheet and magnetic strips for anti-theft tags). An exciting application for these new bulk metallic glass materials is use as membranes for enhancing the efficiency of gas separations both in production processes and for fuel cell usage.

SRNL has previously worked with thin section (melt-spun ribbons) of metallic glass materials for membrane applications, however, with the relatively new ability to cast fully amorphous metallic glasses in bulk sections a new opportunity is opened for bulk metallic glasses (BMG) as hydrogen membranes. The ability to readily cast metallic glass alloys will allow for easier fabrication of membranes—machine thin membranes from larger castings—and will also ease mass production challenges in comparison to thin section (melt spun) metallic glass ribbons. Bulk metallic glass alloys are traditionally processed from multi-component system comprised of metallic species of varying atomic size. It is this vast difference in atomic sizes that results in slow diffusion/redistribution kinetics and allows for deep undercoolings to the point of freezing in the “liquid” structure to produce amorphous metallic alloys at relatively slow cooling rates (10-100 K/s). Figure 1 demonstrates the slower cooling rates that make the formation of a BMG more likely. These metallic glass alloys have been shown to possess high permeation rates. For example the permeation rate for a --Zr-Al-Co-Ni-Cu BMG alloy -- 1.13×10^{-8} mol/m s Pa^{1/2}--is comparable to permeation the rate measured for pure Pd metal. Furthermore, these metallic glass alloys have also been shown to possess high elastic toughness and excellent resistance to hydrogen degradation, i.e., structural changes. Both of these properties—high permeation and high elastic toughness—potentially make these materials attractive for gas separation membranes. In addition to the Zr based BMG, thin foils of Co and Fe based were tested.

The focus of this work is to extend the Nb-Ti-Ni membrane development work with a direct replacement of Nb with V, evaluate the hydrogen permeability of this alloy and four thin foil metallic glasses.

EXPERIMENTAL APPROACH

Sample Preparation

Arc melted buttons of approximately 25 gms each were prepared using a Centorr System VII arc melter system with a tungsten electrode. Arc melting was performed following evacuation to approximately 10^{-4} Torr and backfilled with argon. The V-Ti-Ni alloys were prepared using 99.7%V, 99.95%Ti, and 99.95% Ni raw materials supplied by Alfa-Aesar. The V-Ni-Ti alloy tested as part of this study contained the following alloy composition—53wt%V, 26wt%Ti, and 21wt%Ni. Characterization of the as-cast microstructure was performed using light optical microscopy on polished and etched samples. Scanning electron microscopy and energy dispersive x-ray spectroscopy—including X-ray dot mapping—using a Hitachi S3600 were performed to characterize the phase structure and a alloying element distribution. Disk approximately 12mm in diameter and 0.5-0.75mm in thickness were sectioned from the arc melted buttons and prepared via grinding on SiC papers to provide a 1200 grit finish. Samples, 19 mm diameter and 0.89 mm thick or disks were welded into 2.12" diameter Conflat (CF) flanges. Crevices were seal welded using electron beam welding to minimize the effects of virtual leaks. The sample assemblies were placed in a 1" OD vacuum system fabricated with 2.12" CF flanges. Copper gaskets were used to seal the samples.

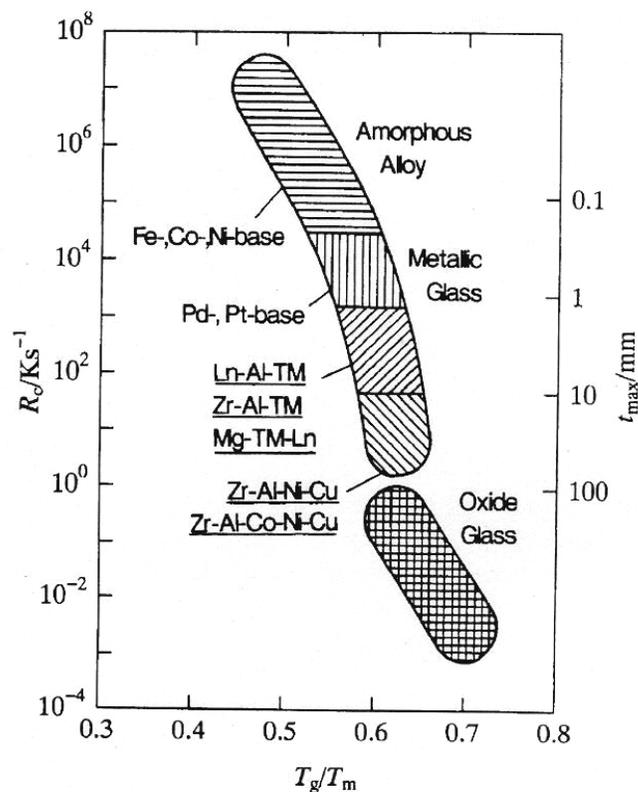


Figure 1. Cooling rate and crystallization temperatures for a variety of metallic glasses⁹, note that modest cooling rates can result in non-crystalline materials for sizeable parts.

A total of four Co and Fe based alloys were procured from a commercial source. Disks were punched from the foil and mounted into VCR vacuum fittings, with a nickel gasket on one surface and the sample in direct contact with the VCR sealing surface on the other. The sample assemblies were leak tested and verified leak tight to 2×10^{-7} sscm He prior to installation in the permeation test apparatus.

GAS PERMEATION TESTING

Hydrogen permeation testing was conducted using the permeation test rig shown in Figure 2. The samples were mounted in the apparatus using copper gaskets, evacuated to at least 1×10^{-6} Torr for a period of at least four hours at room temperature. The samples and support piping were then heated to 100C for 8 to 16 hours to outgas the system and then heated to the final test temperature. A leak rate test was conducted by closing the appropriate valve. If the leak rate was not linear, the sample and support piping were evacuated for additional time, after an acceptable leak rate was obtained, the sample section was evacuated and after at least one hour, the valves were closed and the desired pressure of hydrogen was introduced. It took approximately 2-3 minutes for the pressure to reach the target value. The pressure rise on the low pressure side of the system was monitored. The data were logged at either a ten to 30 second interval. The data were reduced to estimate the diffusivity and permeability.

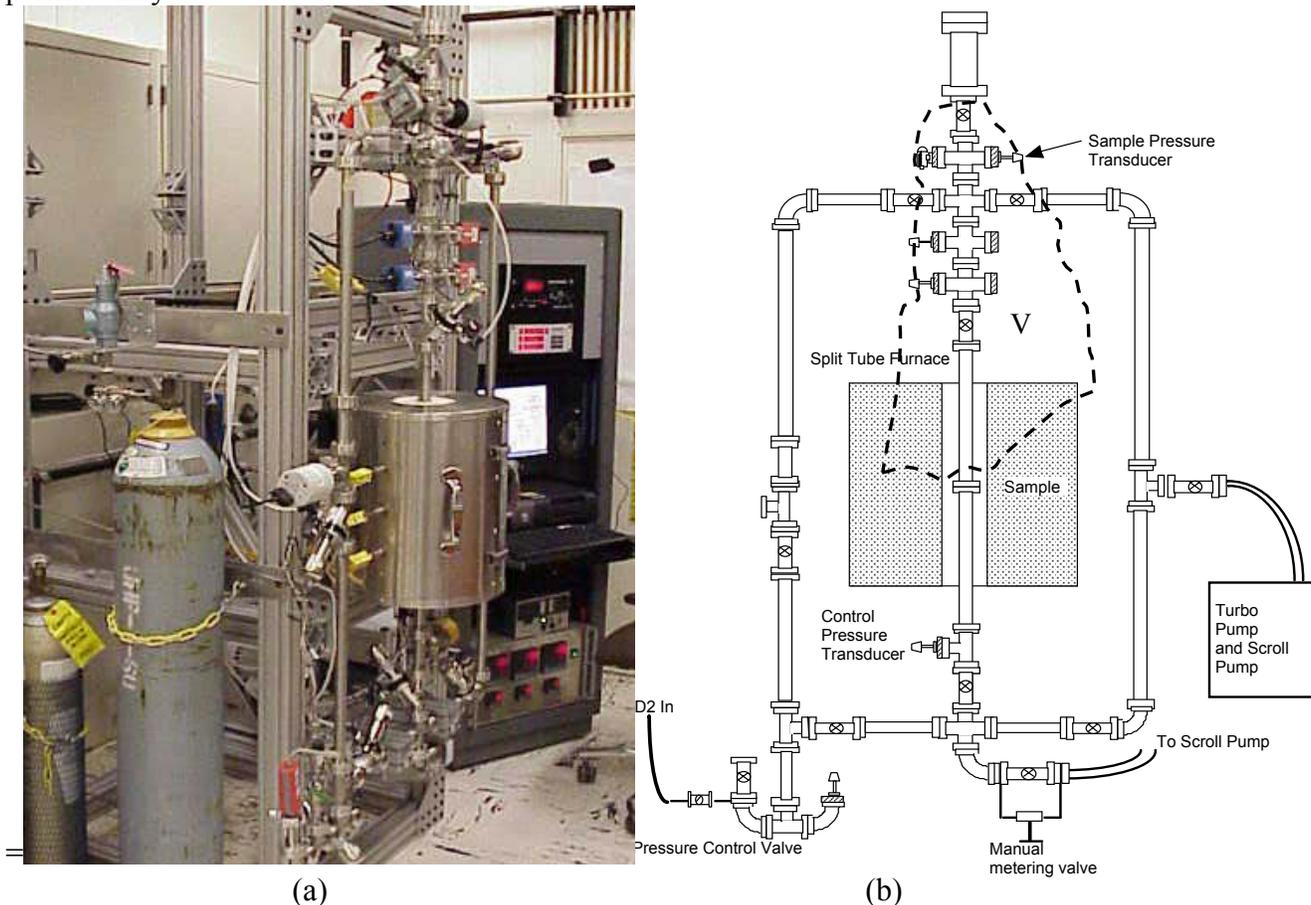


Figure 2. SRNL Gaseous Permeation Test Rig (a) photo and (b) schematic

The raw data were plotted as a function of time. The data exhibit three distinct regions, the background in-leakage region, a transition region, and a steady state region, nearly linear region. The diffusivity (D) was estimated by calculating the slope and determining the x-axis intercept of the linear region using a least squares method. These two experimental variables, in conjunction with the thickness x were then used to determine the lag time (t_l), i.e., the time at which the line crossed the x-axis when the pressure was zero. Lag time, t_l , time was used in the equation:

$$t_l = x^2 / 6 D \quad (1)$$

to determine D . The permeability (Φ) was estimated from the slope (M) of the curve, the system expansion volume (V), the sample area (A), and the test pressure (ΔP) as shown in Eq. 2.

$$\Phi = M * V * x / (A * \sqrt{\Delta P}) \quad (2)$$

The permeability is the product of the solubility (S) and the diffusivity as shown in Eq. 3.

$$\Phi = S * D \quad (3)$$

RESULTS AND DISCUSSION

Microstructure Analysis

Evaluation of the microstructure of the V-Ti-Ni alloy was performed using scanning electron microscopy combined with x-ray mapping of the element constituents. Previous work on Nb-Ti-Ni alloys being investigated for advanced hydrogen separation membrane use has attributed positive results to microstructures consisting of a large primary (P in Fig 3b) $Nb_{83}Ti_{13}Ni_4$ phase surrounded by eutectic (NiTi + NbTiNi) (I in Fig. 3b); $Nb_{83}Ti_{13}Ni_4$ was postulated to be the high diffusivity phase while the eutectic structure contributes to the lack of susceptibility to hydrogen embrittlement [6]. SEM backscattered and secondary electron micrographs of the V-Ti-Ni alloy display a similar microstructure to the Nb-Ti-Ni alloy with a primary phase surrounded by interdendritic eutectic structure—Figure 3. X-ray mapping of the elemental constituents indicated that the primary phase in the microstructure to be high in vanadium content. Additionally, the interdendritic eutectic is rich in Ni and Ti. Semi-quantitative chemical analysis of the composition of the vanadium rich primary phase indicates an approximate composition of $V_{75}Ti_{16}Ni_9$.

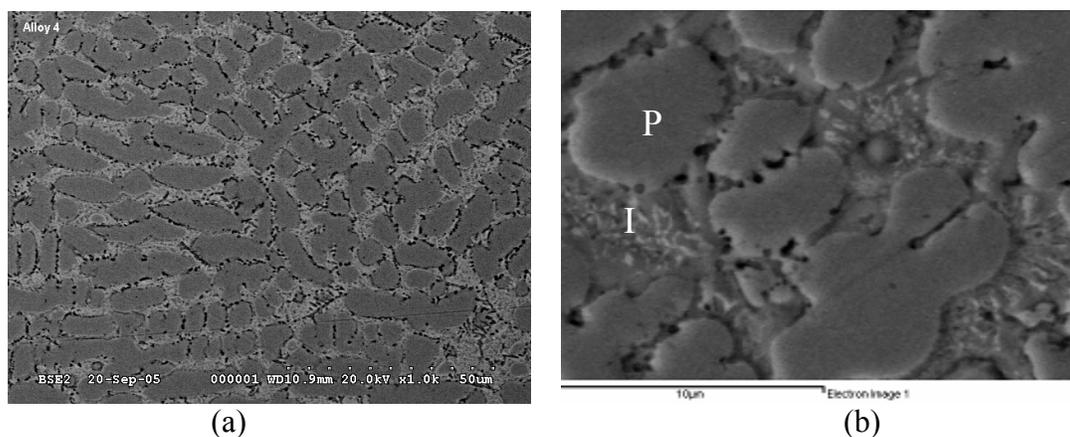


Figure 3. Scanning electron microscope images of a V53-Ti26-Ni21 alloy (a) back-scattered and (b) secondary electron image.

Gaseous Hydrogen Permeation Testing

Measurement of the steady state permeation flux for two crystalline V-Ti-Ni alloys (see microstructure of V51-Ti28-Ni21 and V54-Ti28-Ni18 alloys in Figure 3) and the amorphous metallic glass materials was conducted and compared to literature data for palladium membranes. The testing was conducted under sub-atmospheric pressures but at values typically used at the Savannah River Site for hydrogen isotope purification. A typical raw data curve for sample 3B (V54-Ti28-Ni18) alloy at a temperature of 400°C and pressures of 200 and 400 Torr is shown in Figure 4. While that of sample D2 (V51-Ti28-Ni21) is shown in Fig. 5. The calculated permeabilities from test data collected at 400°C for these alloys are provided in Table I.

Ni-Ti-V 413°C 700T Permeation Test

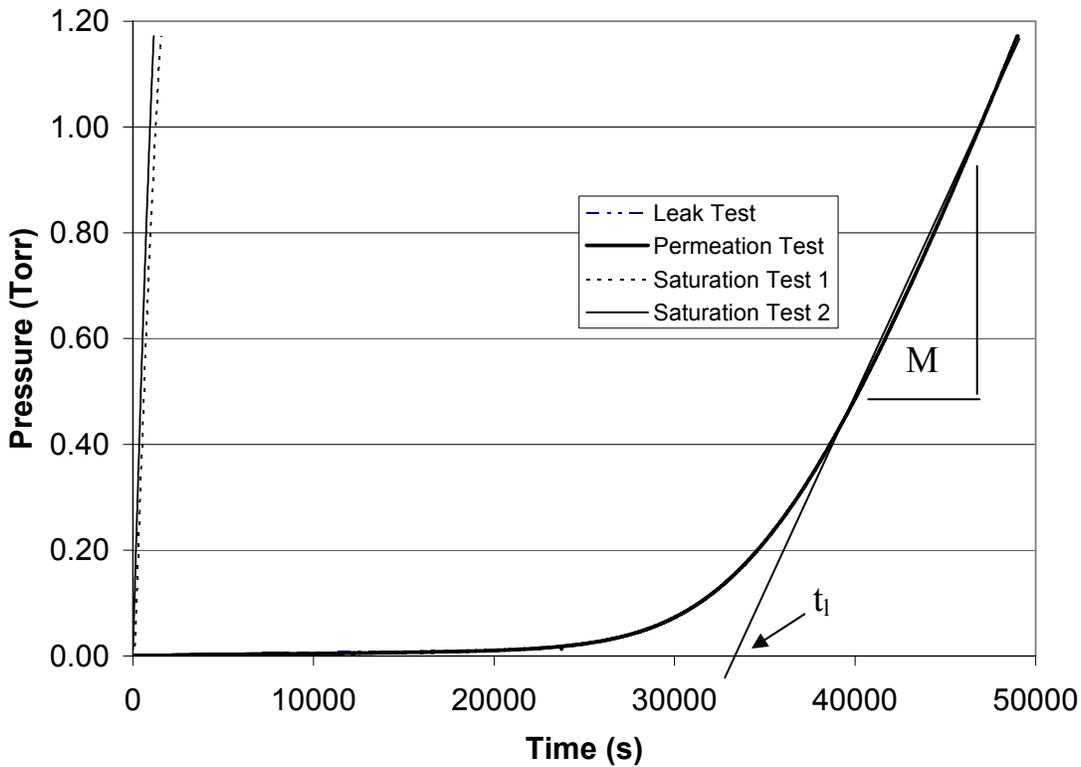


Figure 4. Hydrogen permeation and saturation test data for Sample 3B.

Similar to Pd and Pd-alloy membrane materials the V51-Ti28-Ni21 alloy demonstrated a susceptibility to hydriding when cooled through a critical temperature range in the presence of hydrogen. During testing a system power failure allowed the sample to cool from the test temperature (400°C) to room temperature under hydrogen. During re-start of the system it was determined that the sample has failed and this failed sample was then examined using x-ray diffraction in order to determine the cause of failure. Results from the XRD analysis shown in Figure 6, clearly show the formation of vanadium- hydride phase in this sample which resulted in the subsequent failure of the membrane.

Table I. Permeability values for samples 3B and D2 tested at 400°C

Alloy	Permeability (mol H ₂ m ⁻¹ s ⁻¹ Pa ^{-1/2})*
3B (V54-Ti28-Ni18)	1.26 x 10 ⁻⁸
D2 (V51-Ti28-Ni21)	2.1 x 10 ⁻⁹

*Uncorrected values for system leakage, but leakage was low for these samples.

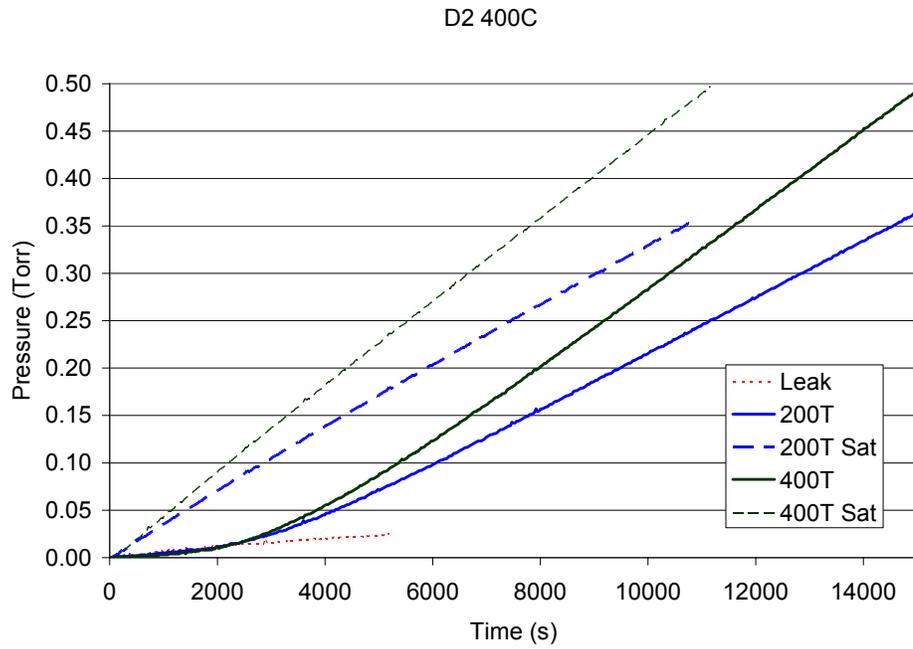


Figure 5. Hydrogen permeation and saturation test data for Sample D2

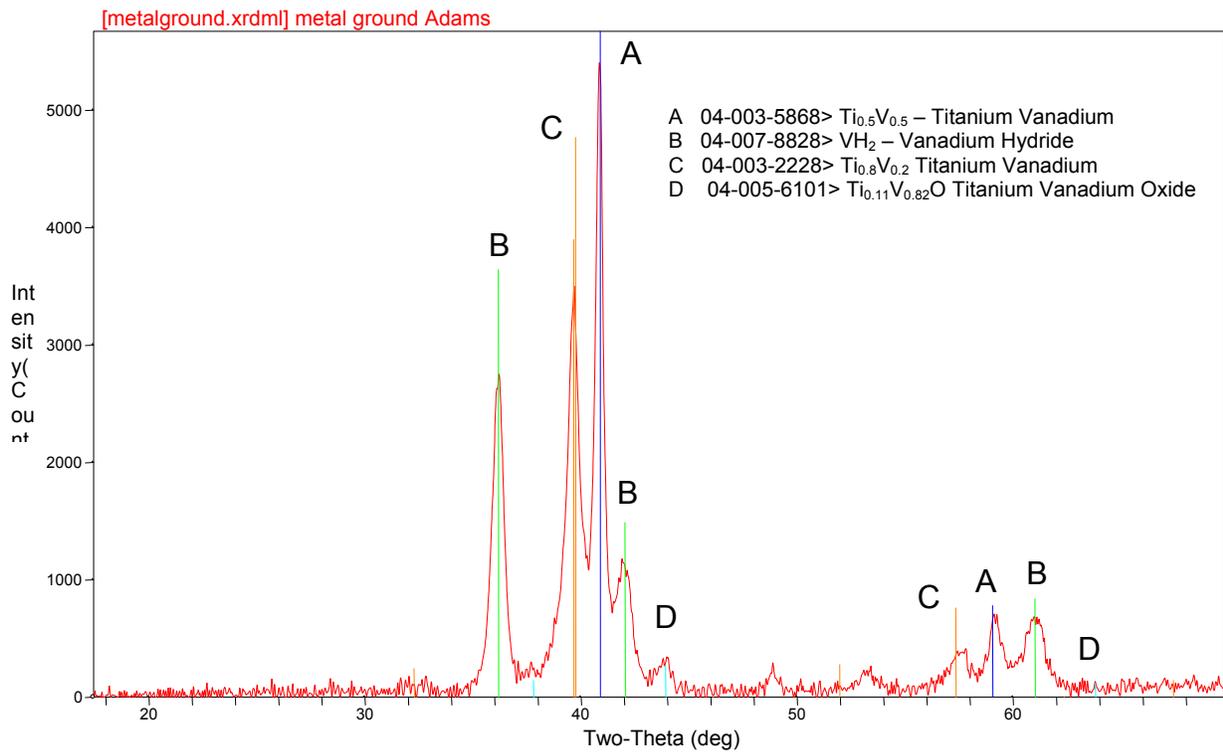


Figure 6. XRD data indicating formation of vanadium hydride on cooling to room temperature under H₂ cover gas.

In addition to the V-based alloys, metallic glass materials have been tested using the same approach, temperature range and pressures. Due to concerns about crystallization of the material, the samples were fixtured in 0.75" diameter VCR fittings using silver plated nickel gaskets rather than being brazed or welded into the fixtures. The samples were verified leak tight to at least 2×10^{-9} sccm He. Four commercial-off-the-shelf (COTS) metallic glass materials tested exhibit a range of permeability and flux within two decades of Pd. The raw data for the four samples at 400C are shown in Figure 7. Due to the low thickness of this sample, approximately $25 \mu\text{m}$, no determination of a lag time was possible. Testing using a mass spectrometer generally indicated hydrogen at or near the saturation levels within the first sampling frequency, which is limited to between seven and 15 seconds for the instrumentation used. The data were analyzed using the standard data reduction method and the permeability of this alloy is indicated in Table II. There is no correction for the amount of in-leakage and one can see that the slope of the leak curve is a significant fraction of the total slope.

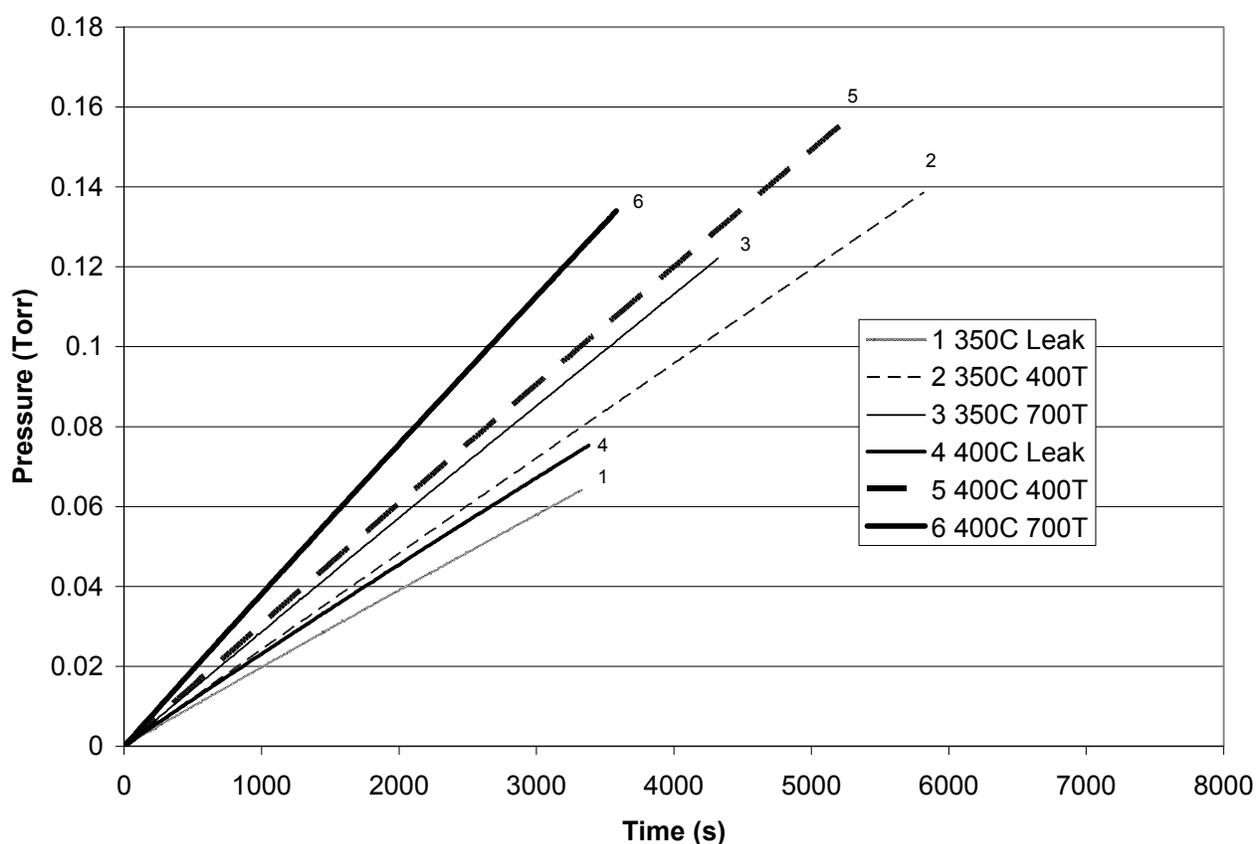


Figure 7. Permeation data for a typical Fe-based MetGlass sample

Table II. Permeability data for COTS metallic glass materials compared to Pd

Alloy	Permeability (mol H ₂ m ⁻¹ s ⁻¹ Pa ^{-1/2})*
Palladium 350°C	1.8 x 10 ⁻⁸
Palladium 400°C	2 x 10 ⁻⁸
MetGlas 12 350°C	1.81 x 10 ⁻⁹
MetGlas 12 400°C	1.94 x 10 ⁻⁹

*Uncorrected values for system leakage, which may be a significant contributor to the slope of the data.

He and H₂ Separation Testing

A Met Glass sample was tested at 400°C with a varying mixture of He and H₂. The desired test gas was introduced into the test chamber and a mass spectrometer was used to monitor breakthrough and gas composition on the test side of the permeation apparatus. The results of the test are shown in Fig. 8. The step pressure changes for the He introduction do not result in He being detected on the sampling side, whereas, when H₂ is introduced a pressure is detected by the mass spectrometers almost immediately.

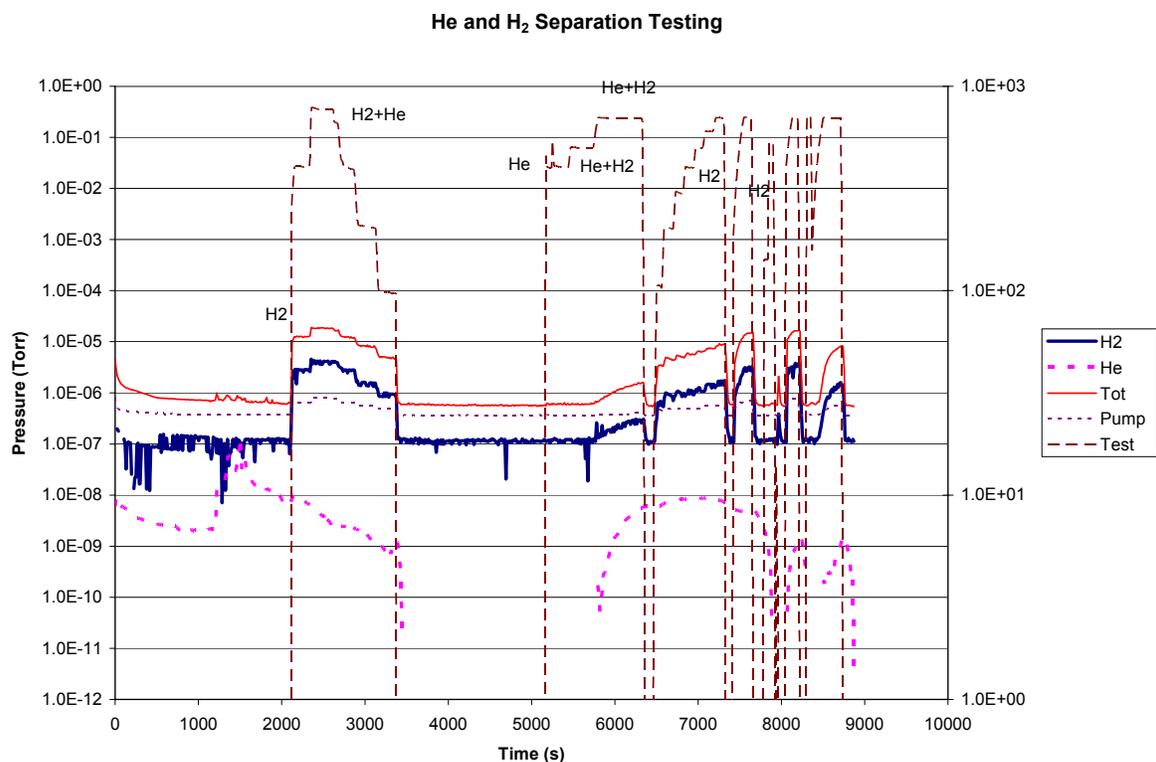


Figure 8. Separation testing of He and H₂ using met glass. Note that the He signal does not change about background when it is present while the hydrogen signal, total system pressure and pump pressure all increase when H₂ + He are introduced.

CONCLUSIONS

V-Ti-Ni alloys and Fe- /Co-Based metallic glasses have been evaluated with respect to hydrogen permeability for potential use in hydrogen purification membrane reactor application. Microstructural characterization of the V-Ti-Ni alloy using SEM has shown similar microstructural features to a previously evaluated Nb-Ti-Ni alloy; namely, the occurrence of a primary phase surrounded by interdendritic eutectic.

Gaseous hydrogen permeation testing of similar V-Ti-Ni alloys once again demonstrated permeabilities on par with commercially available Pd/Pd-alloy membrane materials.

Permeation testing of the Fe-/Co-based metallic glass alloys demonstrated permeabilities slightly lower than Pd/Pd-alloys however, the cost savings afforded by these materials (approximately 650X lower) warrants further study/evaluation of this class of materials.

The Fe-/Co-based metallic glass alloys demonstrated the ability to separate He from H₂ at 400°C.

Additional testing of these membranes is warranted with syn-gas or water shift gas to determine the compatibility with realistic gases that will be present in the hydrogen generation systems.

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