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Hydrogen Permeability of Mulitphase V-Ti-Ni Metallic Membranes

Thad M. Adams* and John Mickalonis
Savannah River National Laboratory, Aiken SC 29803

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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 a Group 5A—Ta, Nb, V—based alloy with respect to microstructural features and hydrogen permeability. Electrochemical hydrogen permeation testing of the V-Ti-Ni alloy is reported herein and compared to pure Pd measurements recorded as part of this same study. The V-Ti-Ni was demonstrated to have a steady state hydrogen permeation rate an order of magnitude higher than the pure Pd material in testing conducted at 22°C.

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 in many applications. Unfortunately, palladium and its alloys are extremely expensive, roughly twice the cost of gold, making them impractical for large-scale 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 allow for 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 permeability[1-3]. 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}.

The most interesting recent result has been the evaluation of Ni-Ti-Nb alloys for hydrogen permeation [6]. 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 a these ternary Nb-Ti-Ni alloy has shown permeation on an order equal to pure Pd and reasonable mechanical stability in hydrogen.

The focal point of this work is to extend the Nb-Ti-Ni membrane development work with a direct replacement of Nb with V. Characterization of the resulting microstructure and measurement of the permeability of the novel V-based alloy is reported.

Experimental Approach

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.

Hydrogen permeation testing was conducted using a Devanathan and Stachurski type-electrochemical apparatus—Figure 1. Permeation testing of V-Ni-Ti alloy was conducted on foils approximately 0.6mm in thickness with an exposed surface area of 0.4 cm^2. The test solution consisted of 0.1M NaOH solution at room temperature. The solution was purged with nitrogen 24 hours prior testing as well as during the test. The electrochemical parameters included a charging current of 100µA/cm^2 on the cathode side and an applied potential of -125mV versus a saturated calomel electrode on the anode side. In an attempt to truly measure the actual permeability of the V-Ni-Ti alloy both sides of the alloy disc were coated with a flash layer of Pd. As a means of comparison Pd foils approximately 0.25 and 0.5mm in thickness have been tested under identical conditions.

Figure 1. Devanathan-Stachurski Electrochemical Hydrogen Permeation Apparatus

Analysis of the electrochemical data provides a measure of the hydrogen flux through the sample by measuring the steady-state current density I_p (A/cm^2) on the anodic side of the cell. This steady state current density can be converted to the steady state hydrogen permeation flux, J_{∞}, (mol/m^{2}s) via equation 1 below.

$$J_{\infty}=I_p/nF \qquad (1)$$

The steady-state hydrogen permeation rate, V, (mol/m s), can be defined according to equation 2

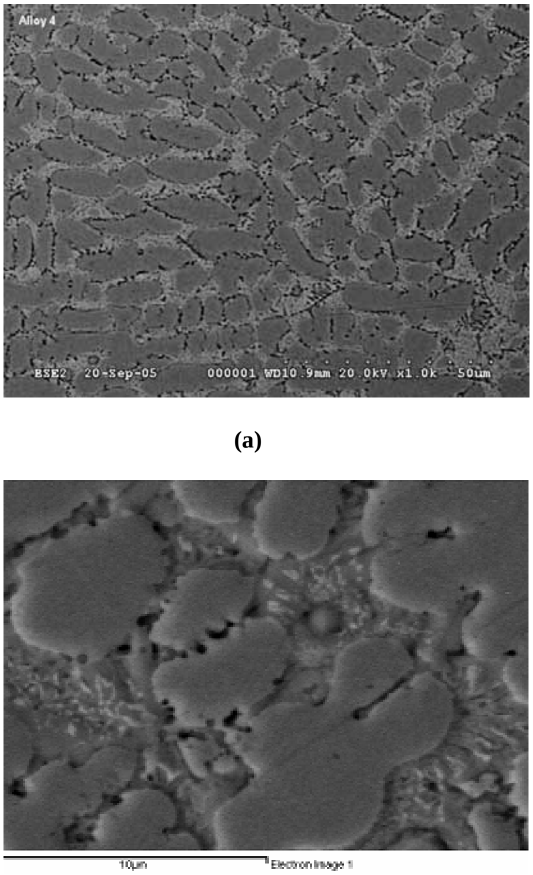
$$V=J_{\infty}L=LI_p/nF \qquad (2)$$

where L is the sample thickness, I_p is the steady-state current density, n is the number of electrons transferred, and F is Faraday's constant.

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 $Nb_{83}Ti_{13}Ni_4$ phase surrounded by eutectic (NiTi +NbTiNi); $Nb_{83}Ti_{13}Ni_4$ 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 2. X-ray mapping of the elemental constituents provided in Figure 3 shows 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 $V_{75}Ti_{16}Ni_9$.



(a)

(b)

Figure 2. Scanning Electron Microscope Images of a V53-Ti26-Ni21 Alloy (a) Back-scattered and (b) secondary electron image.

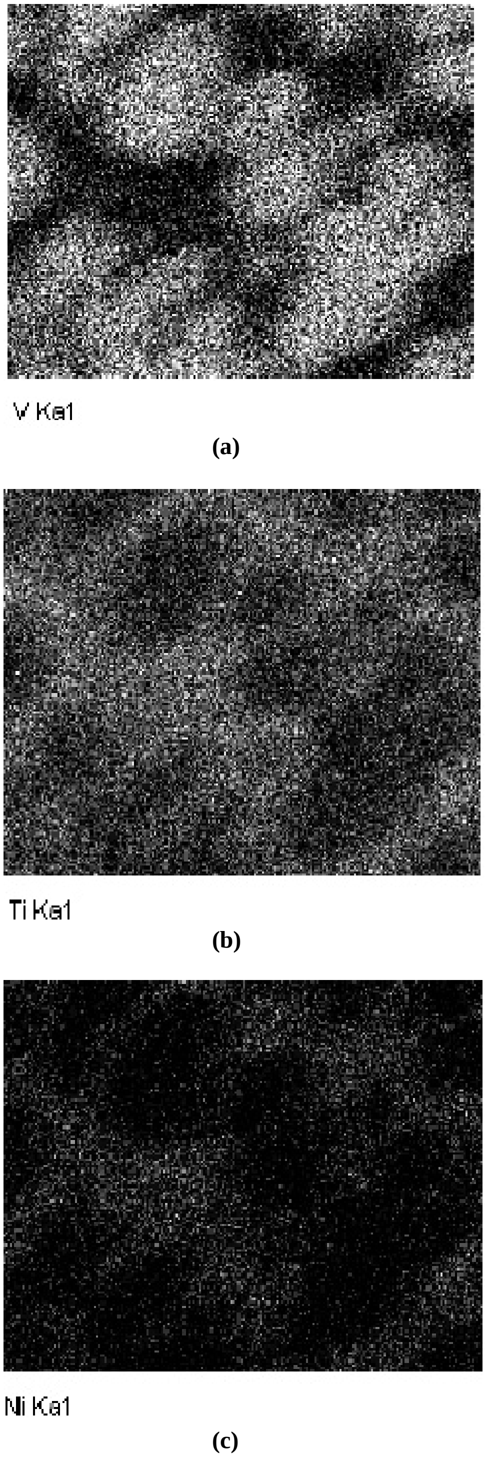


Figure 3. X-ray Mapping of Elemental Constituents within the micrsotructure of a V53-Ti26-Ni21 membrane alloy: (a) V-Kα1 map, (b)Ti Kα1 map, and (c) Ni-Kα1 map.

Electrochemical Hydrogen Permeation

Measurement of the steady state hydrogen permeation flux and rate was conducted and compared to measured values for pure palladium. Comparison of the results for the V-Ti-Ni all to palladium since Pd/Pd-alloys are the current dense metallic membrane materials of choice. The testing was conducted under similar condition—100μA/cm^2 charging current at 22°C-- using the apparatus previously shown in Figure 1. A single set of results are shown in Figure 4, graphed as current density versus time. Examination of the current density plots for the two alloys shows an almost order of magnitude higher steady state current density value for the Pd membrane when compared to the V-Ti-Ni alloy. This higher steady state current density translates into a larger steady state hydrogen flux through the Pd membrane. However, due to the significant difference in thickness between the two membrane materials—L_{Pd}=0.05mm and L_{V51}=0.635mm—the overall hydrogen permeation rate as calculated from equation 2 is larger by an order of magnitude for the V-Ti-Ni alloy. Table 1 displays the calculated steady-state permeation rates for both materials. Thus, from these initial low temperature results the V-Ti-Ni alloy appears to possess a hydrogen permeability greater than Pd under the same conditions. Finally, additional testing at higher cathodic charging currents showed increasing anodic current densities that appeared to saturate .

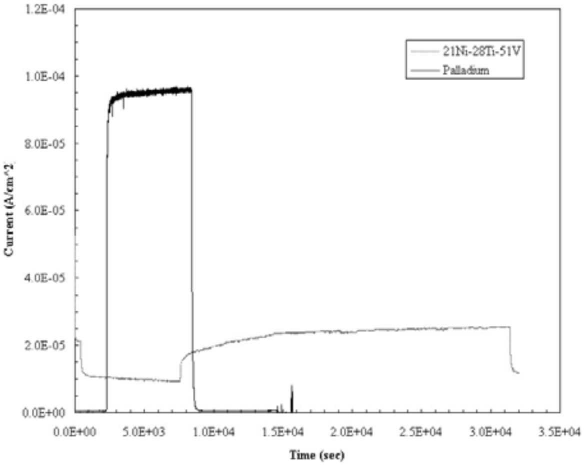


Figure 4. Measured Anodic Current Density During Electrochemical Hydrogen Permeation Testing for Pd and V-53-Ti26-Ni21 materials at 22°C.

Table 1. Steady-State Hydrogen Permeation Rates Measured for Pd and V-Ti-Ni Alloy

Alloy	**Permeation Rate (mol H_2/m s)**
Palladium	**3.3-4.3 x 10^{-10}**
V53-Ti26-Ni21	**1.0-3.7 x 10^{-9}**

Conclusions

A V-Ti-Ni alloy has been evaluated with respect to hydrogen permeability for potential use in hydrogen separation membrane reactor application. Micrsotructural 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..

Hydrogen permeation rates measured electrochemically for the V-Ti-Ni alloy as well as for pure Pd materials have shown the V-Ti-Ni alloy to have a higher permeability and thus, additional evaluation of this alloy with respect to high temperature hydrogen permeability and durability is warranted.

Reference

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