The effect of temperature and pressure on the hydrogen permeation through Pd-coated Ti 26Ni 21V 53 alloy membrane under different atmospheres

ARTICLE *in* MATERIALS LETTERS · AUGUST 2011

Impact Factor: 2.49 · DOI: 10.1016/j.matlet.2011.04.092

4 AUTHORS, INCLUDING:

Sung Il Jeon
Kobe University
15 PUBLICATIONS **52** CITATIONS
SEE PROFILE

Jung Hoon Park
Dongguk University
50 PUBLICATIONS **156** CITATIONS
SEE PROFILE

Yongtaek Lee
Chungnam National University
25 PUBLICATIONS **212** CITATIONS
SEE PROFILE

Materials Letters 65 (2011) 2495–2497

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

The effect of temperature and pressure on the hydrogen permeation through Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane under different atmospheres

Sung Il Jeon [a,b], Edoardo Magnone [a], Jung Hoon Park [a,*], Yongtaek Lee [b]

[a] Greenhouse Gas Center, Korea Institute of Energy Research, 102, Gajung-ro, Yuseong-gu, Daejeon, 305-343, Republic of Korea
[b] Department of Chemical Engineering, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 305-764, Republic of Korea

ARTICLE INFO

Article history:
Received 11 April 2011
Accepted 25 April 2011
Available online xxxx

Keywords:
Hydrogen permeation
Ti–Ni–V
Alloy membrane
Gas mixture

ABSTRACT

The paper introduces $Ti_{26}Ni_{21}V_{53}$ alloy membrane as a potential replacement for Pd-based membrane. The pressure–temperature–hydrogen permeation relationships of Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane have been investigated under pure hydrogen and mixed hydrogen gas with carbon dioxide and carbon monoxide in a pressure range from 0.5 to 2 atm over a wide temperature range including the typical hydrogen membrane operating temperature range (350–450 °C). The experiments show that the hydrogen flux was directly proportional to the temperature at constant pressure according to an Arrhenius-type relationship, whereas it was not proportional to the square root of hydrogen partial pressure in little accordance with the Sievert's law. The hydrogen permeability values obtained for the Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane under present conditions are higher than the pure palladium and those previously published in the Ti–Ni–V ternary systems.

1. Introduction

Increasing the hydrogen productions and lowering the hydrogen costs are two crucial points. Nowadays many scientists believe that non-Pd–alloy membranes for producing high purity hydrogen and for separation process applications are one of the best candidates to help the hydrogen energy technologies [1–4]. The present work introduces a new non-Pd–alloy membrane of Ti–Ni–V ternary system, $Ti_{26}Ni_{21}V_{53}$ alloy. The motivation of this work is based on two fundamental studies and its key observations. First, Hashi and co-workers have investigated the hydrogen permeation, microstructure, and brittleness properties of twenty-one compositions in the Ti–Ni–V ternary system and revealed that only four alloys (designed H, F, G and E in Ref.[2] and shown in Fig. 1a) showed measurable hydrogen permeability [2]. Fig. 1 shows the differences in compositions between the main alloys of the Ti–Ni–V ternary phase diagram [5], according to Ref. [2]. It should be noted that the measurable hydrogen permeability (1) can be placed close the center of the TiNi–V pseudo-binary system in the triangular Ti–Ni–V phase diagram, and (2) this area corresponding to the (βTi,V)-TiNi-σ tie-triangle phase [5]. In particular, there is a systematic trend in the variation of the hydrogen permeability value with vanadium content and, in first approximations, it is possible to conclude that (3) a higher vanadium content corresponds to higher hydrogen permeability at 400 °C [2] in the following order: $Ti_{40}Ni_{29}V_{31}(G) \approx Ti_{30}Ni_{29}V_{41}(E) > Ti_{41}Ni_{39}V_{20}(F) > Ti_{51}Ni_{40}V_{09}(H)$. Among different candidates in the (βTi,V)-TiNi-σ triangle composition, the second motivation of this work is based on the recent observation done on the Ti—26 at.%, Ni—21 at.% and V—53 at.% alloy composition by Adams and Mickalonis [3]. This alloy composition is really attractive for hydrogen membrane applications due to its much higher steady-state hydrogen permeation rate than pure palladium membrane in electrochemical testing conduced at room temperature [3].

The present paper has two aims. The first, to investigate the hydrogen permeation rate through Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membranes over the 350–450 °C temperature range and 0.5–2 atm pressure range with pure hydrogen. This particular alloy composition is represented in Fig. 1 by a star. Its second aim is to offer a preliminary overview of the effect of gas mixture composition, hydrogen/carbon dioxide and hydrogen/carbon monoxide, on the Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane performance. To the best of our knowledge this is the first report describing the Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membranes for hydrogen separation.

2. Experimental

$Ti_{26}Ni_{21}V_{53}$ alloy membranes (diameter = 10 mm; thickness = 0.5 mm) were fabricated by wire cutting from about 25 g cast ingot prepared using vacuum arc melting machine. Reactive ion etching was treated (~500 nm) in order to eliminate the effect of the contamination layer. A thin layer of about 150 nm thick of pure palladium (purity = 99.99%) was deposited by dc magnetron sputtering system on the $Ti_{26}Ni_{21}V_{53}$ alloy surface. The microstructure of the $Ti_{26}Ni_{21}V_{53}$ and Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane was analyzed with a scanning electron microscope. A full description of the hydrogen permeation measurement apparatus is reported in Ref.[6]. The feeding and sweeping flow rates were kept at 40 ml/min in a pressure range between 2 and 0.5 atm controlled via a series of back pressure regulators in function of temperature from 450 and 350 °C. The pressure used in

* Corresponding author. Tel.: +82 42 860 3766; fax: +82 42 860 3134.
E-mail address: pjhoon@kier.re.kr (J.H. Park).

0167-577X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2011.04.092

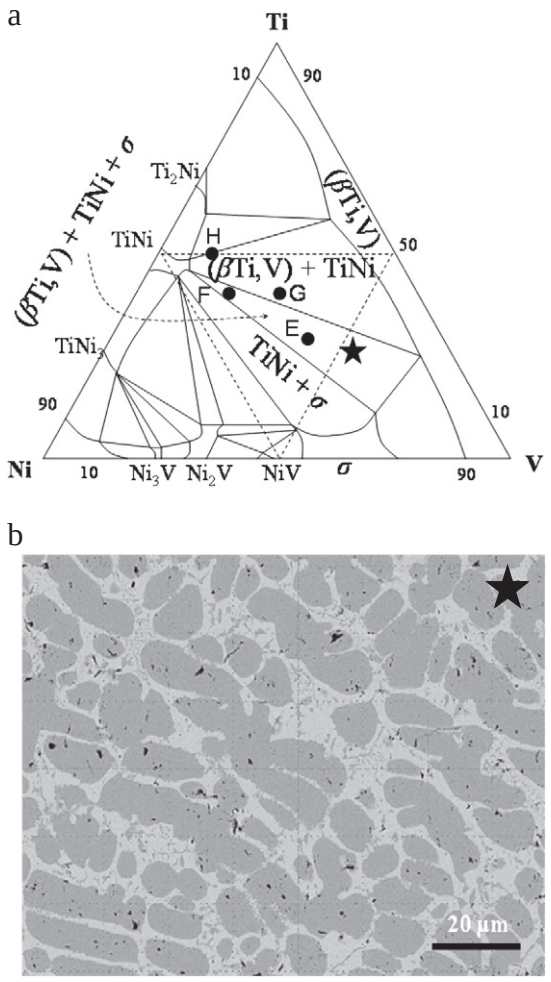

Fig. 1. (a) Ternary equilibrium phase diagram of titanium–nickel–vanadium system (after Ref. [5]). Approximate compositions of alloys H, F, G and E denoted by solid circle (after Ref. [2]) in composition of Ti—26 at.%, Ni—21 at.% and V—53 at.% alloy investigated in this work (denoted by solid star) and (b) SEM image of as-prepared sample.

this experiment means the absolute pressure. A selected amount of carbon dioxide (40% vol/vol) and two different binary mixture of hydrogen with carbon monoxide (0.3 and 1.5% vol/vol) at the total pressure of 0.5–2 atm was also utilized to study the effect of these gas mixture on the hydrogen permeation through Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane. The hydrogen content in the permeate stream was carried away by sweep gas and analyzed using a gas chromatograph. The hydrogen permeation data are obtained in accordance with the time needed to reach the equilibrium state.

3. Results and discussion

As a representative example, Fig. 2a shows the variation of hydrogen permeation flux with time for experiments at a series of pressures ranging from 2 to 0.5 atm under pure hydrogen. The maximum hydrogen flux obtained is ~5.5 ml/min^{-1} cm^{-2} under present conditions. In order to determine the overall parameters of hydrogen permeation process from time–pressure–temperature data it is necessary to adopt a simplified representation of the temperature and pressure dependencies. Thus Fig. 2b and c shows representative curves for the hydrogen permeation fluxes under the different pressure–temperature conditions in pure hydrogen and hydrogen/carbon dioxide gas mixture, respectively. In the latter case the hydrogen permeation flux values were lower than those obtained in pure hydrogen, suggesting a reciprocal relationship between hydrogen flux and carbon dioxide content in the feed side during the

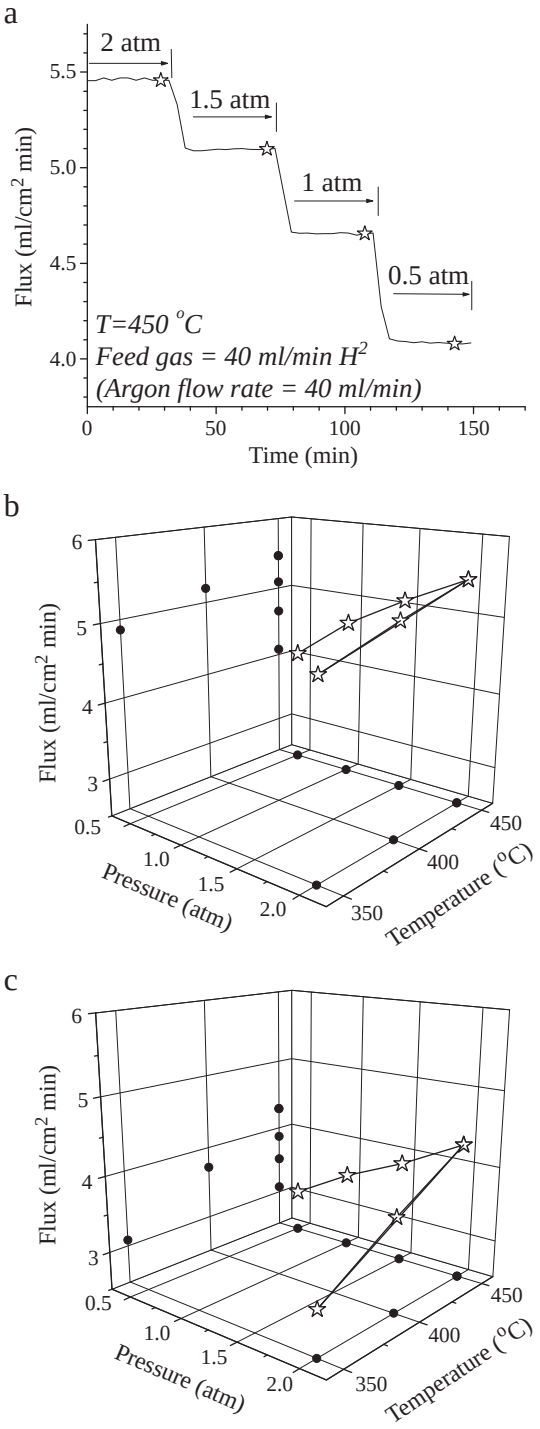

Fig. 2. (a) Representative curves of the isothermal variation of the hydrogen permeation flux of a Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane as a function of pressure and time using pure hydrogen. Variations with pressure and temperature of the hydrogen permeation flux in (b) pure hydrogen and (c) hydrogen/carbon dioxide gas mixture (CO_2 40% vol/vol).

experimental measurements. In general, from Fig. 2b and c we can see that as the temperature and hydrogen pressure were increased in the feed side, the hydrogen permeation flux in the permeate stream increased.

Plotting log hydrogen permeation flux values obtained versus 1/T, the Arrhenius plot (Fig. 3a) was obtained, which was found to be linear in the temperature range examined. The average activation energies (Ea) are 8.17 kJ/mol and 8.31 kJ/mol for pure hydrogen and carbon dioxide, respectively. These results show that the hydrogen fluxes are a thermally activated process in the temperature range studied. The gas dependence

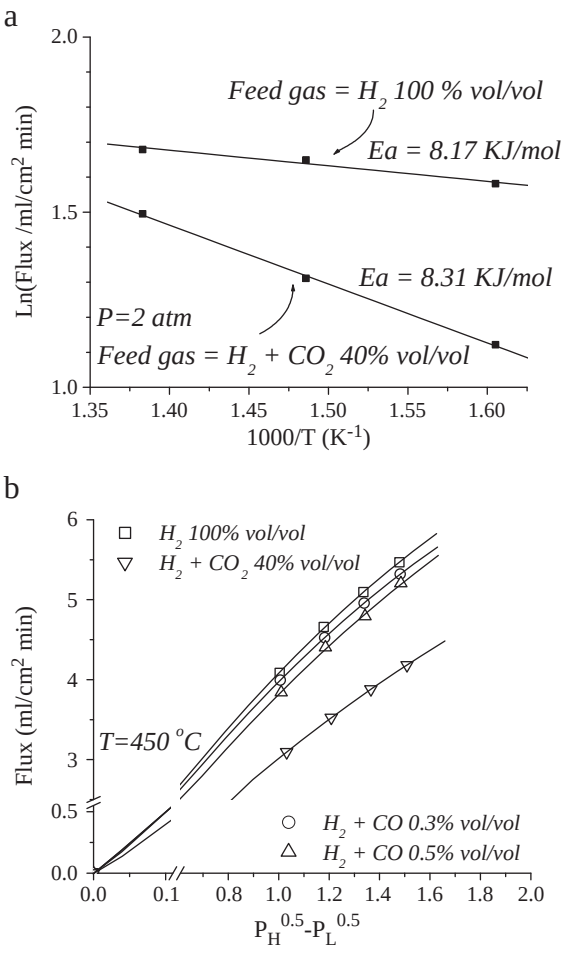

Fig. 3. (a) Temperature dependence of hydrogen flux through Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane at 2 atm. (b) Representative curves of the isothermal variation of the hydrogen permeation fluxes as a function of square root hydrogen pressure difference.

of hydrogen permeation fluxes, determined using hydrogen/carbon dioxide (40% vol/vol) and hydrogen/carbon monoxide (0.3 and 1.5% vol/vol), is plotted against square root hydrogen pressure difference in Fig. 3b. It is clear that simple Sievert-type linear relationships cannot describe satisfactorily the hydrogen permeation fluxes under present experimental conditions. These results are in good agreement with findings of other authors [1,7]. Moreover, in comparison with carbon dioxide, it could be observed that carbon monoxide atmosphere has a minor influence on hydrogen permeation, probably due to different interactions of the two kinds of gas with hydrogen at the active site on the Pd surface [8].

Fig. 4 shows the temperature dependence of the hydrogen permeability for the Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membranes. The hydrogen permeability values obtained in the present work for the Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane are higher than those previously published [2] in the Ti–Ni–V ternary system and it is particularly noteworthy that Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane clearly shows better hydrogen permeability than that of pure Pd. The result seems plausible because similar behaviors emerge from recent hydrogen electrochemical permeation studies, where it was shown that the $Ti_{26}Ni_{21}V_{53}$ alloy appears to possess a hydrogen permeability greater than Pd under room temperature [3].

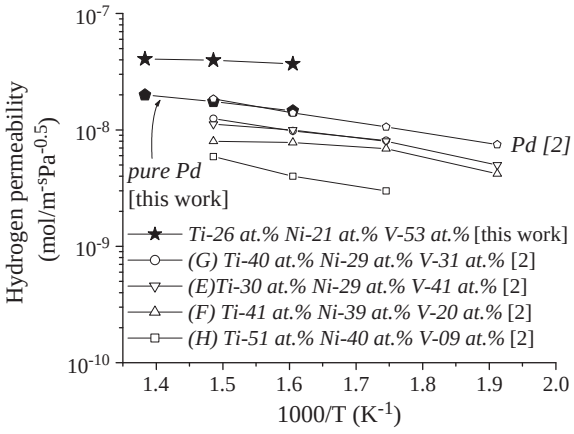

Fig. 4. Hydrogen permeability results with the best experimental conditions of this study (H_2 100% vol/vol; 40 ml/min; 2 atm) for the Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membranes with 150 nm thick Pd layer (the solid symbols are the current work). Open symbols are the data for different compositions (see H, F, G and E in Fig. 1) with a Pd-thickness of 190 nm under H_2 of 0.20–0.97 MPa in the upstream side and 0.1 MPa in the downstream side [2].

4. Conclusions

In this experimental work the influence of co-existing gases on the hydrogen permeation through a Pd-coated $Ti_{26}Ni_{21}V_{53}$ alloy membrane was studied for the first time. A maximum hydrogen flux of ~5.5 ml/min^{-1} cm^{-2} was obtained at 450 °C and 2 atmospheres with pure hydrogen as feed gas. To the best of our knowledge, this is the first result in the literature that provides hydrogen permeation flux performance higher than those previously published in the same ternary system and pure palladium material.

Acknowledgment

This work was supported by the Energy & Resource R&D program (2008-C-CD11-P-09-0-0000) under the Ministry of Knowledge Economy, Republic of Korea.

References

[1] Dolan MD. Non-P B.C.C. alloy membranes for industrial hydrogen separation. J Membr Sci 2010;362:12–28.
[2] Hashi K, Ishikawa K, Matsuda T, Aoki K. Hydrogen permeation characteristics of (V, Ta) Ti–Ni alloys. J Alloys Compd 2005;404:273–8.
[3] Adams TM, Mickalonis J. Hydrogen permeability of multiphase V–Ti–Ni metallic membranes. Mater Lett 2007;61:817–20.
[4] Wang W, Ishikawa K, Aoki K. Microstructural change-induced lowering of hydrogen permeability in eutectic Nb–TiNi alloy. J Membr Sci 2010;351:65–8.
[5] Chen SW, Ho CS, Lin CH, Chen CM. The 900 °C isothermal section of Ti–Ni–V alloys. Metall Mater Trans A 2000;31:1679–82.
[6] Park JH, Jeon SI, Sim WJ, Baek IH, Choi SH. Stability of Ta/YSZ cermet membrane for hydrogen permeation. Energy Procedia 2011;4:756–62.
[7] Catalano J, Baschetti MG, Sarti GC. Influence of the gas phase resistance on hydrogen flux through thin palladium-silver membranes. J Membr Sci 2009;339:57–67.
[8] Catalano J, Baschetti MG, Sarti GC. Hydrogen permeation in palladium-based membranes in the presence of carbon monoxide. J Membr Sci 2010;362:221–33.