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Alloys based on Group 5 metals for hydrogen purification membranes

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ABSTRACT

Production of high-purity hydrogen is required to move to power systems with little environmental impact. The considerable part of hydrogen is suggested to be obtained by methane conversion and its separation from other hydrocarbon gases which are not involved in the energy production process (associated gas, waste gas of petrochemical industry, etc.). The aim of this study was to compare properties of low cost alloys for membranes for hydrogen purification and separation. To investigate the membranes of $V_{53}Ti_{26}Ni_{21}$ and $Ta_{77}Nb_{23}$ (wt.%) alloys, the specific hydrogen permeability and micro hardness tests, metallography and X-ray diffraction were applied. It was concluded the $Ta_{77}Nb_{23}$ (wt.%) alloy has hydrogen permeability parameters and mechanical characteristics that make it suitable for the production of thin membranes.

1. Introduction

Economic production of high-purity hydrogen is required for the future with little environmental impact and transition to environment oriented power systems. Increasing of membrane performance on hydrogen flux and reducing of the membrane prime cost are two important criteria. Considerable part of hydrogen is suggested to be obtained by methane conversion and its separation from other hydrocarbon gases, which are not involved in the energy production process (associated gas, waste gas of petrochemical industry, etc.). A rapid increase of the share of membrane gas separation is expected in the upcoming years. According Ref. [1], to make membrane technology for high-purity hydrogen production efficient and economically reasonable, diffusive filter materials should meet following requirement: temperature (250–500 °C), flux (150 cm^3/cm^2/min with $\Delta P(H_2)$ of 100 psia), cost (~U$ 1000/m^2), and durability (5 years). The alloys developed in 1960s were based on palladium, for example, $Pd_{77}Ag_{23}$ [2] and B1(wt.% Ag 15.2–16.8, Au 1.3–2.1, Ru 0.4–1.1, Pt 0.4–1.1, Al 0.08–0.2, and the balance Pd) [3]. They are efficient, but expensive. Adding other metals was aimed at reducing the temperature of hydride formation, which typically leads to the membrane failure.

Group 5 metals (V, Nb, Ta) are receiving special research attention due to both relatively low price and potential of hydrogen permeability parameters [4]. However, hydride formation is also the weakest point of these metals. Alloying the metals is a way to solve the problem. In our view, the best results for suppression of hydride formation were demonstrated by a series of the alloys with TiNi [5].

For example, the permeability values of (Nb, V, Ta)–TiNi alloys at 673 K are better than $3 \cdot 10^{-8}$ mol H_2 m^{-1} s^{-1} $Pa^{-0.5}$ [1,6–8].

The main difference between hydrogen permeability is based upon the difference of hydrogen solubility of metals. One should note that composite membranes based on Group V metals and plated by Pd have been studied only for the last decades [6–8]. However, there is no information about commercial application of this membrane type.

The hydrogen solubility of $Ta_{70}Nb_{30}$ (at.%) is the highest as reported in the paper [9]. Partial substitution of Nb atoms by Ta atoms has little effect on mechanical properties, hydrogen solubility, and permeability. The smaller hydride formation temperature of the metals Ta (283 K), V (443 K), Nb (444 K) is the additional advantage over Pd (571 K). With regard to cost-effectiveness, production of Ta–Nb membrane systems is potentially profitable as tantalum is a natural impurity of Nb, which means decrease of costs on obtaining Ta–Nb alloys.

The paper aims to look into the development of both affordable and quite technology savvy membranes for diffusive hydrogen purification. The major subject of this work is the $Ta_{77}Nb_{23}$ (wt.%) alloy, its hydrogen permeability was not studied before. Membranes were made by rolling and have no catalytic Pd coating. We do not consider the problems of embrittlement resistance. The paper presents analysis of hydrogen permeable alloys (Group 5 metals with NiTi) and their comparison with the $Ta_{77}Nb_{23}$ (wt.%) alloy.

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2. Experiment

2.1. Sample preparation

As raw materials, Ti (99.98%), V (99.98%), Ni (99.99%), Ta (99.9%), and Nb (99.99%) were used. About 16 g ingots of V–NiTi and Ta–Nb were prepared on a water-cooled copper hearth in argon arc-melting furnace. The fore vacuum in the arc furnace was equal to or more than 10^{-3} Pa. The share of argon impurities was less 10^{-4}. Smelting was carried out using non-consumable tungsten electrode and at the direct current 270 A. The ingots were flipped and remelted to ensure compositional uniformity. Disks of 15 mm in diameter and 0.2–0.25 mm in thickness were cut out from the ingots by precision saw. The obtained samples were cold rolled (at room temperature), than they were polished to thickness of 0.14 mm. Recrystallization annealing at 1373 K during 1 h was carried out in diffusive cell under vacuum 10^{-6} Torr.

2.2. Measurement of hydrogen permeability

Permeation technique has a great variety of experimental ways. Hydrogen permeation test of the $V_{53}Ti_{26}Ni_{21}$ (wt.%) alloy was carried out by the steady state flux method.

The permeation test procedure of the $Ta_{77}Nb_{23}$ sample is described as follows: the diffusive cell with fixed sample was mounted in test system gas line, the helium pressurisation test were performed from the inlet side to confirm the absence of leaks using mass-analyser for control. Then degassing of the sample was performed at 823 K for 24 h in vacuum. Prior to each measurement, the sample out-gassing from two sides were performed at the pressure up to 1.33×10^{-3} Pa followed by sample degassing. The degassing temperature was 50 K higher than for previous measurement. After sample degassing and assigning specified experiment temperature, the working hydrogen pressure was supplied rapidly from the high pressure side in the input chamber with V_{in} known volume and measuring equipment of analytical part of apparatus was activated. The pressure, P_{in}, in the chamber was beginning to decrease. The increase of the pressure, P_{out}, in closed low-pressure chamber with V_{out} known volume was induced by the hydrogen passed through membrane. The obtained pressure–time dependences $P_{in}(t)$ and $P_{out}(t)$ were information for further processing. Experimental data obtained for the $Ta_{77}Nb_{23}$ alloy at the temperature 673 K are shown in Fig. 1a.

2.3. Samples structure and properties

Microhardness of the samples was determined using Micromet-5103/A1K, Buehler with load in the range from 10 to 50 g. The membrane materials were observed using SEM Zeiss Supra 40VP. The sample plates with dimensions 5×9 mm were examined using diffractometer Bruker D8 Advance at room temperature, a Cu Kα X-ray source was used. Patterns were typically recorded over a 2θ range of 10–90°. The database PDF-2 (ICDD) was used to determine composition.

3. Results and discussion

3.1. Hydrogen permeation

The performance of a metal membrane is defined by the density of steady state flux of hydrogen passing through membrane.

$$J_R = \Gamma D \frac{\sqrt{P_{out}} - \sqrt{P_{in}}}{l} \quad (1)$$

Eq. (1) for flux, J_R, is known as Richardson formula in the intermediate pressure range (high, but not ultra-high). Coefficient of hydrogen permeability is defined as $\Gamma D/l$, where Γ is the hydrogen solubility, D is the diffusivity, l is the membrane thickness. The hydrogen permeability varies within several orders of magnitude for different metals and is the key characteristic for assessment of the potential use of a material for hydrogen purification. Thus, for example, the hydrogen permeability of palladium is $1.6 \cdot 10^{-8}$ (mol m^{-1} s^{-1} Pa$^{-0.5}$) and niobium is $3 \cdot 10^{-6}$ (mol m^{-1} s^{-1} Pa$^{-0.5}$) at 673 K [1].

The hydrogen flux through membrane which separates two closed volumes V_{in} (inlet) and V_{out} (outlet) was calculated from the dependences $P_{in}(t)$ and $P_{out}(t)$. The thickness of $Ta_{77}Nb_{23}$ membrane was 0.14 mm, the area was 0.785 cm^2, the initial hydrogen concentration on the membrane surface was zero.

The gas balance equation relating the gas density flux (in terms of entirely molecular hydrogen, further the density will be omitted) passed through membrane and the gas pressure in chamber with volume V is: $J = \frac{V}{RTS}\frac{dP}{dt}$, where T is the temperature, R is the gas constant, S is the area.

We assume that once each experiment starts, the flux rapidly acquires quasi steady state due to the sample thinness, i.e. the flux has to satisfy Eq. (1). If hydrogen storage in membrane is negligible small, the quasi steady state fluxes $J_{out}(t)$ and $J_{in}(t)$, which should match, one can be calculated from the pressure time dependences $P_{in}(t)$ and $P_{out}(t)$:

$$J_{out} = \frac{V_{out}}{RTS}\frac{dP_{out}}{dt},\ J_{in} = -\frac{V_{in}}{RTS}\frac{dP_{in}}{dt} \quad (2)$$

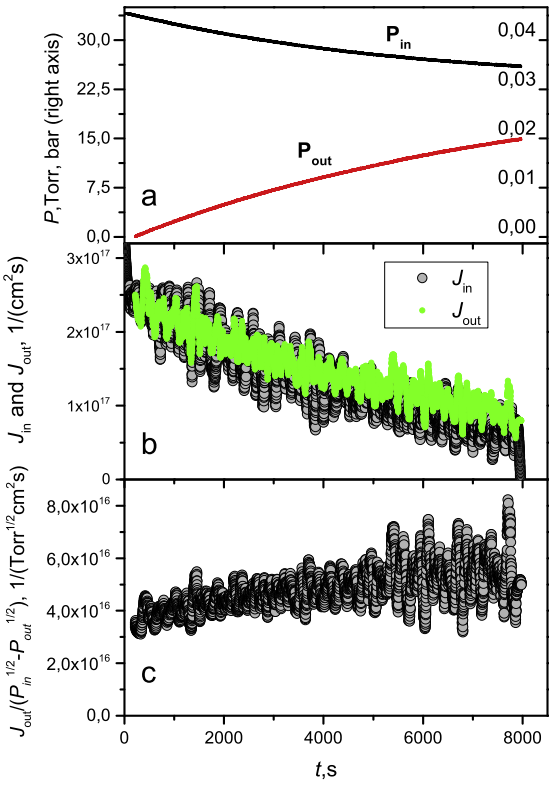

Fig. 1. $Ta_{77}Nb_{23}$ membrane: relation between time and (a) the inlet and outlet chambers pressures, (b) the flux density and (c) the ratio of the flux to $(\sqrt{P_{out}} - \sqrt{P_{in}})$.

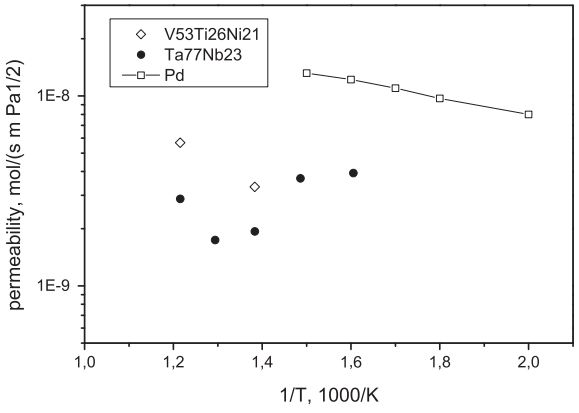

Fig. 2. Arrhenius plot of the hydrogen permeability of palladium, $V_{53}Ti_{26}Ni_{21}$ and $Ta_{77}Nb_{23}$ alloys.