INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 7553–7558

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Ti modified Pd–Ag membranes for hydrogen separation

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ARTICLE INFO

Article history:
Received 23 August 2014
Received in revised form
28 October 2014
Accepted 7 November 2014
Available online 3 December 2014

Keywords:
Hydrogen separation membranes
Sputter deposition
Thin film membranes
Combinatorial approach
Resistivity measurement

ABSTRACT

An investigation was carried out into Pd–Ag separation membranes to check whether a reduction in their Pd content was possible through the incorporation of a third element, namely Ti. For this purpose a combinatorial thin film deposition system was developed incorporating three sputter targets arranged in triangular form. The system had a substrate in the form of a magazine, 6 inch in diameter, accommodating 21 discs arranged again in triangular form aligned with the targets underneath. With this geometry, a library of thin film membranes was obtained in a single experiment covering a wide compositional field, Pd content up to of approx. 75%. The thin film library was then screened with respect their tendency to react with hydrogen. This was accomplished by the resistivity measurements carried out on the membranes, while they are subjected to heating–cooling cycle under hydrogen, the values being compared with identical cycle carried out under argon. Since permeability is a product of hydrogen solubility and diffusivity, membranes that react with hydrogen, i.e. either forming a solid solution or a hydride, delineate compositions which are candidates for separation membranes. In the present work, this procedure was applied to a portion of Ag–Ti–Pd ternary system aiming for separation membranes with f.c.c. crystal structure. Mapping based on the resistivity measurement indicated, Ag35Ti22Pd43, Ag13Ti25Pd62 and their near compositions as possible candidates for separation membranes.

Introduction

Hydrogen separation membranes allow filtration of hydrogen from mixed gases. Such mixtures may be produced via steam reforming of natural gas/coal/lignite [1] or though gasification of municipal wastes [2]. Hydrogen separated in this way may be used in fuel cells to generate electricity or may be fed directly to the natural gas grid. It is likely that the current network of natural gas will soon be transformed into a "gas" grid where hydrogen would be an essential ingredient [3]. All these require the use of efficient separation membranes, which when made possible would lead to an easy availability of hydrogen as is currently the case for natural gas.

Among the all metallic membranes Pd is the most essential element due not only its high permeability but also its catalytic effect and oxidation resistance even at elevated temperature [4]. However, membranes based on Pd are extremely

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http://dx.doi.org/10.1016/j.ijhydene.2014.11.049

expensive and therefore efforts have concentrated either on alloying to reduce Pd content [5,6] or to switch to non-Pd membranes making use of Pd only as a catalytic layer [7]. A reduction in membrane thickness through the use of thin films also reduces Pd content and thus has attracted considerable attention in recent years [8,9]. It is worth emphasizing that even pure palladium has its problems as a separation membrane. As could be verified from Pd–H phase diagram [10] when the Pd–H is cooled form an elevated temperature, initially a single phase f.c.c. alloy is converted into a two-phase structure which results in a considerable volume expansion [11]. This phenomenon lead to the formation of micro cracks which severely affects the durability of the Pd membrane.

There are two approaches in handling this embrittlement problem. One method is to control the temperature and pressure during operation, so that the membrane is always in one phase region. The other is to alloy Pd so that transformation to two-phase structure is avoided. This is most commonly achieved by alloying Pd with Ag. An addition of 20–30 at% Ag is quite common which not only reduces the critical temperature for two-phase transition but also yields the permeability values which are up to 1.7–2.0 times of that of the pure Pd [12]. Similar result could also be obtained via alloying with Cu [13]. It was shown that that 40 wt. % addition of Cu can reduce the critical transformation temperature below the room temperature [14]. This addition also results in a %10 increase in hydrogen permeability [15] which arises mainly from an increase in hydrogen diffusivity [16]. In addition to Ag and Cu, elements such as Y, Fe and Ni could also be used as alloying elements in Pd [12]. Of these, according to Fort et al. [17] Pd–Y is quite comparable to Pd–25%Ag alloy with a higher hydrogen permeability and better durability. Pd–Fe alloy membranes are interesting as they show no phase transformation [18].

All membranes reported above were developed via the traditional approach of synthesizing one membrane composition at a time and testing it for permeability. This is quite time consuming and not always successful. The current work aims for f.c.c. membranes, similar to those reviewed above, but adopts the so-called combinatorial approach that would allow the synthesis of multiple material compositions in a single experiment. A library of thin film membranes produced is then evaluated by a rapid screening to identify the material composition as candidates for separation membrane. This approach was applied to a ternary alloy system Ag–Ti–Pd, i.e. Ag–Pd modified with Ti.

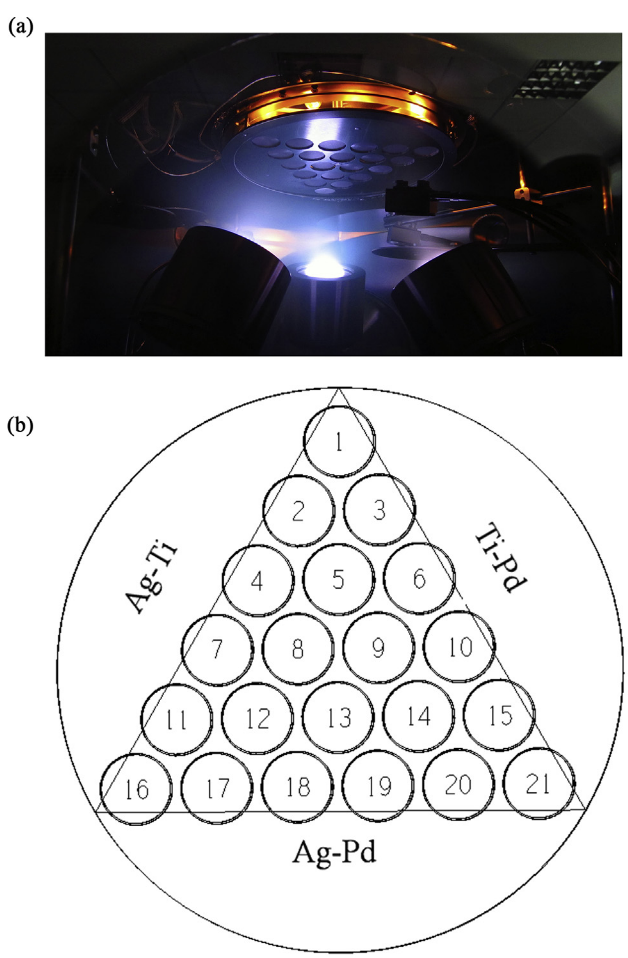

Fig. 1 – Sputter deposition of thin film membranes. a) A viewgraph showing the targets and substrate magazine incorporating 21 glass substrates, b) Triangular distribution of substrates in the substrate magazine.

Experimental

In this work, a thin film deposition system was used, especially designed for the purpose of combinatorial studies. The system had a vacuum chamber 65 lt. in volume with all connections CF type, except for sputter gun stems and the main door. The chamber is connected to a turbomolecular-rotary pump system which can provide a base pressure in the

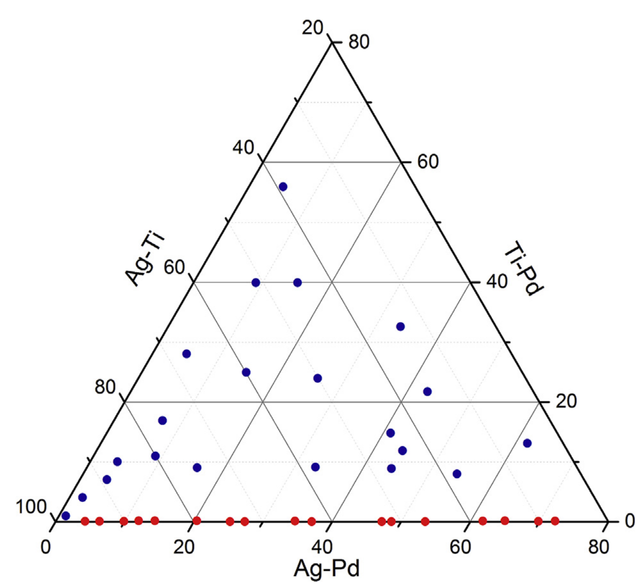

Fig. 2 – Chemical composition of thin film membranes in the ternary diagram. The diagram combines the samples that are generated in two experiments. Compositions of Ag–Pd binary thin films that were deposited separately are also indicated in the diagram.