Short Communication

Palladium-copper membranes for hydrogen separation

Ke Zhang [a],*, J. Douglas Way [b],*

[a] Aramco Services Company, Aramco Research Center—Boston, 400 Technology Square, Cambridge, MA 02139, USA
[b] Department of Chemical & Biological Engineering, Colorado School of Mines, Golden, CO 80401, USA

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A B S T R A C T

This communication summarizes key elements and facts of PdCu alloy membranes for H_2 separation by reviewing fundamentals and literature reports, such as the PdCu phase diagram and its implications toward membrane permeability and stability, the phase and composition segregation behavior, and the intricate phase structure-composition-stability-permeability relationship. The inconvenient challenges for applying PdCu alloy membranes due to its complex alloy phase diagram consisting of more than one phase structure are identified. The sulfur resistance and H_2 permeation hysteresis will also be discussed accordingly. Previously reported permeation data will be revisited by using the insights outlined to explain some of the previous observations of instability for PdCu alloys operating in pure H_2 atmosphere. We conclude the manuscript with a summary, as well as our perspective and outlook on this topic.

1. Introduction

Pd-based membranes have been proposed to produce high purity hydrogen due to their exclusive selectivity for hydrogen via the solution-diffusion mechanism [1]. Over the past two decades, numerous studies have been devoted to developing robust Pd-based membranes for H_2 purification, and great achievements have been obtained in optimizing membrane fabrication, improving membrane stability, and operating membranes under industrial-related conditions [2–4]. Meanwhile, additional challenges have also been identified when utilizing Pd-based membranes in large-scale H_2 separation and purification. For example, hydrogen absorption takes place in two diverse phases for the Pd-H system, i.e. the low-concentration Pd-H solid-solution (α) phase and the high-concentration hydride (β) phase. These two phases have different lattice parameters in the *fcc* structure. Pure Pd membranes usually suffer from hydrogen embrittlement induced by the α-β phase transition at temperatures lower than 298 °C and pressures smaller than 2 MPa [5,6], which is accompanied by a lattice expansion, which often leads to micro-cracks on the membranes. Another issue is the membrane stability at operating conditions involving impurity gas species, especially H_2S. H_2S is a typical byproduct in syngas from coal gasification that can impose severe negative influence on the membrane performance of Pd-based

membranes. Pd membranes can be rapidly poisoned after exposure to a gas stream with H_2S concentrations as low as several parts-per-million (ppm) [7,8]. The poisoning effect consists of significant H_2 permeance inhibition and can cause membrane failure or rupture with the formation of defects on a roughened surface [9–11].

One of the most practical and feasible options for addressing these challenges is to alloy Pd with other metals to modify the geometric and electronic structure and the surface reactivity of metallic Pd. By alloying Pd with other metals, such as Au [12–15], Ag [16–18], Cu [19–23], Ru [24–26], and Pt [27], the chemical stability of alloy membranes oftentimes can be improved and the operating temperature range can be broadened. Among these Pd alloy membranes, PdCu alloys have received great attention due to the low cost of Cu, better H_2S resistance than with Pd alone, and higher H_2 permeability in some PdCu alloys. However, the application of PdCu membranes for H_2 separation also faces inconvenient challenges originated mainly from its complex alloy phase diagram consisting of more than one phase structure and the intricate *phase structure-composition-stability-permeability* relationship for PdCu membranes that needs special attention [28]. In this mini-review communication, key elements of utilizing PdCu membranes for H_2 separation will be summarized by elaborating the PdCu upon phase diagram and its implications toward membrane permeability and stability. Unless specifically identified, the referenced membrane permeation properties were from supported Pd-based membranes, where the top layers were deposited onto various porous substrates. The phase and composition segregation behavior of PdCu alloy membranes will be discussed in detail, and the insights

* Corresponding authors.
E-mail addresses: ke.zhang@aramcoservices.com (K. Zhang), dway@mines.edu (J.D. Way).

will be used to explain some of the previous observations of insta-bility for PdCu alloys operating in pure H_2 atmosphere. We will also discuss the sulfur resistance and H_2 permeation hysteresis for PdCu membranes, followed by a conclusion with our perspec-tive and outlook.

2. Pd-Cu membranes for H_2 separation

2.1. Pd-Cu phase diagram

Pd and Cu form a continuous *fcc* solid solutions at temperatures above 600 °C, while both *fcc* and *bcc* structures can be present below 600 °C in which the two phases are separated by a miscibil-ity gap of a mixed phase region (Fig. 1) [28]. The term "miscibility gap" refers to the region in the Pd-Cu phase diagram where both *bcc* and *fcc* phases exist, thus resulting in a "gap" that partitions the two pure phase regions. Note that this phase diagram does not involve the effect of hydrogen dissolution in the alloy. The *bcc* phase boundary would shift slightly towards higher Pd con-tents in a Pd-Cu-H system [29]. The hydrogen diffusion in *bcc* PdCu is significantly faster than in *fcc* PdCu and is relatively insensitive to alloy composition [30], which may lead to a significant increase in H_2 permeability with the transition from *fcc* to *bcc* phase. At 53 wt% Pd, the *bcc* PdCu phase can exist up to 600 °C. However, H_2 permeability at this composition is extremely low due to the low solubility at higher Cu compositions. In PdCu alloy mem-branes, H_2 permeability experiences a maximum in a very narrow region around 60 wt% (47% mol%) Pd [31]. Within this region, H_2 permeability is very sensitive to alloy composition such that even small deviations of 2–3 wt% Pd from the optimal concentration in either direction result in huge decreases in H_2 permeability by 40–60% when compared to the peak value. The permeability decline on the Cu-rich side can be attributed to the decrease in hydrogen solubility with a slight increase in Cu composition, while a slight increase in Pd content can induce a transition from the *bcc* phase to the mixed phase region with the formation of a less permeable *fcc* phase since the optimal $Pd_{60}Cu_{40}$ wt% concentration

is located adjacent to the boundary of the *bcc* and mixed phases. Thus, the preparation of PdCu membranes requires precise compo-sition control toward $Pd_{60}Cu_{40}$ wt% to obtain membranes with ideal H_2 permeability. Fig. 2 summarizes the correlation of H_2 permeance, top-layer thickness, and H_2 selectivity of Pd-Cu membranes reported in the literature along with representative data of Pd-Ag and Pd membranes for comparison.

2.2. Pd-Cu membrane preparation and alloying

Electroless plating (ELP) is frequently adopted for PdCu mem-brane preparation that typically consists of sequential plating and a subsequent alloying at elevated temperatures since it is dif-ficult to obtain stable deposition rates in co-deposition plating bath and the displacement of deposited Cu by Pd may occur due to the higher reduction potential of Pd. It is thus challenging to accurately control the PdCu membrane compositions by ELP syn-thesis. With the recent development of ELP processes, it is feasible to control PdCu membrane compositions to within 1 mol% by mea-suring the gas evolution in ELP deposition [50].

The alloying of sequentially deposited Pd and Cu layers is a nec-essary step for obtaining homogeneous PdCu membranes with ideal H_2 permeability. The alloying of PdCu can be accomplished at temperatures higher than 600 °C mainly due to the sufficient mobility of Cu atoms. The Tamman temperatures for Cu and Pd are 406 °C and 639 °C, respectively. However, the final resultant PdCu alloy will be in the *fcc* phase at alloying temperatures higher than 600 °C, which is not advantageous for H_2 permeation. On the other hand, the alloying process would be significantly prolonged at lower temperatures. For example, it required more than a week at 500 °C to alloy a 9.5 μm $Pd_{74}Cu_{26}$ wt.% membrane, while the alloying at 450 °C cannot be fully accomplished even after 2 weeks [50]. By studying the PdCu solid-state transformation kinetics, Pomerantz et al. [22] modeled the phase growth process for the Pd/Cu bilayer with roughly 15 wt.% Cu and found that the anneal-ing time needed at 500 °C for the formation of Pd-rich *fcc* alloy is 225 h. Moreover, the annealing time only referred to the formation
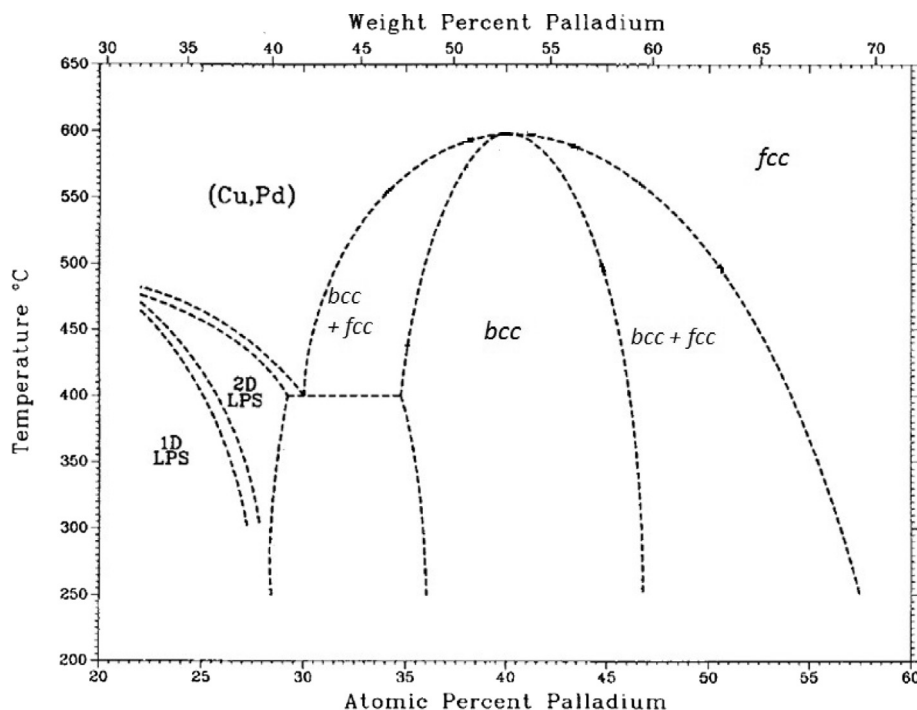

Fig. 1. Pd-Cu phase diagram [28].