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Inhibition of hydrogen flux in palladium membranes by pressure–induced restructuring of the membrane surface

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Abstract

The effects of high pressure gas exposure on the hydrogen flux though Pd films were explored. It was observed that exposure of a Pd membrane to N_2, Ar, or CO_2 at 3.0 MPa and 500 °C caused a substantial decline in hydrogen flux within 24 h that only recovered to ca. 60% of its initial value after 24 h of subsequent hydrogen exposure. Atomic force microscopy images revealed that the Pd surface became smoother with a reduction in density of nanoscale features after high pressure exposure, consistent with an observed transition in rate limiting step from bulk diffusion to surface kinetics. The rate of flux loss was found to have an apparent activation energy of 39 kJ mol^{-1}, which is consistent with values reported for Pd surface self-diffusion. This effect was not observed when the exposure gas was helium or at pressures < 2 MPa, suggesting that impinging gas momentum is an important factor that promotes smoothening of the Pd surface. Lastly, it was observed that the flux loss could be completely reversed by air treatment or prevented by the presence of O_2 impurities (ca. 1%) in the feed.

Keywords: Palladium (Pd) composite membrane; Hydrogen flux depression; Gas bombardment; Surface morphology; Pd surface self-diffusion

1. Introduction

Palladium and its alloys have been studied for decades because of their excellent hydrogen permeation properties that provide high fluxes at moderate temperatures [1,2]. Many studies have reported its use as a separating agent [3–5], in membrane reactors [6,7], and even for tritium separations as part of a nuclear fuel cycle [8]. However, there have been suggestions that some gas species can inhibit permeance by competitive adsorption on the Pd surface.

The study of hydrogen flux inhibition on palladium membranes has primarily been focused on the competitive surface adsorption of either CO [9–12] or H_2S [13–15]. Whereas CO can react with H_2 on the surface to form PdC, H_2S can form a PdS compound directly – both of which may permanently degrade the hydrogen flux and purity of the membrane. Similarly, CH_4 exposure has been shown to form a carbonaceous species [16,17], but hydrogen flux inhibition was only observed above 450 °C [16]. CO_2, on the other hand, has not been shown to induce significant hydrogen flux inhibition or react to form a PdC phase [9,12]. Attempts to lower the materials cost by alloying Pd resulted in similar studies on PdAg alloys for both CO [18–21] and H_2S [15] exposure, but these results showed comparable or worse flux inhibition and membrane degradation compared to pure Pd. Improvements to H_2S exposure tolerance, however, were observed for PdAu [13,22–24] and PdCu [15] alloys.

The effects on hydrogen flux in Pd membranes due to exposure to both N_2 [25,26] and NH_3 [25,27] have also been explored, with an apparent hydrogen flux inhibition attributed to NH_x surface adsorbed species. However, our recent work [28] did not observe any effects from N_2 or