

PdCu B2 Hydrogen Interactions under Advanced Water Gas Shift Membrane Reactor Conditions

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1. Introduction

Advanced water gas shift (WGS) membrane reactors (AWGSMR) use H-selective membranes to continuously remove H₂ in order to increase the equilibrium controlled, exothermic WGS reaction conversion of coal derived syngas to H₂. This low cost H₂ production AWGSMR path eliminates the need for multi-stage WGS reactors, resulting in a single stage, simpler process that provides high purity H₂ with less catalyst and lower reactor volume. This technology requires a durable, H-selective membrane with commercially acceptable permeance in the presence of co-reactants and contaminants like sulfide, H₂S. It has been shown that below 350°C, the Pd_{0.47}Cu_{0.53} ordered body-centered cubic (B2) alloy has a high H permeability and a reported tolerance to H₂S [1]. However, this single B2 phase composition is perilously close to the low Cu B2 + fcc phase boundary and may not be stable under AWGSMR operation. Furthermore CO or H₂S adsorbents could induce surface segregation of Cu, shifting the composition outside of the single B2 phase region [2]. The formation of the fcc phase with a different molar volume could compromise the membrane integrity and H selectivity. This study, carried out under the DOE Advanced Water Gas Shift Membrane reactor Contract DE-FG26 05 NT42453 will present a comprehensive description of H permeation in intermediate range Pd_(1-x)Cu_x B2 alloys in order to benchmark the behavior of the PdCu B2 alloys and to set the stage for developing new alloys with improved stability and H permeability performance

Materials and Methods

Pd-Cu-H system bulk phases were predicted with the first principles (FP) VASP code [3-4] using projector augmented wave potentials. The low energy (110) surface of the stoichiometric PdCu composition was selected to represent surface reactions on the ordered B2 phases. Thermodynamic properties were predicted with the Materials Design MedeA Phonon direct method lattice dynamics [5-6]. Hydrogen solubility measurements were made on a Pd_{0.44}Cu_{0.56} B2 alloy using a Sievert's apparatus over the 100-350 °C temperature range [7]. Selected Pd-Cu-H experimental and theoretical data were fit with thermodynamic models to develop a thermodynamic description for phase diagram modeling over a wide range of conditions.

Results and Discussion

The Pd-Cu-H thermodynamic description was collectively developed from newly obtained Pd_{0.44}Cu_{0.56} B2 H solubility data, established experimental data for H₂ desorption isotherms,

para-equilibrium miscibility gap boundaries, and partial H enthalpies for Pd-Cu-H fcc alloys, and from FP predictions of the thermodynamic stability of the B2 alloys [7]. The thermodynamic modeling showed that solubilized H slightly shifts both B2 phase boundaries towards lower Cu concentrations. The high permeability Pd_{0.47}Cu_{0.53} composition was predicted to be stable in the B2 form and to have near optimum H solubility for AWGSMR operation.

H diffusivity was simulated within a Pd_{0.50}Cu_{0.50} B2 2x2x2 supercell. Direct method lattice dynamic calculations were made to confirm the identity of the transition state. The zero point energy (ZPE) corrections were determined for the interstitial and transition state H positions. The ZPE-corrected activation barrier [$\Delta H_{act} + \Delta ZPE_H$], was 6.96 kJ/mol, yielding a diffusivity of 6.3×10^{-8} m²/s at 673 K (400 °C). Reasonable agreement was found between the FP predicted H diffusivity in Pd_{0.5}Cu_{0.5} and that measured in the Pd_{0.47}Cu_{0.53} B2 by Piper [8] and Völkl [9]. Hydrogen solubility in Pd_{0.47}Cu_{0.53} was calculated from the Pd-Cu-H thermodynamic assessment modeling [7], where the Sievert's coefficient, K_s , is determined from the inverse slope of the square root of H₂ pressure versus the solubilized H/(Pd+Cu) metal ratio. Using the FP calculated diffusivity and the K_s Sievert's coefficient from the thermodynamic assessment, the theoretical H bulk permeability, Q , was estimated to be 8.2×10^{-8} mol s⁻¹ m⁻¹ Pa^{0.5} in Pd_{0.47}Cu_{0.53} at 673 K.

Significance

Atomic-thermodynamic modeling, experimental H solubility measurements, and thermodynamic assessments were used to investigate H adsorption, solubility, and diffusion in PdCu ordered B2 alloys. First principles diffusivity predictions based on direct method lattice dynamics, H solubility measurements, and thermodynamic assessments were used to collectively predict the H permeability in bulk PdCu in the absence of surface contributions.

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