Design of Stable Pd-Based Membranes for Hydrogen Gas Separation: A Statistical Thermodynamics Approach

D.E. Nanu[C, S] and A.J. Böttger
Department of Materials Science and Technology, Delft University of Technology, Delft, Netherlands
d.e.nanu@tnw.tudelft.nl

The demand for hydrogen has increased in the recent years due to its potential as an energy resource. This has motivated intensive research to improve hydrogen production, separation, and purification. Membrane processes are considered one of the most promising technologies for the production of high-purity hydrogen. Pd and its alloys are commonly used as membrane materials. However, the commercial Pd-based membranes are not suitable for long-term use in numerous cycles of hydrogen absorption/desorption. In most of the cases, the failure of the membrane is due to embrittlement caused by the hydride formation/decomposition. The design of stable Pd-based membrane materials calls for a reliable thermodynamic model for H in Pd-alloys. This paper presents a statistical thermodynamic approach for describing the phase stability in Pd-H and Pd-M-H systems, and its application in designing new membrane materials for hydrogen gas separation. The cluster variation method (CVM) is applied to determine the phase stabilities of fcc solid solutions in which the interstitial atoms (H) occupy the octahedral sites formed by the close-packed metal lattice (Pd, Pd-alloys). The tetrahedron approximation of the CVM is used in combination with two approaches for describing the atomic interaction energies i.e., semi-empirical effective pair potentials (EPP) and ab initio derived effective cluster interactions (ECI). Both CVM-EPP and CVM-ECI models are used to calculate the phase diagram of the Pd-H system. While the CVM-ECI approach is an ab initio route, the CVM-EPP model requires experimental data for fitting the atomic interaction parameters. The use of EPP is however much simpler and faster and hence more convenient to use for practical applications. The CVM-EPP model was used to explore the influence of alloying elements on the phase diagrams of Pd-M-H systems. The results illustrate the effect of alloying on the solubility of H atoms and on the lattice parameter. It is shown that in the CVM-EPP approach the strength of the effective field of the metal sublattice and the relative interaction strength between nearest-neighbour occupied and unoccupied interstitial sites determine the phase boundaries and degree of short range order. Examples of using the CVM-EPP model in designing new membrane materials for hydrogen gas separation are discussed.