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First principles screening of B2 stabilizers in CuPd-based hydrogen separation membranes: (1) Substitution for Pd

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ABSTRACT

We report here a screening study using first-principles method in an attempt to identify ternary elements that can extend the CuPd B2 phase field at reduced Pd contents and thus lower cost. A total of 37 alloying elements are included for unbiased screening. The results show that addition of Mg, Al, Sc, Ti, Y, Hf, Zr, Ga, La, and Zn lowers the enthalpy of formation of the B2 phase noticeably. The atomic size, electronic density of states, charge transfer, and electronegativity are analyzed to interpret the results. Compromise between enthalpy and solubility suggests additional potential alloying elements: V, Fe, Cr, Nb, Ta, and Mn. To assess the effects of alloying on mechanical properties, we calculated the equation of states and elastic constants of 10 example alloys at 6.25 at% solute contents.

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1. Introduction

Palladium (Pd) is regarded as an excellent membrane material for hydrogen separation due to its high surface selectivity and high permeability for hydrogen (for reviews, see [1–4]). However, pure Pd membranes are prohibitively costly since Pd is an expensive precious metal with limited supply. Further, pure Pd is vulnerable to surface poisoning, especially in atmospheres containing H_2S [5,6], an impurity typically found in gas streams from coal gasification. The high cost and surface degradation have so far prevented Pd membrane technology from widespread industrial adoption. Furthermore, pure Pd is prone to hydrogen embrittlement that causes cracking [7], which is due to formation of palladium hydride (so called β phase) within solid solution of palladium with hydrogen (so called α phase) at temperature below 300 °C and pressure below 20 atm [1]. Design of a single-phase alloy that eliminates phase change during the operating temperature and pressure ranges can potentially avoid the low temperature embrittlement. As a result, alloying strategies have been sought experimentally [8–10] and theoretically [11–15] to develop robust Pd-alloys with increased chemical stability and hydrogen permeability in aggressive environments. Hydrogen permeability of various Pd-based binary, ternary and quaternary alloys are summarized in [1,3,4]. Several theoretical studies using first-principles density functional theory (DFT) have addressed the "sulphur poisoning" phenomenon [16–20]. Thermodynamic modeling of the Cu–Pd–H [21] and Pd–S [22] systems based on DFT and the CALPHAD (acronym of CALculation of PHAse Diagrams) method have also been reported.

The vast majority of reports are focused on Pd-rich compositions that have a face-centered cubic (FCC) structure. Experimental studies [5,23–25] have shown that alloying with Cu improves resistance against surface poisoning in binary Pd–Cu alloys with the FCC structure. Pd–Cu binary alloys with the ordered body-centered cubic (BCC) structure (*Strukturbericht* Designation B2) should have even higher theoretical H_2 permeability since the BCC lattice has a more open crystal structure compared to the FCC lattice [24–26]. Indeed, Howard et al. [24] studied the hydrogen permeability of a series of binary Pd–Cu alloys over wide compositions between 623 and 1173 K, and found that the H_2 permeability for the 53 and 60 wt.% Pd alloys in B2 structure was several times greater than that of the FCC alloys.

The established Cu–Pd binary phase diagram is based on the data assessed by Subramanian and Laughlin that is collected in the ASM handbook [27]. The B2 phase has a relatively large compositional homogeneity range that is shifted to the Cu-rich side from the stoichiometric 50 at% Pd position. The critical point occurs at about 40 at% Pd and 598 °C. According to the Arrhenius diffusion equation (shown below), diffusivity D increases with temperature:

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$$D = D_o \exp\left\{-\frac{\Delta Q}{RT}\right\} \tag{1}$$

where D_o is the pre-exponential coefficient, ΔQ is the activation energy, R is the gas constant, and T is the absolute temperature. Improving the thermal stability of the B2 phase will allow the membranes to be operated more efficiently at temperatures higher than 598 °C in part due to higher hydrogen diffusivity.

Therefore, it is highly desirable to design and develop new B2 PdCu-based alloys with ternary (or even higher-order) addition aiming to improve their thermal stability at reduced Pd contents. A rational approach is to combine theoretical prediction with critical experiments in order to accelerate the process. In the present study, a total of 37 alloying elements were chosen including all transition metal elements and certain non-transition metal elements. The selection was basically unbiased while available binary phase diagram information [27] in particular terminal solubility in Pd and literature reports on Pd-based hydrogen membranes were also assessed. Some elements such as Tc, Hg, Re, and Pt were included solely for comparison purpose. The enthalpy of formation of a compound is usually a good indicator for its stability, which can be reliably calculated using first-principles DFT methods. For computationally affordable screening of a large number of virtual alloys, we used only enthalpy of formation at zero temperature as the pivot factor to begin with, which was estimated from the cohesive energies with zero-point phonon contributions ignored. We expect the zero point energies (ZPEs) to have very minor effects on the *trend* of enthalpy of formation as shown in our simple estimation of ZPE of example alloys based on Debye's model (see the Supplementary Materials).

Note that a ternary addition that improves the B2 lattice stability may not necessarily enhance the alloy's surface affinity for hydrogen molecules, hydrogen diffusion within the bulk lattice, or resistance against sulphur poisoning. Therefore, a quaternary and even quinary addition may also be needed to balance these properties. Nevertheless, the alloying impact on these properties needs to be examined and addressed separately. Several theoretical studies have detailed the methodologies in predicting hydrogen diffusion in binary Pd alloys [13,28–30]. As a follow-up of the present study, key experiments on down-selected alloys have been performed to examine the phase equilibria, corrosion resistance in presence of H_2S, and hydrogen permeance performance [31–33]. A combined experimental and DFT study on oxygen induced surface segregation in a B2 CuPdY alloy based on the present study was reported recently [34].

2. Computational methodology

The first-principles pseudo-potential plane-wave DFT package of VASP (Vienna *ab initio* simulation package) [35,36] was used to calculate the total energies. For all calculations, we employed the projector augmented-wave (PAW) potentials [37] as supplied with VASP and the Perdew–Burke–Ernzerhof [38] gradient approximation for the exchange–correlation functional. The Brillouin zone integrations were performed on the Monkhorst–Pack k-point meshes [39] using the Methfessel–Paxton [40] method with a smearing parameter of 0.2 eV. All structures were fully relaxed under zero pressure at least twice (both lattice parameters and atomic coordinates) until energy converge reached 1 meV/atom. Reciprocal space (k-point) meshes of $8 \times 8 \times 8$ were shown to be sufficient for structural relaxation. Plane-wave energy cutoff at 500 eV was used for all systems in present study. For all transition metal elements, the semi-core 3p, 4p and 5p electrons were explicitly treated as valence. Only collinear spin polarization was considered in the calculations. The calculations showed that pure Pd was very weakly ferromagnetic at the ground state with an atomic magnetic spin moment of ~0.3 Bohr magnetons [22]. Magnetic contribution to the total energy became noticeable only when elements Cr, Mn, Fe, Co, and Ni were involved.

To study the energy of alloying substitution on the lattice stability of B2 phase, a $2 \times 2 \times 2$ supercell with 16 atoms in total was constructed. As the first step in searching for elements that stabilize the B2 phase at lower Pd contents, only substitutions for Pd sites were considered. A total of 8 compositions for each alloying element were chosen (namely $Cu_8Pd_{8-x}M_x$; where M denotes the alloying element and x = 1–8). The energy can be sensitive to atomic configuration. For each composition, a minimum of 3 representative configurations were tested except the composition of $Cu_8Pd_7M_1$. The lowest energy configuration was used later to calculate the enthalpy of formation. After full relaxation the structure either remained cubic or became slightly distorted as permitted by the symmetry of the lattice. To calculate enthalpy of formation (ΔH_f) of $Cu_8Pd_{8-x}M_x$, a composition-weighted average of the cohesive energies of corresponding pure elements was subtracted from the cohesive energy of a given composition, thereby:

$$\Delta H_f(\mathrm{Cu_8Pd_{8-x}M_x}) \approx \frac{1}{16}\{\mathrm{E(Cu_8Pd_{8-x}M_x)} - 8\mathrm{E(Cu)} - (8-x)\mathrm{E(Pd)} - x\mathrm{E(M)}\} \tag{2}$$

where $E(Cu_8Pd_{8-x}M_x)$ is the cohesive energy of B2 $Cu_8Pd_{8-x}M_x$ compound. E(Cu), E(Pd), and E(M) is the cohesive energy per atom of element Cu, Pd, and M in its ground state structure respectively. The resulting energy is an "enthalpy" because its volume is relaxed at zero pressure.

3. Results

3.1. Enthalpy of formation

DFT calculated formation enthalpy of stoichiometric B2 CuPd is −12.0 kJ/mol of atoms (see Table 1), which agrees well with experimental data of −13.77 ± 0.2 kJ/mol of atoms at 769 K, 827 K, and 866 K for $Cu_{60}Pd_{40}$ (at%) alloy [41] and a recent CALPHAD modeling report [42]. DFT calculated lattice parameter is 3.016 Å which also agrees well with an experimental value of 2.981 Å [43]. Our calculations also agree with earlier DFT studies that reported an enthalpy value of −12.35 kJ/mol of atoms at T = 0 K [15] and of −12.73 kJ/mol of atoms at 298 K [21].

The calculated enthalpies of formation and lattice parameters for $Cu_8Pd_7M_1$ at zero pressure are listed in Table 1. For comparison purpose, atomic radii of all alloying elements studied are also listed. Here we used the *metallic* radii for metals [44] for which the coordination number is 12. For Si, Ga, Ge, Sn, and Sb, the data were taken from [45]. Mind that one may get very different results if different atomic sizes are used. Fig. 1 plots ΔH_f and lattice parameters versus the International Union of Pure and Applied Chemistry (IUPAC) standard group number n of the doping elements in the periodic table for period 3, 4, 5 and 6. Note that 4d and 5d transition metal elements have similar atomic size and electronegativity except for n = 11 and 12. As expected, for enthalpy, the trends in period 5 and 6 are also quite similar, which show increasing enthalpy with n at beginning, reaching peak at n = 7 and decreasing thereafter. The trends in the supercell lattice parameter a versus n for transition metals are strikingly similar to the trends in enthalpy albeit in the opposite direction. The apparent correlation between ΔH_f and lattice parameter a is further examined in Fig. 1c. Although the data points are rather scattered, for models with doping elements in the same period, a general trend towards lower ΔH_f as a increases is evident. Among the compounds with lowest ΔH_f (<−17 kJ/mol of atoms), we found that they all have larger lattice parameters than pure B2 CuPd with the exception of

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