Hydrogen absorption and hydrogen-induced reverse segregation in palladium–silver surface

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ABSTRACT

Hydrogen absorption from surface to second subsurface layer of ordered and substitutionally disordered $Pd_3Ag(110)$ was investigated by performing density functional theory-based calculations. Ag segregation to topmost layer was found to be energetically favored for clean surface structure. The absorption of H in the alloy surface, for both ordered and substitutionally disordered structures, is generally characterized by lower activation barrier as compared to pure Pd surface. When H is present in the surface or subsurface regions, our results strongly suggest the tendency of subsurface Pd atoms to segregate to the surface or near surface region. The reverse segregation of Pd, along with the large lattice constant and the modified electronic structure of Pd atoms in Pd_3Ag alloy could help in understanding the experimentally determined high hydrogen permeability of PdAg membranes.

1. Introduction

Hydrogen production and storage is important for the realization of hydrogen-based fuel cell systems and other related hydrogen-based technologies. Producing high purity H_2, however, is still a major concern at present. Extracting H_2 from mixture of gases with the aid of hydrogen separation membranes is a promising process which is currently the topic of various research works [1–4]. An ideal hydrogen separation and permeation membrane is expected to allow the smooth penetration of H into the bulk and filter the undesired gases. Understanding the interaction of H with the membrane is therefore significant to design efficient hydrogen separation and permeable membranes.

Palladium and its alloys are popular for such applications due to their high H solubility and capability of absorbing large volume of H [5]. Among these alloys, PdAg is often used for hydrogen technology related applications. Compared to pure Pd, PdAg has better permeability and selectivity for H [6–8]. Alloying Pd with Ag also enhances the mechanical strength of the material [8,9]. PdAg has larger lattice constant and could suppress the induced lattice expansion upon storing H that causes the embrittlement of pure Pd [10].

Indeed, the importance of this alloy as hydrogen separation membrane or permeable film is evident as it was the subject of several investigations [6–9,11–27]. Aside from this, describing the properties of bimetallic surfaces and their interaction with adsorbates attract the attention of

researchers due to the different properties of the metal alloy with reference to the component metals that comprise it. For a clean PdAg surface, Ag is known to segregate to the surface [11–14]. However, in the presence of adsorbate, it was experimentally observed that reverse surface segregation of Pd atoms takes place [14,15]. Few works have been conducted to study the extent of this complex but fascinating phenomenon, especially for the case of H–PdAg system [25–27], which could be the key in understanding the efficient permeation of H.

In particular, it was identified that PdAg with 23% Ag atomic percentage gives the highest hydrogen permeability [8]. Theoretical works were conducted on the adsorption and absorption of hydrogen in $Pd_3Ag(111)$ [17,18,26,27]. Nevertheless, a recent experimental study investigated the surface composition of $Pd_3Ag(100)$ surface [12] and a theoretical work examined the effect of alloying Pd(100) with other metal on H atom adsorption [23]. The mechanism for oxygen reduction by hydrogen, on the other hand, was studied on PdAg(110) surface [16]. These studies signify the growing interest and the demand to study the different surface facets of PdAg other than the highly-densed (111) facet.

This present work investigates the absorption of hydrogen atom in $Pd_3Ag(110)$ surface by performing density functional theory-based calculations. The absorption of H from the surface to 2nd subsurface region (2nd topmost atomic layer) is studied in which the reactivity of the $Pd_3Ag(110)$ surface is compared with Pd(110). Specifically, both the ordered and substitutionally disordered $Pd_3Ag(110)$ were considered. A model that predicts the difference in total energy of substitutionally disordered $Pd_3Ag(110)$ surfaces was also designed. The effect of the presence of Ag atoms in the topmost layer on H absorption was equally discussed. Moreover, by placing H atom on the surface and in the subsurface regions of several substitutionally disordered $Pd_3Ag(110)$ surfaces, the tendency of surface adsorbed and subsurface absorbed H atom to induce reverse segregation of subsurface Pd atoms is predicted. The results presented here could aid in understanding the behavior of H in Pd_3Ag systems.

2. Computational method

Density functional theory calculations were performed as implemented in Vienna ab initio Simulation Package (VASP) [28,29]. Generalized gradient approximation (GGA), within the Perdew–Burke–Ernzerhof (PBE) functional [30], was used to treat the exchange-correlation energy. Ionic cores were described by the projector augmented-wave (PAW) method [31] and the Kohn-Sham one-electron valence states were expanded in a basis of plane waves with energy cutoff of 400 eV. This guarantees the convergence of H adsorption energies within ∼15 meV. We used potentials with electronic configurations of Pd ($4 d^9 5 s^1$) and Ag ($4 d^{10} 5 s^1$). The calculated lattice constant of Pd_3Ag is 4.00 Å and is in good agreement to previous computational and experimental results [12,19].

Six atomic layers of Pd_3Ag in (110) facet with four atoms in each layer were used to represent the surface unit cell. To account for surface relaxation, the three-topmost atomic

layers of the clean surface models were allowed to relax. A vacuum region of ∼15.0 Å was introduced to avoid the interactions of the periodically repeated slab in the direction perpendicular to the surface. Brillouin zone integration was performed on a grid of $4 \times 6 \times 1$ Monkhorst-Pack k-points. Energy convergence tests were carried out to guarantee the accuracy of the parameters used in the calculations. The methods of Methfessel–Paxton [32] and tetrahedron with Blöchl corrections [33] were used as smearing methods for calculations that involve relaxations and for total energy calculations, respectively, with a smearing width of 0.2 eV. Calculations that involve relaxations were executed until the forces on the unconstrained atoms were less than 0.01 eV/Å.

The ordered structure of Pd_3Ag bulk system yields two possible (110) surface structures: a surface that is completely covered by Pd atoms and a surface that has two Ag atoms in the top-most layer. These structures were referred to as (020202) and (202020) in this manuscript, respectively. The integers inside the ( ) correspond to the number of Ag atoms in each layer where the first integer refers to the topmost layer. The clean surface models of (020202) and (202020) – $Pd_3Ag(110)$ are shown in Fig. 1. In (202020), Ag atoms in the topmost layer protrude in the vacuum side, 0.165 Å higher than the surface Pd atoms. It denotes the preference of Ag to segregate to the surface which was also identified from previous studies [11–14] and is attributed to the lower surface energy of Ag as compared to Pd. Aside from the ordered structures, various substitutionally disordered $Pd_3Ag(110)$ surfaces were considered, in which, the atomic composition of the surface layers were varied.

For H-surface systems, 0.25 monolayer (ML) of H was introduced to accurately describe its absorption behavior with negligible hydrogen–hydrogen interaction. The stable positions of H atom in the surface and subsurface regions were determined by initially placing it in high symmetry sites. Relaxation process was then carried out by allowing the H and the three topmost layers of the surface to move. Hydrogen is basically identified to be energetically stable in pseudo-threefold and long bridge sites of the surface region and in tetrahedral and octahedral sites of the subsurface region, in agreement with previous studies [34,35]. Using these stable sites, absorption of H from the surface to 2nd subsurface layer was investigated. In this paper, we referred to 2nd and 3rd topmost atomic layers as 1st and 2nd subsurface layers, respectively. The binding energy of H is calculated by using the equation

$$E_b = E_{H+Surface} - \tfrac{1}{2} E_{H2} - E_{Surface}, \tag{1}$$

where $E_{H+Surface}$ is the total energy of the H-surface system, E_{H2} is the total energy of hydrogen molecule in gas phase and $E_{Surface}$ is the total energy of the isolated surface. Employing this equation, a more negative value implies stronger binding energy.

The reaction paths were investigated by employing climbing image – nudged elastic band (CI-NEB) method [36], where the H and the three top-most layers were allowed to relax during calculation. It was reported from our previous work that relaxation of the surface atoms of Pd(110) significantly influenced the energetics and pathway of H atom [34]