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Various properties of Pd_3Ag/TiAl membranes from density functional theory

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ABSTRACT

First principles calculation reveals that the Pd_3Ag/TiAl interface structure terminated with Pd atoms at the top of the octahedral interstitials of TiAl possesses higher interface strength and better thermal stability than other interface structures, which should be fundamentally due to a stronger chemical bonding formed in the interface. Calculation also shows that hydrogen diffusion between surface layer and inter-site seems energetically more favorable than diffusion within the surface layer, and that the small energy barrier suggests the easy diffusion of hydrogen across the Pd_3Ag/TiAl interface. Moreover, hydrogen diffusion would have a small effect to increase the interface energy and decrease the interface strength. The calculated results are in good agreement with experimental observations in the literature, and demonstrate that the Pd_3Ag/TiAl membranes should be a good candidate for hydrogen permeation.

1. Introduction

The noble metal palladium (Pd) has sparked great research interests during the past decades [1–3], as Pd membranes possess perfect selectivity and high permeability of hydrogen [4,5], and have been widely used in various hydrogenation and dehydrogenation processes [6,7]. Nevertheless, the hydrogen embrittlement is apt to occur in Pd membranes due to frequent lattice expansion and contraction as a consequence of the well-known $\alpha \leftrightarrow \beta$ phase transition [8], and the hydrogen permeability of Pd is easily deteriorated by the poisoning of several gases such as H_2S, CO, etc. [9–13].

One of the solutions to the above problems is to alloy Pd with such elements as Ag, Cu, Ru, Ni, Y, and Au, etc. [12–16]. Among all these Pd alloys, the binary Pd–Ag system has been commonly regarded as a significant and superior candidate for hydrogen separation due to the following facts. First, the addition of Ag could eliminate the hydrogen embrittlement in Pd membranes, and therefore enhance the lifetime of Pd membranes [17]. Second, the alloying of Ag would greatly improve the capability of hydrogen separation of Pd, and the PdAg alloy with an Ag composition of 23 wt% may have a hydrogen permeability about twice of pure Pd [18–22]. Third, the solution of Ag in Pd seems very easy, and single FCC solid solutions are formed within the entire composition range. Fourth, Ag lowers the operation temperature of hydrogen separation, and PdAg alloys are also cheaper than pure Pd [17].

It is well known that to achieve higher permeability and lower cost, the PdAg membranes should be kept as thin as possible, and various porous supports, such as ceramics [23], glasses [24,25], and stainless steel [26] have been therefore developed to maintain the mechanical stability of PdAg membranes. Nevertheless, the interface cohesion between the membranes and supports has become a challenging problem, mainly due to the big difference of coefficients of thermal expansion or atomic interdiffusion within the interface region [27,28]. Very recently, a porous TiAl alloy has been fabricated by means of the Kirkendall effect [29], and is therefore proposed as a promising support for Pd membranes [30], based on its good properties and wonderful match with Pd [31,32].

Prior to practical application of the PdAg/TiAl membranes, it is of vital importance to find out the cohesion properties of PdAg/TiAl interfaces, as well as the effect of H on interface properties during the process of hydrogen separation. In this respect, however, there is no report regarding PdAg/TiAl membranes in the literature. By means of highly accurate first principles calculations, the present study is dedicated to investigate the cohesion properties of PdAg/TiAl interfaces and the behaviors of H diffusion within the interface region. Specifically, the PdAg phase with the atomic compositions of Pd_3Ag is selected in the present study, as this composition is very close to the experimentally observed PdAg alloy with the highest hydrogen permeability as related before [18–22]. It will be shown that the present findings are not only in good agreement with experimental results in the literature, but

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also provide a deep understanding of the underlying physics of Pd_3Ag/TiAl membranes.

2. Method of calculation

All calculations are performed by means of Vienna ab initio simulation package (VASP) [33] with the plane-wave basis and a projector-augmented wave (PAW) method [34]. The electron exchange correlation effects are described by local density approximation (LDA) of Perdew and Zunger [35], and the plane-wave cutoff is 400 eV. It should be indicated that LDA gives a better description of the work function for transition metals than generalized gradient approximation (GGA) [36]. For each calculation, periodic boundary conditions are added in all three principal axes, and the energy criteria are 0.01 and 0.001 meV for relaxation and static calculations, respectively. For k space integration, the temperature smearing method of Methfessel and Paxton [37] is used for relaxation calculation, and the modified tetrahedron method of Blöchl–Jepsen–Andersen [38] is performed for static calculation.

For the bulk calculation, a unit cell of four atoms is adopted for FCC Pd, Ag, and $L1_2$ Pd_3Ag with a k-mesh of $13\times13\times13$. The elastic constants are calculated according to the universal-linear-independent coupling-strain method (ULICS) of Yu [39] based on the stress–strain theory [40–42]. For the surface calculation, the low-index surfaces of (1 0 0), (1 1 0), and (1 1 1) are selected for Pd, Ag, and Pd_3Ag, due to their close-packed nature and lower energy state. It should be mentioned that there are two types of surfaces for both (1 0 0) and (1 1 0) Pd_3Ag, i.e., the surface terminated with the Pd atoms is named type I, and the surface terminated with both Pd and Ag atoms is called type II. After the test, seven surface layers with the vacuum distance of 30 Å are selected for each surface, and the k-meshes of $13\times13\times1$ and $17\times17\times1$ are used in relaxation and static calculations, respectively.

The present interface calculation is focused on the interface structures between (1 0 0) surfaces of $L1_2$ Pd_3Ag (overlayer) and $L1_0$ TiAl (substrate), and such a selection is mainly due to the low surface energy of (1 0 0) surface of $L1_0$ TiAl as well as the good match between (1 0 0) surfaces of $L1_2$ Pd_3Ag and $L1_0$ TiAl. A surface unit cell of 1×2 and the optimized lattice constants of $L1_0$ TiAl bulk (a=3.913 Å, c=3.999 Å) from our previous work [43] are selected for the (1 0 0) Pd_3Ag/(1 0 0)TiAl interface. Accordingly, Fig. 1 shows the six possible interface models of (1 0 0) Pd_3Ag/(1 0 0)TiAl. For each interface model, there are seven TiAl layers and (4+4) Pd_3Ag layers with a vacuum distance of 36 Å.

For H diffusion in the (1 0 0)Pd_3Ag/(1 0 0)TiAl interface, the climbing image nudged elastic band method (cNEB) [44] is used to find out the minimum energy path and corresponding energy barrier for the process of H diffusion. In this approach, the diffusion path is discretized between the initial and final configurations. These discrete configurations or images are linked to each other by elastic springs. All images are optimized simultaneously with a k-mesh of $7\times7\times7$ along the reaction path until the forces acting on the atoms in each image are smaller than 0.02 eV/Å.

3. Results and discussion

3.1. Surfaces of Pd, Ag, and Pd_3Ag

Before surface calculations, various properties of FCC Pd, FCC Ag, and $L1_2$ Pd_3Ag bulks are first calculated, and the derived results are in good agreement with experimental data in the literature [45–47]. For instance, the present lattice constants (Pd: a=3.85 Å; Ag: a=4.01 Å; Pd_3Ag: a=3.89 Å) are consistent with corresponding experimental values in the literature (Pd: a=3.89 Å [45]; Ag: a=4.06 Å [46]; Pd_3Ag: a=3.96 Å [47]). The obtained bulk modulus B and elastic constants of C_{11}, C_{12}, and C_{44} for Pd bulk are 2.24, 2.60, 1.97, and 0.74 Mbar, respectively, which match well with the corresponding experimental data of 1.95, 2.34, 1.76, and 0.795 Mbar [45].

After a series of surface calculation, the surface energy (σ) and work function (Φ) of Pd, Ag, and Pd_3Ag surfaces are derived by means of the following formulas:

$$\sigma=\frac{1}{2}(E_{\mathrm{tot}}^{slab}-E_{\mathrm{tot}}^{bulk}), \tag{1}$$

$$\Phi=V_{\mathrm{vac}}-E_{\mathrm{f}}, \tag{2}$$

whereE_{tot}^{slab} is the total energy of the slab, E_{tot}^{bulk} is the total energy of the corresponding bulk, V_{vac} is the vacuum level in the vacuum region, E_{f} is the Fermi energy of the slab, and the factor 1/2 in Eq. (1) is due to two equivalent surfaces in the slab used in the present work. It should be noted that the work function is the minimum energy needed to remove an electron from the solid to a point in the vacuum immediately outside the solid surface.

Consequently, Table 1 lists the obtained surface energy and work function of various Pd, Ag and Pd_3Ag surfaces. It could be seen from this table that the derived work function and surface energy of Pd and Ag from the present calculation are in good agreement with available experimental results in the literature [48–54]. For instance, the present surface energies of Pd (1 0 0) and (110) surfaces are 2.12 and 2.22 J/m^2, respectively, which match well with the corresponding values of 2.00 and 2.05 J/m^2 from experiments [51,52]. In addition, one can also observe from Table 1 that the descending sequence of surface energy of Pd, Ag, and Pd_3Ag surfaces is as follows: (110)→(1 0 0)→(111), suggesting that the close-packed (111) surface is the most stable one with the lowest surface energy. Specifically, for (1 0 0) and (1 1 0) surfaces of Pd_3Ag, the type-II terminated with both Pd and Ag atoms would be more stable with lower surface energy than its type-I counterpart terminated with Pd atoms, and such a feature should be mainly due to the lower surface energy of Ag as shown in Table 1.

It is of interest to investigate the layer spacing of surfaces, and the change of interlayer spacing (Δd_{ij}) due to surface formation is presented by:

$$\Delta d_{ij}=(d_{ij}-d_0)/d_0 * 100\%, \tag{3}$$

where d_0 is the distance between two adjacent layers of the bulk, and d_{ij} is the distance between two adjacent surface layers of i and j after relaxation. After the calculation, it can be discerned that compared with the bulk, the present interlayer distance between the surface and sub-surface layers of Pd (100) and Ag (100) experiences a contraction of −1.17% and −1.54%, respectively, which are consistent with the calculated values of −0.6% and −1.9% [54]. Moreover, the Δd_{ij} value between the surface and sub-surface layers of Pd_3Ag (100)-I surface is −1.47%, which is bigger than the corresponding value of −0.7% for Pd_3Ag (100)-II surface.

In order to further understand the surface formation, Fig. 2, as a typical example, shows the comparison of total density of states (DOS) of Pd_3Ag (100)-II surface and bulk. It can be seen clearly that compared with the bulk, the Pd_3Ag surface has a smaller bandwidth of DOS, and its electronic structure is more localized with higher values of DOS peaks near the Fermi level. In addition, the two DOS peaks of bulk atoms at about −3.0 eV and −5.2 eV are combined into one DOS peak centered at about −4.0 eV for Pd_3Ag surface. Such comparison of DOSs implies that surface formation should have induced the changes of electronic distribution, and the total energy of the surface atoms is higher than that of bulk atoms.

3.2. Pd_3Ag/TiAl interface

It is well known that the cohesion properties of the interface between PdAg and its support have a decisive effect on the