Fusion Engineering and Design xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Fusion Engineering and Design

journal homepage: www.elsevier.com/locate/fusengdes

Hydrogen diffusion mechanism on α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) interface: A first-principles study

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HIGHLIGHTS

- The α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) interface structural model was established.
- The adsorption sites and adsorption energy of α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) interface were calculated by density functional theory, and transition states of adsorption sites were determined based on transition-state search.
- The hydrogen resistance mechanism of α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) interface was discovered by first-principles.

ARTICLE INFO

Article history:
Received 30 October 2016
Received in revised form 7 May 2017
Accepted 8 May 2017
Available online xxx

Keywords:
α-$AlPO_4$
α-Al_2O_3
Interface
First-principles
Tritium permeation barriers

ABSTRACT

α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) fabricated by selective laser sintering could improve the performance at protection against H permeation compared with that of single phase α-Al_2O_3 and α-$AlPO_4$. In this study, the possible interfacial structures, thermodynamics and kinetics of hydrogen diffusion in heterojunction α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) coating were investigated based on the density functional theory. The adsorption energy and the adsorption sites are calculated in order to obtain the most stable configuration. The hydrogen isotopic diffusion in heterojunction α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) is also compared with that in α-Al_2O_3 (0001) or α-$AlPO_4$ (0001) surface. The interfacial binding illustrates that hydrogen is more difficult to diffuse through the grain compare with α-Al_2O_3 (0001) or α-$AlPO_4$ (0001). Due to the higher saddle point energy of hydrogen migration and potential well, the hydrogen resistivity property of α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) is better than the single phase materials. The interface of α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) is predicted to be effective at suppressing hydrogen permeation.

1. Introduction

Operating of radioactive tritium, optimizing of tritium balance and controlling tritium inventory play crucial roles in fusion reactors similar to the International Thermonuclear Experimental Reactor (ITER). The utilization of a coating, namely, hydrogen permeation barrier (HPB), deposited on structural material of steel is an effective way to hinder tritium migration [1]. The hydrogen permeation barrier is one of the key technological developments of fusion reactor cladding, and is an important safeguard to reach the safety tritium radioactive environmental standards [2]. There are several materials posing as formidable candidates for tritium permeation barrier (TPB) coatings, such as the BN [3], Cr_2O_3 [4], ZrO_2 [5], Er_2O_3 [6] and Y_2O_3 [7]. Among all of the HPB materials, Al_2O_3 [8–14] has received the most widespread attention. Owing to low permeability, low conductivity, structural stability, corrosion resistance, the feasibility of the process, and so on, the α-Al_2O_3 coating was carried out earlier and has become one of the tritium candidate coating materials of fusion reactors [15,16]. Tritium barrier effect of the α-Al_2O_3 coating was corroborated by the experiment, and its mechanism was discovered. For hydrogen isotopes permeation through HPB material, the hydrogen isotopes could be absorbed on the surface of the upstream side and firstly dissociated into atoms, then dissolved into the material, followed by diffusing through the material, and finally recombining into molecules on the downstream side [17,18], which is calculated based on first-principles. First-principles is widely used in the H diffusion and obtains the H site.

Many researchers have obtained the properties and mechanisms of HPB through first-principles. Hydrogen sites are calculated in previous density functional theory (DFT)-local density approximation (LDA) at a tetrahedral site in bulk FeAl [19]. Johnson

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http://dx.doi.org/10.1016/j.fusengdes.2017.05.039
0920-3796/

et al. have calculated the hydrogen site on the FeAl (110) surface by GGA-PBE (Perdew-Burke-Ernzerh), while hydrogen adsorbs on top of Al atoms of the FeAl (100) surface [20]. Zhang et al. [21] utilized PW91 (Perdew-Wang)-GGA (generalized gradient approximation) to carry out first-principles total energy calculations in α-Al_2O_3/FeAl, and revealed the mechanism of hydrogen diffusion in the interfacial slab. Next, thin ceramic coatings, such as SiO_2, act as TPB material to suppress tritium permeation through structural materials [22]. The α-$AlPO_4$ crystal structure is derived from the SiO_2. The investigation of α-$AlPO_4$, whose tritium simulation has not been reported, could reveal the effect of tritium resistance to the tetrahedral crystal. Moreover, the hydrogen isotope diffusion mechanism from the α-Al_2O_3 to α-$AlPO_4$ is unknown. The diffusion of hydrogen isotopes and stability will depend on the structure of the oxide interface, and the lattice mismatch degree between the components further affects the performance of HPB [21]. Therefore, the diffusion of tritium in α-Al_2O_3 and α-$AlPO_4$ interface region, which is also lacking in a clear structure, is distinct from that in single phase α-Al_2O_3 and α-$AlPO_4$. The simulation can reveal the diffusion mechanism of tritium to α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) interface and predict the new material of HPB. It is reasonable to do theoretical studies for diffusion of hydrogen in α-$AlPO_4$ (0001)/α-Al_2O_3 (0001).

In the present paper, the structure of α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) interface was established and relaxed. Macroscopic experiments have found that hydrogen isotopic permeation through such aluminum rich coating based HPB is predominantly controlled by hydrogen diffusion in bulk [23,24]. Thus it is reasonable to use hydrogen atoms instead of tritium atoms for simulation. Based on the interface structure, composite interfacial adsorption sites and the adsorption energy were also calculated by first-principles calculation. Utilizing transition-state search method by Dmol3, the diffusion process of H atoms from α-$AlPO_4$ (0001) into the α-Al_2O_3 (0001) were then also well-studied in this paper.

2. Computational method and model

2.1. Method

Dmol3 [16] program package in Materials Studio 8 of Accelrys Inc. by first-principles was used to calculate total energy in the PW91 [25] -GGA. The parameters used in the α-Al_2O_3 calculation [26] were selected most likely on account of the lack of reports on hydrogen isotope penetration to α-$AlPO_4$. The double numerical quality basis set with polarization functions (DNP) [27] had to be adapted, and the semi-core pseudopotential [28] could be utilized. Spin-polarized and Monkhorst-Pack mesh [29] k-points of $3 \times 3 \times 1$ for bulk and surface calculations were selected. All calculations were utilized a convergence tolerance of energy of 2.0×10^{-4} Ha/atom (1 Ha = 27.21 eV), a maximum force of 0.004 Ha/Å, and a maximum displacement of 0.005 Å, allowing the energy of the model to converge. Maximum SCF cycles were turned into 200. The cut-off energy were 300 eV.

The three potentials chosen to optimize the structure of α-$AlPO_4$ include GGA, LDA, and PBE. The result demonstrates that the PW91-GGA is the best suitable potential to approach the experiment result. Lattice constants were a = b = 4.949 Å, c = 10.945 Å for α-$AlPO_4$ which is consistent with the experimental value a = b = 4.944 Å, and c = 10.946 Å. The optimized lattice constants for the bulk α-Al_2O_3 were a = b = 4.806 Å and c = 13.133 Å which were the same parameters to the experimental value.

Adsorption energy is defined as:

$\Delta E_{ads} = E_{[slab+H]} - (E_{[slab]} + E_{[H]})$ where $E_{[slab+H]}$, $E_{[slab]}$, and $E_{[H]}$ are the calculated total energy of the H atom on the α-$AlPO_4$(1000)/α-Al_2O_3(0001) slab, a clean α-$AlPO_4$(1000)/α-Al_2O_3(0001) slab and a gas-phase H atom. With the definition, negative values of ΔE_{ads} signifies adsorption is more stable than the corresponding clean surface and H atom. The complete linear synchronous transit/quadratic synchronous transit (LST/QST) method is used to locate the transition states (TS) for hydrogen dissociation and hydrogen diffusion. Frequencies of hydrogen are determined by all critical points identified on the potential energy surface (PES) to determine minima and transition states.

2.2. Established and relaxed geometric structures

The α-Al_2O_3 belongs to the hexagonal close pack (hcp). The O atoms in the unit cell are the cubic close-packed structure on α-Al_2O_3 (0001). Among the numerous α-Al_2O_3 crystal planes, α-Al_2O_3 (0001) is the most stable juxtaposed with α-Al_2O_3 (1–102) and α-Al_2O_3 (11–20) [30]. The lattice constants of α-Al_2O_3 (0001) are a = b = 4.754 Å, c = 12.988 Å compared with the experimental values (a = b = 4.759 Å, c = 12.992 Å [31]). α-$AlPO_4$ has a hexagonal structure whose close-packed plane is (0001). The crystal structure of α-$AlPO_4$ (0001) whose lattice constants are a = b = 4.944 Å, c = 10.946 Å is shown in Fig. 1. In crystallography, lattice mismatch degree is defined as:

$$\delta = (a_\beta - a_\alpha)/a_\alpha$$

Where a_α, a_β refers to the lattice constant. With the calculation, α-$AlPO_4$ (0001) and α-Al_2O_3 (0001) have small lattice mismatch degree with 2.795% (less than 5%). It implies that this interface is a coherent interface [32]. (2×2) Supercell flat slab model was used to simulate the interface configuration. To simulate the actual surface, it is necessary to add a sufficiently large vacuum in the direction perpendicular to the surface of the α-$AlPO_4$. Interaction of the adjacent unit cell can be ignored when the vacuum layer spaced between the alumina surfaces equals to 15 Å [21]. Therefore, the interfacial lattice constants are a = b = 9.698 Å, c = 40.000 Å.

As the structure shown in Fig. 1(A), a possible mechanism contributing to the instability of the structure is the existence of a separate oxygen atom at the interface. With the addition of an Al atom, the total energy of the interface declined by 11.94 eV compared with the sum of original structure's energy and single Al atomic energy. Consequently, Al atoms were added to relax all geometric structures. For the cyclical principle, 13 kinds of supercell flat slab models were established, having six possible configurations, as shown in Fig. 1(B).

The final geometric structure of the α-Al_2O_3 (0001)/α-$AlPO_4$ (0001) slab is shown in Fig. 2. Two slabs are made of 22 layers. The α-$AlPO_4$ (0001) surface was modeled by a slab consisting of 10 layers, whereas α-Al_2O_3 (0001) surfaces were modeled by a slab composed of 12 layers (*i.e.,* four O layers). Compared with others, the structure, as shown in Fig. 1(B) (b), was thought as the general construction in the material because it is the most representative structure.

As shown in Fig. 2, the O5-Al3-O4 bond angle is 137.135° in the optimized structure which has smaller repulsive force compared with it in the original structure. In the original structure, the distances of Al3-O4, Al3-O5, Al3-O6 and Al3-O7 are 2.192 Å, 1.978 Å, 1.727 Å and 1.850 Å, respectively. With the relaxed geometric calculation by Dmol3, the distances of Al3-O4, Al3-O5, Al3-O6 and Al3-O7 are 1.812 Å, 2.012 Å, 1.787 Å and 1.826 Å, respectively. The interatomic distances (Al-O) in the interface region of both slabs are very close to corresponding experimental values (1.86-1.97 Å [26]). The result considers that proper binding between α-$AlPO_4$ (0001) and α-Al_2O_3 (0001) was obtained, providing support to the real relevance of the models.

Please cite this article in press as: L.Y. Wang, et al., Hydrogen diffusion mechanism on α-$AlPO_4$ (0001)/α-Al_2O_3 (0001) interface: A first-principles study, Fusion Eng. Des. (2017), http://dx.doi.org/10.1016/j.fusengdes.2017.05.039