Computational Materials Science 144 (2018) 56–63

Contents lists available at ScienceDirect

Computational Materials Science

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

Oxygen diffusion and migration in clean and defective uranium nitride UN (0 0 1) surfaces

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ARTICLE INFO

Article history:
Received 6 November 2016
Received in revised form 28 November 2017
Accepted 1 December 2017

Keywords:
DFT
UN
Adsorption
Vacancy
Inclusion
NEB

ABSTRACT

This study focuses on the diffusion of atomic and molecular oxygen through the uranium mono-nitride UN (0 0 1) surface. The adsorption of oxygen at the most favorable sites has been checked on different surface states namely: clean surface and surfaces containing defects such as inclusion atoms.

Inclusions atoms are positioned at a uranium U atom vacancy or at a nitrogen N atom vacancy location of the UN (0 0 1) surface. Neptunium, plutonium, protactinium, silver and neodymium which are the most probable nuclear reactions (n, U) products have been selected as U atom substitute. Some light elements such as carbon, chromium and silicon were used to replace an N atom.

The first principle calculation, based on Density Functional Theory (DFT) was used, taking into account the Generalized Gradient Approximation (GGA) and the Projector-Augmented Wave (PAW) to describe the exchange-correlation functional.

The purpose of this work is to verify the oxygen adsorption energy variations performed across all the studied surfaces. The most favorable sites of UN (0 0 1) clean and defective surfaces to oxygen O atom diffusion were preliminary identified. In the second step, atomic dynamical Potential Energy Surface (PES) was used to study the interaction between O atom and UN (0 0 1) surfaces at these sites. Finally, Nudged Elastic Band (NEB) method was used in order to investigate the migration of O atom through the UN (0 0 1) surfaces.

The results show that at the bridge site, the adsorption and incorporation energies of oxygen atom on and in the UN (0 0 1) surfaces respectively, do not substantially vary with the type and position of the studied impurities. But, at the N vacancy site, the adsorption energy of the O atom decreases practically when UN (0 0 1) surfaces contain inclusion atoms compared to the clean surface case.

Furthermore, the NEB calculations show discrepancies for the Minimum Energy Path (MEP) during the migration of the O atom at the bridge site through the studied UN (0 0 1) surfaces and depending on the type and position of the added impurities. Among the studied MEPs, protactinium is found to be the most suitable barrier to the diffusion of oxygen through the UN surface as an inclusion on UN (0 0 1).

1. Introduction

Uranium mono-nitride (UN) is a promising fuel material for Generation-IV fast breeder nuclear reactors because of some interesting physical properties compared to classical fuels such as UO_2. The UN phase stability, the high thermal conductivity and the high uranium density in the fuel constitute some of the advantageous characteristics compared to oxide fuels [1–3]. UN as an actinide compound suffers from the oxidation process, even for the case of the low oxygen content in the fuel pin, which deteriorates its effectiveness in the nuclear reactors [4–7]. Oxidation mechanism simulations were studied in various references with several experimental and theoretical works which were carried out to explain this behavior [8–11].

The most energetically favorable UN (0 0 1) surface is frequently used for the theoretical studies and analyses: namely the studies of the spontaneous of the molecule dissociation of oxygen (O_2) or the comprehension of the diffusion mechanism of the oxygen O atom [12,13].

The diffusion phenomenon of oxygen on UN (0 0 1) depends on the surface quality. Indeed, energy of adsorption of the O atom at the most favorable interstitial (bridge) site for a clean surface increases if this surface loses a nitrogen N atom (vacancy of N). Besides, this last position (N vacancy site) becomes even more

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https://doi.org/10.1016/j.commatsci.2017.12.003
0927-0256/

favorable to an adsorption of atomic oxygen on this same surface [12–15].

The aim of this work is to bring more details about the way the oxygen is diffused on UN (0 0 1) clean surface and other surfaces containing vacancies or impurities (atomic inclusions) substituted with the U or N atoms of surface. The migration of the O atom through UN (0 0 1) surface is also studied at the bridge site for various surface qualities: clean surface and those containing inclusion atoms using the concept of the Nudged Elastic Band [16,17].

The selection of the inclusion atoms is performed by using two categories: the first category consists of heavy atoms resulting from the most probable nuclear reactions (n, U) such as Pa, Nd and Pu. Considering that the fuel will undergo these modifications during its employment in the nuclear reactor operations. These inclusions replace a U atom of UN (0 0 1) surface.

The second category of inclusion atoms consists of some light elements which can be encrusted in the fuel during the manufacturing process such as C, Cr or silicon. These inclusions replace an N atom of UN (0 0 1) surface.

The most favorable positions to O atom diffusion on clean and defective UN surfaces were identified by using the ionic relaxation method of density functional theory. Adsorption energies of the O atom during its diffusion on surfaces were calculated using the concept of the static and dynamic Potential Energy Surface.

The theory of the NEB makes it possible to identify the MEPs of atomic oxygen through the various considered surfaces and thus, determining the inclusion atom UN (0 0 1) surface which is the most appropriate effective barrier to oxygen diffusion.

2. Computational details

Density functional theory which is an *abinitio* method was used to carry out for this study. The well-known Vienna Simulation Package (VASP 5.3) code was used to perform all the structural and diffusion calculations [18–21]. The Projector Augmented Wave method was used, in which the Uranium $6s^2 6p^6 6d^2 5f^2 7s^2$ and nitrogen $2s^2 2p^3$ electrons are considered as valence electrons. The standard Generalized Gradient Approximation (GGA) as an exchange correlation functional is taken into account [22,23]. A ferromagnetic configuration of UN is considered in all this simulation since, it has been demonstrated that it is energetically more favorable than other magnetic phases [14].

The UN supercell $2 \times 2 \times 1$ is used in all our calculation with a slab of 5 layers and a space vacuum of 20 Å. The first two layers of the UN slab are kept fixed (see Fig. 1). The asymmetric model of surface is applied and the induced dipole moment is taken into account by applying a dipole correction [24].

The wave functions are expanded in a plane wave basis set with an energy cutoff of 550 eV. A $3 \times 3 \times 1$ Monkhorst-Pack special k-point grid in the Brillouin zone (BZ) is used for surface calculation [25].

The adsorption energy ($E_{adsorption}$) is considered as a measure of strength of the adsorbate–substrate adsorption. It is then defined as [26,27]:

$$\boldsymbol{E_{adsorption}} = -[\boldsymbol{E_{adsorbate\_substrate}} - (\boldsymbol{E_{substrate}} + \boldsymbol{E_{adsorbate}})] \quad (1)$$

$\boldsymbol{E_{adsorption}}$: Adsorption energy.
$\boldsymbol{E_{adsorbate\_substrate}}$: Total energy of adsorbate–substrate system in the equilibrium state.
$\boldsymbol{E_{substrate}}$: Total energy of substrate alone.
$\boldsymbol{E_{adsorbate}}$: Total energy of free adsorbate alone.

With this definition, positive values of $\boldsymbol{E_{adsorption}}$ reflect a strong interaction of adsorbed species with atoms of the surface. The average adsorption energy per oxygen atom on the UN surface, E_{ad_O}, is defined as:

$$\boldsymbol{E_{ad\_O}} = -\frac{1}{\boldsymbol{N_O}}[\boldsymbol{E_{O/UN}} - (\boldsymbol{E_{UN}} + \boldsymbol{N_O E_O})] \quad (2)$$

where N_O is the number of oxygen atoms in the surface unit cell, and $E_{O/UN}$, E_{UN}, and E_O represent the total energy of the adsorbate-substrate system, the clean surface, and the free oxygen atom energy, respectively. So, the positive number indicates that the adsorption is exothermic (stable) and the negative number indicates endothermic process.

3. Results and discussion

3.1. Bulk and surface calculations

UN belongs to the space group $fm\bar{3}m$ (No. 225), with fcc NaCl type ionic structure [28]. Our calculated UN cell parameter is 4.86 Å in the same order of magnitude of the experimental value (4.886 Å) [29] and some theoretical results (4.83 Å, 4.95 Å [30,31]. Our calculated cohesive energy is 13.64 eV analogous to the experimental (13.6 eV) [29] and other theoretical values (14.7 eV, 13.4 eV) [30–32]. The bulk modulus which was derived from the fitting of the energy-volume data using the third-order Birch-Murnaghan equation of states (EOS) [33] is 201.9 GPa and this value shows good agreement with some theoretical data (182 GPa, 277 GPa) [30–32] and the experimental result (194 GPa) [29]. The shear modulus G = 85.4 GPa, Poisson's ratio $\nu = 0.33$ and anisotropic factor A = 0.41 which were calculated using the Voight-Reuss-Hill (VRH) method [34,35] show close agreement with the theoretical values (G = 79.0 GPa, $\nu = 0.33$ and A = 0.41) [36] and have the same order of magnitude of the experimental values (G = 104 GPa and $\nu = 0.26$) [37].

The most favorable position for O diffusion through UN (0 0 1) clean surface was established to be the bridge (interstitial) site for both on and in surface. Considering this site, it has been demonstrated that the dissociation of oxygen molecule O_2 is occurring when it is approaching UN (0 0 1) surface for several state of surface: clean and U or N vacancies surfaces. The UN (0 0 1) N-vacancy surface shows the most probabilistic surface to the dissociation of O_2 molecule with more ability to the adsorption of both molecule atoms compared to the UN (0 0 1) clean or the U vacancy surfaces. It has been also found, that the N vacancy site becomes the most favorable UN (0 0 1) on-surface atomic adsorption of oxygen [38,39,12,15].

3.2. Oxygen diffusion on UN (0 0 1) surface containing inclusion atoms

3.2.1. Methodology

Some of the most probable (n,U) nuclear reactions products were selected as an atomic inclusion at the uranium U-vacancy atom position of the UN (0 0 1) surface, whereas some light elements were selected as inclusion atom at an N-vacancy emplacement (see Fig. 2).

The binding energy of the atomic inclusion is initially calculated to ensure the stability of the system i.e. assuring that incorporation of the inclusion atom in surface is energetically favorable.

The energy of adsorption (see Eqs. (1) and (2)) of the oxygen atom on various surfaces is then calculated at two most favorable UN (0 0 1) surface positions: the interstitial site (bridge) and the N vacancy site.

3.2.2. Binding energy of inclusion atom on UN (0 0 1) surface

The atoms studied as inclusions at a U vacancy position of UN (0 0 1) surface are listed in Table 1. The binding energy of the