Ab initio modeling of UN grain boundary interfaces

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Motivation

Uranium mononitride (UN) is a compound with metallic properties possessing rock-salt *fcc* structure over a wide temperature range and considered as a promising candidate for Generation-IV nuclear reactors [1]. Unfortunately, chemically aggressive oxygen can affect UN performance and stability [2]. Therefore, it is necessary to understand the mechanism of oxygen adsorption and further oxidation of uranium mononitride bulk, surface and complicated systems. Recently, we performed a detailed study on oxygen interaction with UN surface using density functional theory (DFT) calculations [3]. We were able to identify a mechanism of UN surface oxidation consisting of several important steps starting from oxygen molecule dissociation and finishing with oxygen atom incorporation into vacancies on the surface.

Nevertheless, many questions on UN oxidation are still opened. Taking into account the fact that synthesized specimens of polycrystalline fuel powder contains particles with differently oriented crystallographic facets and a wide variety of interfaces between the grains [4], we consider here a role of grain boundaries (GB) in UN oxidation. This makes theoretical simulation of grain boundaries between different UN facets and their interaction with defects and O impurities very important for realistic description of actinides. It's also significant to study out similarities and differences in oxygen incorporation processes energetic on both single surface and grain boundary.

In this work we suggest a simplest grain boundary interface (310)[001](36.8°) model and present first result of energetic of N vacancy formation on grain boundaries as well as oxygen incorporation into pre-existing vacancies.

Computational details

The results were obtained using the *VASP* computer code, employing a plane-wave basis set combined with PAW pseudopotentials for U, N and O atoms (containing 14, 5 and 6 valence electrons, respectively) [5].

In this study, we have generated *k*-points using the Monkhorst-Pack's technique [6] whereas the electron populations were determined following the method of Methfessel and Paxton [7] as implemented in the *VASP* code. For each series of calculations, we have found the optimal *k*-point mesh that provides convergence of the results: the 4×4×4 mesh for grain boundary calculations (the 4×4×1 and 8×8×1 meshes was used for previous surface calculations).

We have performed spin-relaxed calculations using an initial ferromagnetic state for the UN. It is usually convenient to start from the larger local magnetic moments. This is why in the spin-relaxed FM calculations we have started from the value of 2 μ_B *per* U atom. The smearing parameter of 0.2 eV has been found to be optimal for reasonable convergence suggesting the electronic entropy contribution of the order of 10 meV. The optimal cut-off energy has been found to be equal to 520 eV. In this study, we present results of first DFT calculations on oxygen behaviour between UN grain boundaries.

Model

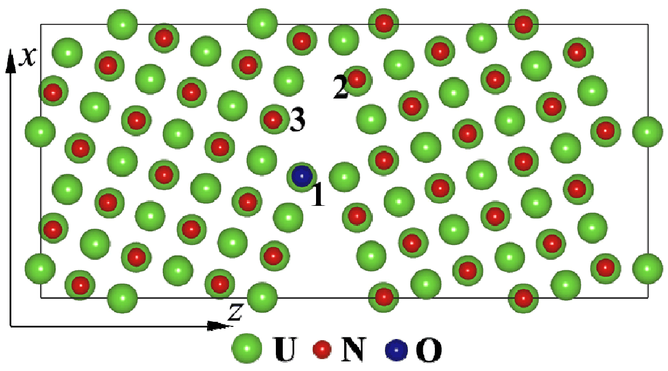

Figure 1. Cross-section of the (310)[001](36.8°) tilt grain boundary supercell (15.40 Å × 4.87 Å × 34.13 Å) for UN slab model with oxygen incorporated into one of possible positions (here position 1).

We consider a model of (310)[001](36.8°) tilt grain boundary used previously for describing of electron-trapping in MgO, NaCl and LiF compounds [8]. The periodic supercell with 15.40 A˚ × 4.87 A˚ × 34.13 A˚ linear dimensions contains 160 atoms (or 159 for N vacancy calculations). We have considered three positions of incorporated O atoms or N vacancies, enumerated as 1 to 3 in Fig. 1. The lattice constant of UN slabs is fixed at 4.868 Å, taken from the lattice relaxation of UN bulk [9]. In all calculations we performed a complete structure optimization within the supercell of fixed linear dimensions using criterion of the total energy minimization.

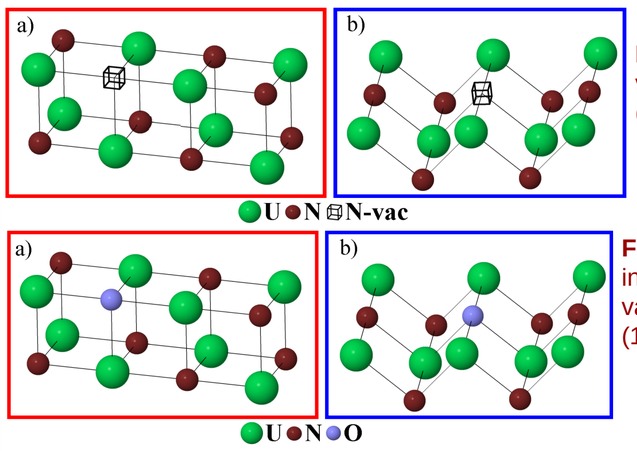

Fig. 2. 2-layer models of N vacancy on UN (001) (a) and (110) (b) surface

Fig. 3. 2-layer models of oxygen incorporation into surface N vacancy on UN (001) (a) and (110) (b) surface

Results and discussion

For three considered positions (1 to 3 in Fig.1) we estimated N vacancy formation energy or oxygen incorporation and solution energy, respectively. The formation energy of nitrogen vacancy was calculated as

$$E_{form}^{N\_vac} = E_{GB(N\_vac)} + m_{N\_atom} - E_{GB}$$

the oxygen incorporation energy for the first time was suggested by Grimes and Catlow [10]:

$$E_{inc} = E_{GB(O\_inc)} - E_{GB(N\_vac)} - E_{O\_atom}$$

and oxygen solution energy was calculated as

$$E_{sol} = E_{inc} + E_{form}^{N\_vac}$$

where $E_{GB(N\_vac)}$ is the total energy of a fully relaxed grain boundary containing N vacancy in one of considered positions $E_{GB(O\_inc)}$ is the total energy for the grain boundary with incorporated O atom in one of positions, E_{GB} is the same for grain boundary without defect, and, finally, m_{N_atom} (m_{O_atom}) is the chemical potential of an atom in the N_2 (O_2) molecule at 0 K.

Table 1. Formation energies $E_{form}^{N\_vac}$ (in eV) for nitrogen vacancy on UN (001) and (110) slab surface (outer, Fig. 2) and mirror layers and on a grain boundary for three different positions (Fig. 1) as well as average magnetic moment μ_{av} of U atoms in these systems

Number of layers in slab	Surface layer of slab (Fig. 2) (001) surface $E_{form}^{N\_vac}$	$\mu_{av}(\mu_B)$	Surface layer of slab (Fig. 2) (110) surface $E_{form}^{N\_vac}$	$\mu_{av}(\mu_B)$	Central layer of slab (001) surface $E_{form}^{N\_vac}$	$\mu_{av}(\mu_B)$	Central layer of slab (110) surface $E_{form}^{N\_vac}$	$\mu_{av}(\mu_B)$	position in Fig. 1.	Grain boundary $E_{form}^{N\_vac}$	$\mu_{av}(\mu_B)$
7, 2×2	3.706	1.548	3.028	1.585	4.431	1.494	4.520	1.513	**(1)**	3.472	1.457
9, 2×2	3.708	1.452	3.036	1.512	4.417	1.412	4.350	1.493	**(2)**	3.343	1.457
11, 2×2	3.712	1.392	3.026	1.453	4.423	1.364	4.418	1.434	**(3)**	3.477	1.456
7, 3×3	3.646	1.487	2.966	1.498	4.417	1.487	4.558	1.471			

Table 2. Incorporation energy E_{inc} and solution energy E_{sol} (in eV), average spin magnetic moments of U atoms μ_{av} as well as effective charge on O atoms for oxygen incorporated into N vacancy on UN (001) and (110) slab surface (outer, Fig. 3) atomic layers, into N vacancy in central layer of UN(001) slab as well as in grain boundary three different positions (Fig. 1)

	O incorporation into surface layer of slab (Fig. 3) (001) surface				(110) surface			
Number of layers	E_{inc}	E_{sol}	$\mu_{av}(\mu_B)$	$q_{eff}(e^-)$	E_{inc}	E_{sol}	$\mu_{av}(\mu_B)$	$q_{eff}(e^-)$
7, 2×2	-6.181	-2.476	1.495	-1.36	-5.822	-2.794	1.516	-1.29
9, 2×2	-6.186	-2.479	1.412	-1.36	-5.820	-2.784	1.472	-1.29
11, 2×2	-6.195	-2.483	1.365	-1.35	-5.817	-2.791	1.416	-1.29
7, 3×3	-6.126	-2.480	1.463	-1.36	-5.748	-2.783	1.471	-1.28

	O incorporation into central layer of (001) slab				O incorporation on grain boundary				
Number of layers	E_{inc}	E_{sol}	$\mu_{av}(\mu_B)$	$q_{eff}(e^-)$	position in Fig. 1.	E_{inc}	E_{sol}	$\mu_{av}(\mu_B)$	$q_{eff}(e^-)$
7, 2×2	-6.611	-2.180	1.47	-1.42	**(1)**	-5.922	-2.450	1.447	-1.406
9, 2×2	-6.608	-2.192	1.39	-1.38	**(2)**	-5.669	-2.326	1.442	-1.382
7, 3×3	-6.599	-2.182	1.45	-1.42	**(3)**	-5.920	-2.444	1.439	-1.363

Oxygen incorporation energy and solution energy are summarized in Table 2. These energies for the vacancies on the GBs (-5.6÷-5.9 vs. -2.3÷-2.5 eV, respectively) are close to those for the UN surface (-5.7÷-6.6 eV for O atom incorporation and -2.4÷-2.8 for O atom solution).

N vacancy formation energies are summarized in Table 1. The results on grain boundaries are compared here with the previous results for N vacancies on the UN (001) and (110) surfaces [3]. We clearly see spin-distribution similar tendencies for both systems (UN surface and UN grain boundary). The formation energies of N vacancy on the GB are 3.3-3.5 eV. These values are comparable with analogous values for UN (001) (3.6-3.7 eV) and (110) (2.9-3.1 eV) surface but are smaller than those in the bulk material (~4.4 eV) or in the (001) or (110) slabs central layer (4.3-4.6 eV). It indicates a clear trend for segregation of vacancies towards the grain boundaries.

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Summary

- The *ab initio* DFT method was used to analyze a role of point defects and oxygen interaction with UN grain boundaries using (310)[001](36.8°) tilt grain boundary model.
- We obtained for the first time the energies of nitrogen vacancy formation and O atom incorporation into N vacancy on the GB and compared these results with previously obtained results for both UN(001) and (110) surfaces.
- We have observed a clear trend for vacancy segregation at the interfaces, open surfaces and GBs.
- Calculated energies for the UN interface very well correlate with the relevant energies for UN surfaces.

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