



First-principles study of fission gas incorporation and migration in zirconium nitride



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ABSTRACT

To evaluate the effectiveness of ZrN as a diffusion barrier against fission gases, we investigate the incorporation and migration of fission gas atoms, with a focus on Xe, in ZrN by first-principles calculations. The formations of point defects in ZrN, including vacancies, interstitials, divacancies, Frenkel pairs, and Schottky defects, are first studied. Among all the defects, the Schottky defect with two vacancies as first nearest neighbor is predicted to be the most favorable incorporation site for fission gas Xe in ZrN. The migration of Xe gas atom in ZrN is investigated through two diffusion mechanisms, i.e., interstitial and vacancy-assisted diffusions. The migration barrier of Xe gas atom through the intrinsic interstitials in ZrN is considerably lower than that through vacancies. Therefore, at low temperatures fission gas Xe atoms diffuse mainly through interstitials in single crystal ZrN, whereas at high temperatures Xe may diffuse in ZrN assisted by vacancies.

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1. Introduction

Uranium-molybdenum alloys are under investigation as candidate fuels for future high-performance research reactors using low-enriched uranium [1,2]. When used as dispersion fuel with aluminum, a significant amount of interaction products form at the interface between the U-Mo fuel particle and the surrounding Al during in-pile radiation tests, which results in unacceptable swelling in the U-Mo/Al dispersion fuel at high burnups [3]. Several coating materials, including Si [4], ZrN [4], U-silicide [5], and U-nitride [5], were proposed as diffusion barriers to reduce the interaction between the fuel particle and the Al matrix. These coatings help reduce the formation of the interaction layer and therefore decrease the fuel swelling. Because of its superior thermophysical properties, ZrN is currently selected as a candidate diffusion barrier material for the U-Mo dispersion fuel lead by the European Dispersion Fuel program. Under neutron irradiations, various kinds of defects can form in the diffusion barrier coatings, which may act as incorporation sites for fission gases. The fission gases generated from the U-Mo fuel can form solution in ZrN or migrate out of the coating. Meanwhile, ZrN has also been investigated as a nuclear fuel component in mixed nitride fuels, such as (U,Zr)N and (Pu,Zr)N. Research shows that nitride fuels, if in solution with ZrN, exhibit better swelling behavior and thus a reduced interaction

between the cladding and the nitride fuel [6]. Therefore it is important to study the fission gas behavior in the nonfissile components of the mixed nitride fuels, i.e., ZrN.

Recently we studied the thermodynamic and kinetic stability of ZrN coatings with respect to the Al matrix and U-Mo fuel using first-principles calculations [7]. However, few studies have been done on the diffusion behaviors of inert gases in ZrN. Tsetseris et al. studied the structure and interaction of point defects in transition-metal nitrides, including ZrN, using first-principles calculations [8–11]. A limitation of their work is that the crystal structure for defective system was not fully relaxed, which can lead to overestimated formation energy for interstitials and underestimated formation energy for vacancies. Pukati et al. studied the defect formation energy in ZrN and the diffusion of inert gases, including He, Kr, and Xe, using first-principles calculations [12]. The incorporation sites and vacancy-assisted migration for fission gases, however, were not systematically studied in their work, both of which are critical for understanding the diffusion mechanism of fission gases in ZrN coating under irradiation.

To address these limitations, we investigated the incorporation and migration behavior of inert gases, such as He, Kr, and Xe, in ZrN using first-principles calculations based on density functional theory. We systematically studied the formation energies of point defects and the incorporation energies of inert gases in these point defects. The diffusion of the gas Xe in ZrN was investigated under two mechanisms: interstitial and vacancy-assisted diffusion. Our

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goal is to obtain a better understanding of fission gas migration behavior in the ZrN coating and nitride fuels.

The rest of the paper is organized as follows. The computational methods are briefly described in Section 2. Detailed results and discussion of the incorporation and migration of inert gases in ZrN are presented in Section 3. In Section 4 we briefly summarize our work.

2. Computational methodology

The first-principles calculations are performed by the projector augmented wave method as implemented in VASP [13,14] within generalized gradient approximation (GGA) parameterized by Perdew et al. [15]. The semi-core *s* and *p* states are treated as valence electrons for Zr. In all cases, the total energies are converged to at least 10^{-6} eV/atom. ZrN adopts the rock salt structure at ambient conditions. The lattice constant of ZrN after full relaxation is predicted to be 4.596 Å, close to the experimental measurement of 4.585 Å [16]. The relaxed lattice constant is used to generate a $3 \times 3 \times 3$ supercell with 108 Zr and 108 N atoms, in order to study the defect formation and migration in ZrN. Previous studies showed that the $3 \times 3 \times 3$ supercell is sufficient to satisfy the convergence criterion of the defect formation energy and migration energy, less than 0.04 eV [9]. During the total energy calculations, a plane-wave energy cutoff of 400 eV and a Monkhorst-Pack mesh of $3 \times 3 \times 3$ *k*-points in the Brillouin zone are employed. The atomic position, cell volume and shape are fully relaxed for all the structures. In order to find the structure with the lowest energy, the symmetry is turned off during the relaxation.

The formation energy E_f of a single defect is calculated with the formula,

$$E_f[A] = E_{\text{tot}}[A] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i, \quad (1)$$

where $E_{\text{tot}}[A]$ is the total energy of a supercell containing a defect *A* and $E_{\text{tot}}[\text{bulk}]$ is the total energy for the perfect crystal using an equivalent supercell. The integer n_i indicates the number of atoms of type *i* that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell to form the defect, and the μ_i is the corresponding chemical potential of the species. For comparison, HCP Zr metal and the N_2 molecule in vacuum are often used as the reference states for Zr and N species to study the defect formation energies [9]. It should be pointed out that point defects in ZrN are often charged. However, as adopted in many other DFT studies of defects in nitrides [9,12,19], the neglecting of the charge state of defect won't affect the incorporation and migration energies of inert gases in ZrN predicted in this work.

When isolated defects get close, they may interact with each other and form a defect complex. The binding energy E_{bonding} of defects *A* and *B* in a defect complex *AB* is obtained by comparing the energy difference between the supercells with single defects *A* and *B* and the supercell containing the defect complex *AB*:

$$E_{\text{bonding}} = E_{\text{tot}}[A] + E_{\text{tot}}[B] - E_{\text{tot}}[AB] - E_{\text{tot}}[\text{bulk}]. \quad (2)$$

In this formulation, a positive binding energy indicates an attraction between defects *A* and *B*.

The incorporation energy of an inert gas *X* in the defect *A* of ZrN crystal is described as,

$$E_{\text{inc}}[X] = E_{\text{tot}}[X + A] - E_{\text{tot}}[A] - E_{\text{tot}}[X], \quad (3)$$

where $E_{\text{tot}}[X + A]$ is the energy of the supercell containing an inert gas *X* and defect *A*, $E_{\text{tot}}[A]$ is the energy of the supercell containing defect *A*, and $E_{\text{tot}}[X]$ corresponds to the energy of an isolated inert gas *X* in vacuum. The incorporation energy E_{inc} is defined as the energy needed to incorporate an atom at a pre-existing defect site.

Therefore, the solution energy of an inert gas atom *X* in the defect *A* can be defined as,

$$E_{\text{sol}}[X] = E_{\text{inc}}[X] + E_f[A]. \quad (4)$$

The solution energy describes the energy required to form the defect-inert gas associations.

The migration barriers of inert gas atoms in ZrN are calculated by the nudged elastic band (NEB) method [17] to simulate the minimum energy path that passes through the transition state of a diffusion process. To determine the minimum energy path through the NEB method, at least three replicas of the system are created, in each of which the diffusing atom is moved by equidistant steps to intermediate positions between the initial and final states, as obtained by linear interpolation of the path. A large $3 \times 3 \times 3$ supercell is used to ensure that the atoms are separated from their periodic image and provide a more reliable result for the migration barriers of fission gas Xe and defects in the diluted limit.

3. Results and discussion

We first discuss the formation of vacancies, interstitials, and possible pairs of vacancies and interstitials in ZrN. Next, we investigate the incorporation of the fission gas Xe at several potential sites in ZrN, and compare its incorporation energy in ZrN with other fission gases and host materials. We finally study the migration behavior of Xe in ZrN with different diffusion mechanisms.

3.1. Single point defects

We first study the formation of single-point defects, such as vacancy and interstitial, in ZrN. Several configurations are possible for N and Zr self-interstitials in ZrN. We consider three possible configurations: tetrahedral interstitial, $\langle 110 \rangle$ dumbbell (denoted as DB110), and $\langle 111 \rangle$ dumbbell (denoted as DB111). The $\langle 100 \rangle$ dumbbell configuration is excluded for N or Zr interstitial due to high energy cost. Using HCP Zr metal and the N_2 molecule in vacuum as the reference states for Zr and N species, the predicted formation energies of vacancies and interstitials in ZrN are shown in Table 1. Among the three configurations of N interstitials, the tetrahedral interstitial has the lowest formation energy in ZrN, followed by DB110 and DB111 interstitials. The formation energy of the N vacancy in ZrN is higher than that of the tetrahedral interstitial but lower than the formation energies of the dumbbell interstitials. The formation energies of Zr interstitials are found to be considerably higher than that of N, because of its large atomic size. The DB111 interstitial of Zr is the most stable configuration among the three configurations studied, followed by tetrahedral and DB110 interstitials. Overall, the current prediction of the defect stability in ZrN is consistent with the study by Tsetseris et al. [11]. However, our predicted formation energies of N interstitials

Table 1
Point defect formation energies in ZrN.

Defect	E_f (eV) ^a	E_f (eV) ^b	E_f (eV) ^c
N vacancy	3.22	1.29	3.15
N DB110 interstitial	3.41	5.34	3.97
N DB111 interstitial	3.71	5.64	4.30
N tetrahedral interstitial	2.72	4.65	3.53
Zr vacancy	2.91	1.29	2.79
Zr DB110 interstitial	11.16	12.78	10.93
Zr DB111 interstitial	10.41	12.03	10.11
Zr tetrahedral interstitial	11.02	12.64	10.11

^a HCP Zr metal and N_2 gas in vacuum as the reference states for Zr and N species.

^b The chemical potentials of Zr and N species set as $\mu_{\text{Zr}} = -10.14$ eV and $\mu_{\text{N}} = -10.23$ eV, respectively.

^c Results from Ref. [9] with HCP Zr metal and N_2 gas in vacuum as the reference states for Zr and N species.

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