First-principles study for strain effects on oxygen migration in zirconium

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ABSTRACT

Oxygen interstitial atom diffusion in bulk α-Zr is studied using first-principles calculation and nudged elastic band method under various tetragonal strain conditions. Octahedral site is a stable position for an oxygen interstitial in α-Zr. An oxygen interstitial atom may diffuse from one octahedral site to another via a tetrahedral site or a crowdion site. An oxygen atom can travel around zirconium bulk with various combination of these diffusion processes. The diffusion from an octahedral site to a tetrahedral site or a crowdion site is the controlled step. The strain effects on the two diffusion mechanisms are different. In general, the diffusion rate decreases under certain tetragonal compressive strain conditions. As a result, the oxidation rate decreases under certain compressive strain conditions.

Since surface coating may be used to protect zirconium metal surface from oxidation, the surface strain generated from the interfacial mismatch can be used for the material design. In our calculations, SiC, TiN, and Al_2O_3 coatings may slow down the oxidation rate of zirconium because they can induce compressive strain on zirconium near the interfacial region.

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1. Introduction

Zirconium alloys have been developed and widely used for fuel cladding in water cooled reactors because of their unique properties, such as low thermal neutron cross section, high melting point, and good corrosion resistance in low temperature water [1–4]. Many zirconium alloys, such as Zircaloy-2, Zircaloy-4, ZIRLO™ alloy (Zr–1Nb–1Sn) from Westinghouse [5], M5® (Zr–1Nb alloy) from AREVA [6], and E-serials from Russia [7] have been developed to improve the corrosion resistance in service and increase the burn-up for reactor economy. Since the degradation of Zr alloys due to corrosion can limit the cladding life during service [8], for example, water oxidation [9] and oxidation of Zr alloys in air [6], how to understand the oxidation mechanism of zirconium is of great scientific and industrial interest.

Native oxide films are easily formed on zirconium or zirconium alloy surfaces [10]. For example, tetragonal phase of zirconium dioxide is found at the oxide/metal interface of zirconium alloy [11–18]. Once oxide film is formed on the zirconium surface, oxygen atoms diffuse from the zirconium dioxide to the bulk zirconium metal via the Zr/ZrO₂ interface [19]. Davies et al. studied oxygen migration in zirconium dioxide during oxide film growth process with experimental approach [20]. Oxygen diffusion in metal zirconium is an interesting topic and it is studied for a long time [21,22]. Hood et al. found that oxygen diffusion in α-Zr is not a strong anisotropy process [23]. Chiang et al. calculated diffusion barriers of oxygen atom migration in bulk and on the surfaces of metal zirconium using density functional theory (DFT) calculations [24]. Wang et al. investigated strain effect of on oxygen adsorption on a Zr(0001) surface [25]. Bai et al. investigated the strain effect on oxygen transport in tetragonal ZrO₂ using temperature accelerated dynamics and molecular dynamics simulations [26].

Surface coatings on the zirconium surfaces are proposed to protect zirconium from corrosion in reactor service. A variety of cladding coatings have been studied, such as Cr [27], TiN-based nanocomposites [28], TiAlN [29], Al₂O₃ [30], and TiO₂ [31] surface coating. Without modifying the commercial zirconium alloy fabrication processes seriously, the coating materials with high melting point and high oxidation resistance can improve the corrosion resistance of zirconium in water cooled reactors. However, weak adhesion may strip the coating on zirconium alloy surfaces.

Upon the classical Wagner theory of oxidation, the oxidation rates are controlled by ionic diffusion through the oxide layer [19]. The lattice mismatch between oxides and zirconium metal substrate generates strain in the interfacial region [32,33]. The

interfacial strain may affect oxygen diffusion into the zirconium or metal oxidation rate. Surface coatings may also generate strain in the interfacial region due to the lattice mismatch between substrate zirconium and coating materials. Once surface coating materials are used, oxygen atoms may diffuse cross the zirconium alloy-coating interface and the oxidation happens from the interfacial area. Although the above studies have provided insights into the oxidation process of zirconium alloy, the strain effect on oxygen diffusion in zirconium metal has not been addressed.

In this study, the strain effects on oxygen interstitial atom diffusion in bulk α-Zr are calculated using DFT calculations. First, the meta-stable configurations of an oxygen interstitial in α-Zr are investigated. Second, the diffusion energy barriers and diffusion paths of an oxygen atom in bulk α-Zr are calculated with nudged elastic band method. Third, the tetragonal strain effects on oxygen atom diffusion rates are evaluated. Finally, several surface coatings are discussed for the purpose of corrosion resistance for bulk zirconium metal.

2. Calculation methods and models

2.1. Calculation methods

Density functional theory (DFT) calculations are performed to calculate the ground state energies of the systems and the energy calculations are performed with the Vienna Simulation Package (VASP) [34,35] code. The projected augmented wave (PAW) [36,37] method is used to deal with the wave functions near the core region. The exchange-correlation energy is described by the generalized gradient approximation (GGA) of Perdew-Burke-Enzerof (PBE) [38,39]. In the energy calculations for structure relaxation and diffusion path search, the summations over the Brillouin zone are performed with a $3 \times 3 \times 3$ Monkhorst Pack k-point mesh for the diffusion calculation. The direct inversion of the iterative subspace algorithm, which is a fast band-by-band residual minimization method (RMM-DIIS) is applied in the calculation of the ground state charge density and the energy convergence criterion is 10^{-4} eV. The conjugate gradient method is used to minimize the Hellmann-Feynman [40] forces in the ionic relaxations with the force stopping criterion of 0.02 eV/Å. The cutoffs of the plane-wave kinetic energy for is 400 eV. Spin-polarization is used in all calculations.

The climb image nudged elastic band (CI-NEB) [41] method is used to search the minimal energy paths and the saddle points of an oxygen interstitial diffusion in bulk α-Zr. The quick-min method (QM) is used to relax the NEB forces. In all calculations, there are four images between the initial and final configurations. The spring constant of the NEB calculations is 5.0 eV/Å^2 and the force convergence criterion is 0.05 eV/Å.

In order to investigate how coating materials affect the oxidation process of zirconium metal, several types of coatings are chosen to protect zirconium metal. For the interfacial calculations, a $5 \times 5 \times 1$ Monkhorst Pack k-point mesh is used for the system relaxation. A vacuum layer on the top of the surface of the coating layer is used to eliminate the interaction between the neighbor slabs since the periodic boundary condition is applied. The thickness of the vacuum layer is 11 Å. The ionic positions are relaxed until the residual forces are less than 0.05 eV/Å. During the interfacial optimization process, the two bottom zirconium atom layers are fixed, and all the other atoms in the supercell are allowed to fully relax. Because of the interface mismatch, the mean dimensional values of the cross sections of the coating material and the zirconium slab are chosen for the cross section values of the supercell.

The adhesion energy E_{ad} is defined as the energy to break the Zr (0001)/coating interface into the isolated Zr(0001) and coating slabs. That is,

$$E_{ad} = (E_{Zr}^{slab} + E_{coating}^{slab} - E_{Zr/coating}^{tot})/S \qquad (1)$$

where E_{Zr}^{slab} and $E_{coating}^{slab}$ are the total energy of isolated Zr and coating slabs, respectively. And the $E_{Zr/coating}^{tot}$ is the total energy of the Zr (0001)/coating interface system. S is the interface area. With this definition, larger adhesion energy indicates stronger binding of the interface [42].

2.2. Simulation models

The space group of α zirconium is P6$_3$/mmc [43]. There are two atoms in its primitive cell of the hexagonal-close-packed (HCP) structure. A $3 \times 3 \times 2$ zirconium super cell is generated to simulate oxygen atom diffusion in α-Zr (see Fig. 1). In this structure, an oxygen interstitial atom may diffuse via octahedra or tetrahedra sites. In Fig. 1, atoms E, A, B, C, D, and F form an octahedra site and atoms B, C, F, and H form a tetrahedra site. With the PBE pseudopotential, our optimized lattice parameters for the bulk α-Zr are $a = 3.24$ Å, $c = 5.16$ Å, which agree with experiment data ($a = 3.231$ Å, $c = 5.147$ Å) [44] and DFT calculations data ($a = 3.237$ Å, $c = 5.188$ Å) very well [45].

2.3. Configurations of oxygen interstitial atom in bulk α-Zr

In order to study oxygen diffusion inside bulk α-Zr, meta-stable configurations of oxygen interstitial inside bulk α-Zr are investigated. Four types of oxygen interstitial configurations are found via structure optimization. Schematics of the four meta-stable configurations are shown in Fig. 2. The four configurations are:

BO: the oxygen interstitial atom is on the basal plane of an octahedra structure.
BT: the oxygen interstitial atom is on the basal plane of a tetrahedra structure.

Crow: the oxygen is between two Zr atoms and a crowdion is formed. For example, the oxygen atom is between atom A and C, or between B and D (Fig. 2(c)).
Octa: the oxygen interstitial atom is at the cental position of an octahedra structure.

For an oxygen interstitial atom in bulk α-Zr, the interstitial formation energy ΔE_i^f is defined as:

$$\Delta E_i^f = E_i - E_O - E_{Pure}. \qquad (2)$$

where E_{Pure} represents the total energy of the α-Zr super cell without any oxygen atom; E_i represents the total energy of the α-Zr super cell with an extra oxygen interstitial atom; E_O is the ground
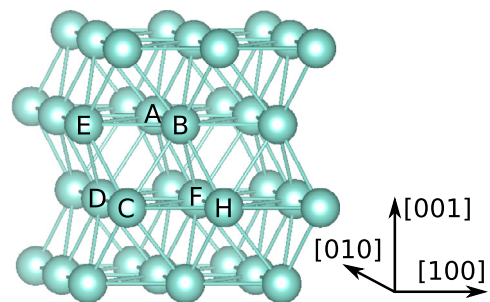

Fig. 1. A $3 \times 3 \times 2$ α-zirconium super cell.