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Anisotropy in oxidation of zirconium surfaces from density functional theory calculations

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ABSTRACT

This work uses density functional theory calculations to analyze the energy barriers for oxygen migration into the basal and prismatic surfaces of zirconium. Specifically, the migration energy barriers between each octahedral site and tetrahedral site in the basal surface, prism surface, and the bulk are determined. The possible oxygen migration paths in each system are also analyzed. Oxygen has higher energy barriers to penetrating the basal surface than the prism surface. It also has a lower energy barrier to escape from basal surface than from the prism surface. This is consistent with the experimental observation that the prism plane of zirconium oxidizes more quickly than the basal plane.

1. Introduction

Zirconium (Zr) based alloys are widely used as the clad for nuclear fuel because of their structural stability and low thermal neutron absorption cross-section [1]. The prototypical clad in boiling water reactors and pressurized water reactors is Zircaloy 2, which is more than 98% Zr, with 1.5% Sn, 0.12% Fe, 0.1% Cr, 0.1% Ni and other components [2]. More recent clads, such as Zircaloy 4, Zirlo™ or M5® [3], contain slightly different compositions than Zircaloy 2 and are engineered for optimal performance in a number areas, including oxidation.

The oxidation of Zr based alloys has been widely investigated because a thin film of zirconium oxide has a dense structure that can inhibit fission gas penetration through the metal. As long ago as 1970, a study by Fehlner and Mott [4] of the transition from chemisorption to 3-D oxide and anion migration during oxide growth showed that at low temperature (~300 K) the oxidation process depends on the oxygen partial pressure. The metal crystallographic orientation could not influence the oxidation rate. In a study of anodic oxidation, Davies et al. found that Zr oxidation behavior only involves the oxygen migration rather than Zr migration [5]. It has also been determined that the presence of oxygen in Zr subsurface interstitial sites can prevent the further penetration of oxygen, leading to a decreased diffusion rate [6,7].

There have been a number of experimental studies of oxygen absorption on the basal (0001) Zr surface. A study by Wang et al. [8] showed that at 0.5 monolayer (ML) coverage, half of the O atoms (i.e., 0.25 ML) occupy the octahedral sites between the first and second layers of the Zr subsurface, while the other half occupy octahedral sites between the second and third layers. They also showed that once the oxygen coverage reaches 2 ML, the oxygen ions reside in the surface face centered cubic (SFCC) sites and in the tetrahedral sites between first and second subsurface layers [9]. Other studies characterized the oxidation rate using electron microscopy (TEM and SEM) [10,11]. These studies found that the prismatic $\{10\bar{1}0\}$ surface has a much faster oxidation rate than the basal (0001) surface.

Studies using density functional theory (DFT) calculations with the local-density approximation (LDA) approximation have also analyzed oxygen absorption by the Zr basal surface [12–14]. These concluded that the energetically favored oxygen absorption sites are the octahedral sites between the second and third layers [12]. However, more recent calculations with the generalized gradient approximation (GGA) using the double oxygen layer model, in which oxygen is placed in two layers, arrived at a different conclusion: the energetically favored sites are the SFCC sites [13], as seen in Fig. 1. Another GGA study using a multiple-layer adsorption model (MLAM), with oxygen in multiple layers, indicated that at 0.25 ML the SFCC site is energetically favored. In this model, as the coverage increases to 0.5 ML a combination of SFCC sites and octahedral sites is the most stable, as indicated in Fig. 1 [14]. These

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GGA calculations [13,14] also suggest that while thermal diffusion allows oxygen to cross the energy barrier from the SFCC sites to the subsurface, the occupation of subsurface sites can prevent further oxygen penetration [13]. A recent LDA calculation determined [15] that strain on the surface can change the most stable sites on Zr basal surface from SFCC sites to octahedral sites.

Little attention has focused on analyzing the energy barriers for oxygen penetration into the Zr basal and prism surfaces. These energy barriers are important because they can be expected to play an important role in oxidation. While one DFT study found that oxygen has a lower energy barrier for migration between SFCC sites than from SFCC sites to subsurface octahedral interstitial sites, it did not compare the basal and prism surfaces [16]. Hence, with the objective of understanding the large difference in their oxidation rates, in this work we determine the paths and energy barriers associated with the oxygen migration into Zr basal and prism surfaces.

2. Methods and bulk migration barriers

The DFT calculations are performed using the Vienna ab initio Simulation Package (VASP) [17,18] with the projector augmented-wave (PAW) method [19]. The GGA approximation is chosen since it performed well in the study of the multiple-layer adsorption model [14]. The Perdew–Burke–Ernzerhof density functional (PBE) [20] is used to describe the exchange-correlation energy. The kinetic energy cutoff is 400 eV, which is the same as used in an earlier DFT study of Zr [14]. An $8 \times 8 \times 8$ k-point mesh is used for the bulk supercell. HCP-structured single crystal Zr structure yields a lattice constant of $a = 0.324$ nm, $c = 0.515$ nm, which gives $c/a = 1.595$. These calculated values are consistent with the experiment values of $a = 0.323$ nm, $c = 0.515$ nm and $c/a = 1.593$, and in good agreement with previous DFT results [14,21]. Previous experimental work showed that the Zr thermal expansion does not significantly affect the c/a ratio. At 950 K, the experimental c/a is measured to be 1.597 [22], which is only 0.25% different from the calculated 0 K value. Moreover, the volume expansion at 950 K is also less than 1% [22]. Thus, the structure found in $T = 0$ K DFT calculations can reasonably be compared to previous experimental studies [8,10].

The climbing image nudged elastic band (cNEB) method [23,24] is used to calculate the atom migration saddle points and the migration energy barriers. In each migration path considered here, six images are used. Before structural equilibration, the interval of oxygen between each image along the migration path is about 1 Å

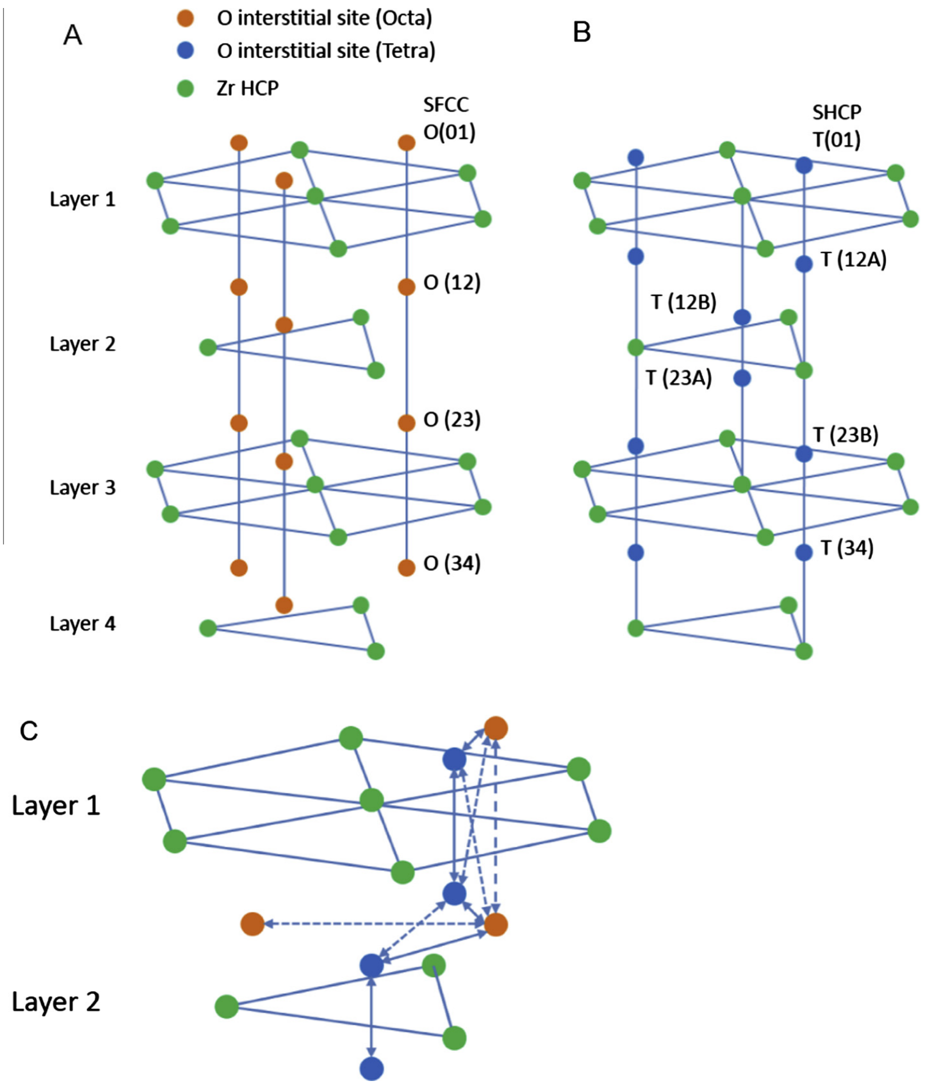

Fig. 1. (A) Oxygen octahedral and (B) tetrahedral interstitial sites in (0001) oriented HCP on Zr. The notation for the oxygen sites follows Yamamoto et al. [12]. (C) Oxygen migration paths in bulk. The solid lines indicate the low energy paths, while the dashed lines indicate the high energy paths.