First-principles study of solute diffusion in zirconium: Vacancy-mediated and interstitial mechanisms of N, O, Si, and U

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Abstract

The fuel-cladding chemical interaction (FCCI) between uranium-based fuels (UO2 , UN, U3Si2) and Zr cladding poses a critical challenge for accident-tolerant fuels; however, the atomic-scale diffusion behaviors of key elements (N, O, Si, U) in the hexagonal close-packed (hcp) Zr matrix remain insufficiently elucidated. Herein, we systematically compare the diffusion mechanisms of these four solutes in hcp-Zr using first-principles calculations combined with the eight-frequency model for vacancy-mediated diffusion and a mean jump frequency method for interstitial diffusion.We find that atomic size mismatch governs site preference: small N and O atoms spontaneously occupy octahedral interstitial sites and diffuse via an interstitial mechanism, whereas larger Si and U favor substitutional incorporation. Although Si and U both prefer substitutional sites, their vacancy-mediated diffusion mechanisms differ qualitatively: Si exhibits near-random diffusion, whereas U experiences significant solute-vacancy binding that produces frequent back-jumps and significantly reduces its net diffusion efficiency. Furthermore, when thermal expansion and the entropy change associated with interstitial formation are taken into account, interstitial diffusion becomes increasingly favorable at elevated temperatures, suggesting a transition for U from vacancy-mediated to interstitial-dominated diffusion at high temperatures, in contrast to N, O, and Si which are interstitial diffusers. These findings demonstrate that FCCI kinetics is collectively governed by intrinsic mobility and solubility, both of which are modulated by atomic size and temperature, thereby offering a quantitative framework for the rational design of diffusion-resistant

Full Text

Preamble

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Abstract

The fuel-cladding chemical interaction (FCCI) between uranium-based fuels (UO2, UN, U3Si2) and Zr cladding poses a critical challenge for accident-tolerant fuels; however, the atomicscale diffusion behaviors of key elements (N, O, Si, U) in the hexagonal close-packed (hcp) Zr matrix remain insufficiently elucidated. Herein, we systematically compare the diffusion mechanisms of these four solutes in hcp-Zr using first-principles calculations combined with the eight-frequency model for vacancy-mediated diffusion and a mean jump frequency method for interstitial diffusion. We find that atomic size mismatch governs site preference: small N and O atoms spontaneously occupy octahedral interstitial sites and diffuse via an interstitial mechanism, whereas larger Si and U favor substitutional incorporation. Although Si and U both prefer substitutional sites, their vacancy-mediated diffusion mechanisms differ qualitatively: Si exhibits near-random diffusion, whereas U experiences significant solute-vacancy binding that produces frequent back-jumps and significantly reduces its net diffusion efficiency. Furthermore, when thermal expansion and the entropy change associated with interstitial formation are taken into account, interstitial diffusion becomes increasingly favorable at elevated temperatures, suggesting a transition for U from vacancy-mediated to interstitial-dominated diffusion at high temperatures, in contrast to N, O, and Si which are interstitial diffusers. These findings demonstrate that FCCI kinetics is collectively governed by intrinsic mobility and solubility, both of which are modulated by atomic size and temperature, thereby offering a quantitative framework for the rational design of diffusion-resistant fuel-cladding interfaces.

Keywords

First-principles calculation; Interstitial diffusion; Vacancy-mediated diffusion; Fuelcladding chemical interaction (FCCI); hcp zirconium

1. Introduction

In light water reactors (LWRs), the conventional UO2-Zr fuel system has long served as the standard configuration for nuclear fuel elements, owing to the high melting point and irradiation stability of UO2, as well as the neutron economy and excellent mechanical properties of Zr alloys [1]. However, UO2 and Zr are thermodynamically unstable; the diffusion of O and U from UO2 into the Zr cladding leads to the formation of a ZrO2 layer, an α-Zr brittle phase, and (U,Zr) intermetallic phases, thereby reducing the safety and service life of the fuel element [2]. After the Fukushima accident, UN and U3Si2 fuels, which possess higher thermal conductivity, higher uranium density, and better fission product retention capability, have emerged as important candidate materials for accident-tolerant fuel (ATF) [3]. UN demonstrates vigorous interfacial reaction with Zr, forming complex multilayered phases at 500 °C and low-melting liquid phases above 1130 °C, which impairs fuel-cladding compatibility [4]. U3Si2 also exhibits significant

interfacial interdiffusion with Zircaloy cladding at 800 and 1000 °C, forming various intermetallic compounds and low-melting-point phases [5]. These deleterious interactions in all three fuel systems—UO2, UN, and U3Si2—ultimately originate from the atomic diffusion of specific elements into the Zr cladding, namely O, N, Si, and U.

Despite extensive experimental observations of these diffusion-driven phenomena, a systematic comparative understanding of how O, N, Si, and U atoms migrate in the hexagonal close-packed (hcp) Zr matrix remains lacking. For instance, in UO2-Zr, the rapid diffusion of O forms an oxygen-rich α-Zr brittle phase, while U atoms penetrate Zr to form (U,Zr) intermetallics [1]. In the UN-Zr system, N atoms readily dissolve into Zr and promote extensive interfacial interdiffusion [4]. In U3Si2-Zr, Si diffuses faster than U, leading to complex phase formation [5].

However, these experimental observations alone are insufficient to uncover the underlying atomistic mechanisms–specifically,

whether

solute

follows

vacancy-mediated

substitutional path or an interstitial path, and how their diffusion rates compare quantitatively.

Therefore, a mechanistic understanding of FCCI requires a systematic investigation of the atomic diffusion of these key elements.

The diffusion of dilute solute atoms proceeds mainly via two mechanisms: vacancy-mediated substitutional diffusion and interstitial diffusion [6]. In hcp-Zr, the dominant diffusion mechanism of each solute is known to correlate roughly with the metallic radius of the solute [7]. For solutes such as Fe, Co, and Ni, ultra-fast interstitial diffusion has been observed experimentally [6, 8, 9].

Specifically, when the ratio of the metallic radii (for 12-fold coordination) of the impurity and the solvent atoms in their pure states is below a certain value, the solute tends to exhibit ultra-fast interstitial diffusion [10]. The critical radius ratio for this size effect has been determined by Nascimento and Lu et al. to be 0.85 [11] and 0.92~0.99 [7], respectively.

The diffusion rate, occupation site (substitutional or interstitial), and directional anisotropy of the diffusion path of solute elements determine the interfacial reaction layer thickness, phase evolution, and mechanical degradation of the cladding. First-principles calculations provide an effective route to obtain impurity stability and diffusion coefficients. For substitutional diffusion in

hcp lattices, several theoretical models have been developed, including the eight-frequency model [12], the thirteen-frequency model [13], and the Green' s function method [14]. Regarding interstitial diffusion, the stability of interstitial sites is strongly correlated with the solute atomic radius and electronic configuration [15]. Various methods exist to evaluate the interstitial diffusion rate, including the mean jump frequency method [16], the multi-state diffusion method [17], and the Green' s function approach [18].

For oxygen interstitial diffusion in α-Zr, first-principles studies have systematically identified the octahedral site as the most stable configuration and quantified the diffusion barriers [19, 20].

In contrast, for N interstitial diffusion in hcp-Zr, systematic first-principles calculations are still lacking: most existing studies have focused only on its formation energies and static site preferences [21, 22] rather than explicit diffusion barriers and pathways. For Si and U, quantitative first-principles calculations of their diffusion coefficients in hcp-Zr are also scarce. Meanwhile, existing studies have primarily focused on solutes with atomic radii similar to that of Zr [7], leaving the diffusion behaviors of both small atoms (N, O) and large atoms (Si, U) in the Zr matrix poorly understood.

To address this gap, we perform a systematic first-principles investigation of the diffusion mechanisms of N, O, Si, and U in hcp-Zr. First, we determine the preferential site occupation (substitutional vs. interstitial) for each solute and establish its correlation with atomic size mismatch. Second, we quantify the vacancy-mediated and interstitial diffusion coefficients using the eight-frequency model and mean jump frequency method, respectively, and validate our calculations against available experimental data. Finally, we compare the dominant transport pathways and demonstrate how the interplay between intrinsic diffusivity and solid solubility governs the experimentally observed FCCI kinetics. This work provides a unified atomic-scale framework for understanding and predicting FCCI behavior across different uranium-based fuel systems.

2.1. Density functional theory settings

To investigate the diffusion mechanisms of N, O, Si, and U in hcp-Zr, all structural relaxations and electronic property calculations were carried out within a density functional theory (DFT) framework, employing the plane-wave pseudopotential formalism as implemented in the Vienna Ab initio Simulation Package (VASP) [23, 24]. The exchange-correlation energy was described using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [25], while the projector augmented wave (PAW) method [26] was adopted to represent ion-electron interactions. Full atomic relaxation was performed until the residual force on each atom fell below 0.02 eV/Å, with total energy convergence set to 10−5 eV. A plane-wave cutoff energy of 500 eV was used. The computational parameters were validated through systematic convergence tests. The plane-wave cutoff energy was converged to 500 eV (within

0.001 eV/atom) using a fixed 4 × 4 × 3 Monkhorst-Pack k-point mesh. A 4 × 4 × 3 supercell containing 96 atoms with the same k-point sampling was then adopted for bulk Zr to balance accuracy and computational cost.

For N, O, Si, and Zr, the standard GGA-PBE functional is well established to accurately describe their structural properties. In contrast, uranium possesses a valence electron configuration of 6s26p65f36d17s2 and exhibits strong electron correlation effects arising from its f electrons.

Therefore, the Dudarev GGA+U formalism [27] was employed, incorporating an additional onsite repulsion term for the 5f electrons. Previous validation studies on U and U-Zr systems have established an optimal effective Hubbard parameter (Ueff) in the range of 1.0~1.5 eV, with 1.24 eV being the statistical optimum for U metal and concentrated U-Zr alloys [28]. However, the required Ueff is known to be system-dependent. Larger values are often required for uranium compounds [29] to correctly capture their electronic structures. Considering the dilute nature of U and to maintain consistency with the broader range of validated parameters for uranium-bearing systems, Ueff

of 1.5 eV was adopted in this study. Spin-polarization was included in all density

functional theory calculations involving U to account for its magnetic ground state. Minimum energy paths for migration were identified using the climbing-image nudged elastic band (CI-NEB) method [30], and migration barriers were extracted from the saddle points of the energy profiles.

To validate our computational approach for Zr, we first calculated the lattice parameters of pure α-Zr. The optimized values are a = 3.235 Å and c = 5.170 Å, which are in good agreement with previous theoretical results [7]. The calculated vacancy formation energy of Zr is 1.96 eV, which is consistent with both reported DFT calculations [7] and experimental measurements (>1.5 eV [31, 32]). Furthermore, the self-diffusion migration barriers of a Zr vacancy in the basal plane and along the c-axis are calculated to be 0.51 eV and 0.62 eV, respectively, which closely match previous DFT values [18, 33].

2.2. Crystal structure and defect sites

Hcp-Zr crystallizes in the space group P63/mmc with two atoms per primitive cell. In such a hcp lattice, a solute atom can reside either on a substitutional site or on an interstitial site.

Symmetrically, there is only one type of substitutional site in the hcp Zr lattice. In contrast, multiple high-symmetry interstitial sites exist. To systematically explore the possible interstitial configurations, we consider nine distinct sites, as illustrated in Fig. 1 [Figure 1: see original paper]: octahedral (Oct), split dumbbell along the c-axis (S), crowdion out of the basal plane (C), tetrahedral (T), basal octahedral (BO), split dumbbell in the basal plane (BS), crowdion in the basal plane (BC), hexahedral (H), and split dumbbell along the diagonal direction (DS) [7, 34]. To ensure a complete sampling of potential interstitial sites, we examined these nine configurations and applied small symmetry-breaking displacements to the initial atomic positions in selected cases [7]. Although previous studies have identified additional low-symmetry interstitial configurations in hcp Zr [15, 18, 35], systematic site searches show that the lowest-energy configurations are consistently

among the high-symmetry sites examined here [18]. Therefore, the nine high-symmetry interstitial sites considered in this study are sufficient to capture the dominant diffusion behavior of these solutes in the Zr matrix.

2.3. Defect formation and binding energies

The formation energy of a single vacancy of Zr atom, substitutional solute (XZr), and interstitial solute (Xi) is defined as

Evf = Ev + mZr - Eperfect

E fX Zr = E X + m Zr - m X - E perfect

E fX i = E X - m X - E perfect

where E v , EX , E X , and Eperfect are respectively the total energies of supercell with a vacancy,

substitutional solute X, interstitial X, and that of a perfect supercell, respectively. mZr and m X is respectively the chemical potential of Zr and X element. Lower formation energy reflects easier formation of defect.

The interaction between two atoms can be evaluated by the binding energy (Eb), which is defined as

EAb - B = éë Etot (A, B) + E perf ùû - éë Etot (A) + Etot (B) ùû

where Etot (A, B) is the total energy of supercell containing both A and B atoms. E tot (A) and E tot (B) are the total energy of supercell containing A atom and B atom, respectively. The positive

and negative binding energies represent the repulsion and attraction between two independent atoms, respectively.

2.4. Vacancy-mediated diffusion: eight-frequency model

To model vacancy-mediated diffusion of substitutional solutes in hcp Zr, the eight-frequency model developed by Ghate [12] was employed, as it provides diffusion activation energies comparable to those obtained from more sophisticated models [7, 18]. As illustrated in Fig. 2 [Figure 2: see original paper], this model accounts for the anisotropic nature of the hcp lattice by considering eight distinct atomic jump frequencies [7, 36]: ω a and ω a ' for vacancy-solute rotation jumps between adjacent basal planes; ω b and ωb ' for rotation jumps within the basal plane and along the c-axis, respectively; ω c and ω c ' for dissociation jumps; and ω 2 and ω 2 ' for direct vacancy-solute exchange jumps

within the basal plane and between adjacent basal planes, respectively. -Em / kBT

Each of these jump frequencies follows the Arrhenius form w =ue

, where E m is the

migration barrier and u is the attempt frequency. The attempt frequencies for solute and solvent jumps were calculated using Vineyard' s harmonic transition state theory [37, 38] based on phonon

frequencies obtained from partial Hessian matrix calculations, considering only the vibrational modes of the migrating atom [39, 40]. The resulting approximation is

3 N -4

saddle

3 ini

saddle

Thus, its attempt frequency is estimated using only three vibrational modes at the initial site uiini and two at the saddle point u isa d d le Due to the anisotropy of the hcp lattice, two distinct diffusion coefficients are obtained: D (perpendicular to the c-axis) and D|| (parallel to the c-axis). Following Ghate' s formalism [12], these coefficients are expressed as:

D^ = CV-S a 2 3 f Bxw X + f Abw X

D|| = CV-Sc 2 f Azw,

where a and c are the hcp lattice parameters, and fAz, fBx, and fAb are the correlation factors that correct for non-random sequences of atomic jumps. These correlation factors depend on the eight jump frequencies and the displacement vectors S, and are calculated following the procedure detailed in Ref. [7].

We note that more sophisticated models for hcp impurity diffusion, including the thirteenfrequency model [13] and the Green' s function method [14] have been developed. However, the thirteen-frequency model primarily improves the drag ratio rather than the diffusion coefficient [18]. Moreover, the activation energy differences between the eight-frequency model and these more advanced methods are small: within 0.1 eV compared to the thirteen-frequency model [7], and below 20 meV compared to the Green's function method [18]. Therefore, the eight-frequency model employed in this work is sufficient for obtaining reliable diffusion coefficients and for determining the dominant diffusion mechanisms of the solutes considered. The activation energy Q and prefactor D0 for each diffusion direction are then obtained by fitting the temperature-

÷ . kB is the è k BT ø

dependent diffusion coefficients to the Arrhenius equation D = D0 exp ç Boltzmann constant, and T is the temperature.

2.5. Interstitial diffusion: mean jump frequency method

To evaluate the interstitial diffusion rate, a mean jump frequency method [16] that accounts for site occupancy and diffusion anisotropy is employed. For anisotropic hcp lattices, the diffusion coefficients perpendicular and parallel to the c-axis are expressed as:

wij (Drij^) 4 i, j ntotal

wij (Drij||) 2 i, j ntotal

D|| =

where the factors 1/4 and 1/2 arise from the dimensionalities of diffusion in the basal plane (two^

dimensional) and along the c-axis (one-dimensional), respectively. Drij

and D rij

are the

projected jump distances in the basal plane and along the c-axis, respectively. ni is the occupancy of interstitial site i following the Boltzmann distribution, ntotal is the total number of interstitial sites considered. For solutes with multiple stable interstitial sites, the occupancy factor ni/ntotal naturally accounts for the relative probability of occupying each site. When one site has a

substantially lower formation energy than the others, its occupancy approaches unity, and the diffusion is dominated by jumps from that site. Since the jump frequency wij Arrhenius law, the resulting diffusion coefficients D

follows the

and D|| naturally obey the Arrhenius form.

To identify the dominant diffusion mechanism for each solute„ we adopt the approach proposed by Lu et al. [7] for estimating the interstitial activation energy. Three quantities are defined for each solute: 1) Lower bound -taken as the formation energy of the most stable interstitial configuration (assuming zero migration barrier). 2) Best estimate -the sum of the formation energy of the most stable interstitial site and the lowest relevant migration barrier. 3) Upper bound -the sum of the formation energy of the octahedral (Oct) site and the migration barrier along a representative pathway, ensuring that any realistic interstitial diffusion mechanism cannot exceed this value.

For solutes whose most stable interstitial site coincides with the Oct site, the upper bound and best estimate become identical. The difference between the upper and lower bounds reflects the magnitude of the migration barrier.

However, the above activation energies are purely enthalpic (0 K). At finite temperatures, vibrational entropy plays a non-negligible role, especially for interstitial diffusion, where the interstitial atom introduces additional low-frequency vibrational modes. We do not explicitly calculate the formation entropy but instead rely on literature values for qualitative discussion [7].

Specifically, the vacancy formation entropy in hcp Zr is reported as 3.19 kB [41], and the

self-interstitial formation entropy is estimated as 7kB [42]. At 1073 K, the entropic contribution T∆S amounts to approximately 0.65 eV for interstitial defects, which can significantly alter the effective activation energy. These entropic effects will be considered when comparing the dominant diffusion mechanisms at elevated temperatures.

3. Results and discussion

3.1. Preferential site occupation of solute atoms

To identify the most favorable defect configurations of N, O, Si, and U atoms in hcp Zr, we calculated the total energies of the system with each solute occupying one substitutional site and nine high-symmetry interstitial sites, and analyzed their formation energies. The formation energies of stable defects after relaxation are summarized in Table 1 , together with the final sites occupied by initially unstable defects after relaxation. The calculations reveal that the substitutional configurations of N and O in hcp-Zr are unstable: when an N or O atom is initially placed on a Zr lattice site, it spontaneously relaxes into an interstitial site during structural relaxation, leaving behind a Zr vacancy. This indicates that the substitutional configurations of N and O are energetically much less favorable than their interstitial configurations. In contrast, for

the larger Si and U atoms, they can stably reside on substitutional sites, with substitutional formation energies lower than those of all interstitial configurations. This stems from size mismatch relative to Zr (1.60 Å). The small N/O atoms (~0.73 Å) favor interstitial sites.

Conversely, Si (~1.17 Å) and U (~1.56 Å), being much closer to Zr in size, prefer substitutional sites, where lattice distortion is minimal.

For N and O atoms, the most stable interstitial sites are the octahedral (Oct) and hexahedral (H) sites, which exhibit the lowest formation energies. The formation energies we obtained for the Oct and H sites are in good agreement with those reported in the literature for N and O in Zr [21, 22]. We find that, apart from the O and H sites, all other initial high-symmetry interstitial configurations (e.g., T, BO, C, BC) for N and O spontaneously relax into neighboring Oct or H sites upon relaxation. This discrepancy with some previous reports arises likely because we removed symmetry constraints and applied small symmetry-breaking displacements, thereby preventing the system from being trapped in local metastable configurations. The lower formation energy of O compared to N implies a higher solubility of O in Zr, attributable to the smaller atomic size, higher electronegative, and stronger bonding capability of O with Zr relative to N [21].

In contrast, Si and U atoms can stably exist in a greater variety of interstitial sites. Si preferentially occupies the Oct interstitial site, followed by DS site. U preferentially occupies BO interstitial site, followed by the DS site. The DS site here is essentially the basal-plane edge-toedge split-dumbbell interstitial, analogous to the IS3 interstitial defined in [15]. For Si and U, the initial crowdion (C) configurations, upon relaxation, spontaneously push aside a neighboring Zr atom and ultimately transform into the widely documented low-symmetry C’ configuration as reported in [35].

3.2. Dominant transport pathways

Having established the preferential site occupation of each solute, we now turn to their diffusion kinetics. Since the substitutional configurations of N and O are unstable, we only consider Si and U, which can stably reside on substitutional sites, for vacancy-mediated diffusion.

correlation factor at 1000 K for Si and U in hcp-Zr, calculated by the eight-frequency model.

Compared to U, Si exhibits higher attempt frequencies and migration energies for direct solute-vacancy exchange jumps (ω 2 and ω 2 ’), whereas showing comparable attempt frequencies and lower migration energies for other jumps. The displacement parameter S (which measures the tendency of a solute to back-jump after exchanging with a vacancy) is negative for both solutes.

Correspondingly, the correlation factor f at 1000 K is close to unity for Si (near-ideal random diffusion) but significantly below 1 for U. This indicates that after a U atom exchanges with a vacancy, the attraction interaction (Eb $= -0.19$ eV eV) drives U to immediately jump back to its original site, severely reducing the net diffusion efficiency. For Si, the near-zero binding (Eb $= 0.02$ eV eV) leads to negligible back-jump, and the diffusion approaches the classical

random-walk model. The activation energies for vacancy-mediated diffusion of Si and U were obtained by fitting the diffusion coefficients from the eight-frequency model, with the resulting diffusion coefficients to be presented later in this paper.

To evaluate the interstitial diffusion behavior of all four solutes, we adopted the approach proposed by Lu et al. [7] for estimating the activation energies associated with interstitial migration. In this scheme, three quantities are defined for each solute: a lower bound, an upper bound, and a best estimate, as illustrated in Fig. 4 [Figure 4: see original paper]. For N, O, and Si, the octahedral (Oct) interstitial site is the most energetically favorable. Consequently, their upper bound and best estimate coincide. In contrast, U prefers the basal octahedral (BO) site, which makes its upper bound slightly higher than the best estimate. The gap between the upper and lower bounds reflects the magnitude of the migration barrier. Although the diffusion barriers between octahedral (Oct) sites of U are lower (0.20 eV perpendicular to the c-axis and 0.79 eV parallel), the barriers between the most stable BO sites (0.62 eV and 0.97 eV, respectively) were adopted for plotting.

The migration barriers for the four elements increase in the order Si $<$ U $<$ O $<$ N. Si has the lowest barrier because of weak interaction with Zr and small atomic size. U, being similar in size to Zr, requires displacing host atoms, which raises its barrier. N and O interact strongly with Zr, leading to high migration barriers. Despite O having a higher barrier than Si and U, its much lower interstitial formation energy yields the smallest overall activation energy. For both substitutional and interstitial solutes, the migration energies for jumps within the basal plane (perpendicular to the c-axis) are lower than those for jumps along the c-axis. According to previous literature, for substitutional solutes, the diffusivity in the basal plane (D) is larger than that along the c-axis (D||) [7, 43]. However, for interstitial solutes, the relationship between D and D|| is not fixed [18].

Comparing interstitial and vacancy-mediated activation energies, we find that for N, O, and Si, the interstitial activation energies are evidently lower than their vacancy-mediated counterpart, indicating that interstitial transport likely dominates. This prediction for Si (radius ratio ~0.73) is fully consistent with the conclusion of Lu et al. [7] that solutes with a radius ratio below 0.92

favor interstitial diffusion. For U, its radius ratio of ~0.98 places it exactly within the transition range of 0.92~0.99 proposed by Lu et al. [7] for Hf, Zr, and Sn. The diffusion activation energies of the two competing mechanisms are comparable for U, making its dominant pathway less obvious at first glance.

To assess how thermal expansion affects the relative stability of interstitial solutes, we compare the formation energies at 0 K and 1073 K (Table 3). The reduction in interstitial formation energy from 0 K to 1073 K is negligible for N and O (0.06 and 0.04 eV) but substantial for Si and U (0.30 and 0.32 eV), due to greater lattice distortion caused by their larger atomic sizes.

This trend is consistent with Ref. [7], which reports a ~0.4 eV reduction for similarly large solutes.

Furthermore, the self-interstitial formation entropy is estimated as 7kB [42]. At elevated

temperatures, this entropic contribution (e.g., ~0.65 eV at 1073 K) further favors interstitial

diffusion over vacancy-mediated diffusion. Drawing upon these enthalpic and entropic considerations, we therefore propose that U, like Hf and Zr in the study by Lu et al. [7], is expected to undergo a transition from vacancy-mediated diffusion to interstitial-dominated diffusion at sufficiently high temperatures. This prediction provides a direct extension of the radius-ratio criterion to an even larger solute (U) and is in excellent agreement with the established framework.

3.3. Calculated diffusion coefficients and validation

Following the identification of the dominant transport pathways, we now proceed to calculate the diffusion coefficients. The interstitial diffusion coefficients of U are derived using the following approach. As illustrated in Fig. 3 Figure 3: see original paper, each BO site has six equivalent BO neighbors lying in the basal plane at a distance a. Along the c-axis, each BO site is adjacent to six equivalent Oct neighbors with a spatial offset of (a/√3, c/2). The diffusion coefficients can be simplified as

D^{BO}-BO =

basal basal × (a 2 × 6wBO-BO = a 2wBO-BO

BO-BO

1 æcö = × ç ÷ × 6wBO-B wBO-BO 2 è2ø

To validate the accuracy of our calculated diffusion coefficients, we compared the vacancymediated and interstitial diffusivities of U in Zr, as well as the interstitial diffusivity of Si in Zr, with available experimental and theoretical data, as shown in Fig. 5 [Figure 5: see original paper]. The diffusion coefficient of Si in Zr obtained from our eight-frequency model is higher than those reported in Ref. [44], where only a single jump pathway was considered. Furthermore, the vacancy-mediated diffusion coefficient of U in Zr calculated in this work agrees well with the experimental data reported in Ref. [45]. Since all experimental data up to 1118 K are consistent with the vacancy-mediated model, the crossover to interstitial-dominated diffusion for U is expected to occur above 1118 K.

Additionally, we compared the vacancy-mediated diffusion coefficients in hcp Zr obtained from the eight-frequency model with those in body-cantered cubic (bcc) Fe from our previous work

calculated using the nine-frequency model [44], revealing distinctly different trends. The diffusion coefficients for both systems are presented in Fig. 5.

For O and N, however, a more sophisticated treatment is required because direct Oct-Oct jumps alone are insufficient to capture the true diffusion kinetics. To obtain more accurate diffusion coefficients that can be meaningfully compared with experimental data, the Oct-H-Oct diffusion network is further incorporated into the model. As shown in Fig. 3(b), In the basal plane, each Oct site has six equivalent Oct neighbors at distance a. Along the c-axis, each Oct site has two equivalent Oct neighbors at distance c/2. Thus,

D^{Oct}-Oct =

basal × a × 6wOct-Oct = a 2 wObacsat-Ol ct

Oct-Oct

1 æcö = × ç ÷ × 2wOct-Oct = wOct 2 è2ø

The effective jump frequency from Oct, through H, to a new Oct site is G = 5wOct-Oct , where the prefactor 5 accounts for the six equivalent H neighbors of an Oct site and the 5/6 probability that the subsequent jump from H lands on a different Oct site. Among the six possible final Oct destinations (including the original one), geometric analysis shows that three produce a net c-axis displacement of ±c/2 and three produce no c-axis displacement; similarly, three produce a net basal displacement of a and three produce no basal displacement. This yields the compact expressions for the Oct-H network contribution:

D^{Oct}-H-Oct = G Dx 2 + Dy 2 = (4wOct-H) × a 2 = wOct-H

G Dz 2 = (3wOct-H) × c 2 = c 2wOct-H

D||Oct-H-Oct =

Owing to the high formation energy of the H site relative to Oct, the H occupancy is negligible, and the H site acts solely as a transient intermediate in the diffusion network. Direct HH jumps, whether in the basal plane or along the c-axis, are therefore not included in the model.

Combining Oct-H with direct Oct-Oct jumps in the basal plane and along the c-axis gives the total diffusion coefficients:

3 2 basal a wOct-Oct + a 2wOct-H

D|| =

w Oct-Oct + c 2w Oct-H

Using the expressions derived above, we have obtained the interstitial diffusion coefficients for N and O in hcp Zr. The results are displayed in Figs. 6(a) and 6(b), respectively, where they are benchmarked against previous DFT calculations and experimental measurements from the literature. The diffusion coefficients of N calculated in this work are slightly lower than the experimental values [46, 47], whereas those of O agree well with previous theoretical calculations [20, 48, 49] and experimental measurements [50-53].

In the basal plane, the diffusivity of N is slightly higher than that of O. This trend is consistent when comparing the experimental values of N and O separately. However, parallel to the c-axis, the diffusion coefficient of N is markedly lower than that of O, and N exhibits a more pronounced diffusion anisotropy (D / D||) than O. This difference can be attributed to the higher migration barriers of N compared to O along the c-axis, for both the direct Oct-Oct jump and the Oct-H-Oct pathway.

3.4. Comparative diffusion of N, O, Si, and U

To compare the calculated diffusivities of N, O, Si and U, we have plotted the diffusion coefficients summarized in Fig. 7 [Figure 7: see original paper]. Si exhibits significantly higher diffusivities than N, O, and U in both the perpendicular and parallel directions relative to the c-axis. The diffusion coefficients of

UZr perpendicular to the c-axis are comparable to those of N and O, whereas in the parallel direction they are about 1~2 orders of magnitude lower. Although the diffusion coefficients of interstitial U are higher than those of N and O, they remain lower than that of Si. This observation is consistent with diffusion couple experiments in the U3Si2-Zr system, where U diffuses more slowly than Si [5].

The intrinsic diffusivity alone, however, does not fully determine the macroscopic diffusion flux, which also depends on the solute’ s solid solubility. Si occupies substitutional sites in α-Zr with a negative formation energy (-1.06 eV), implying a high solid solubility that enables a large concentration gradient to develop at the interface and drive a substantial flux. In contrast, U has a positive substitutional formation energy (0.74 eV), yielding a lower solubility; therefore, even though its intrinsic diffusivity is not extremely low, the resulting macroscopic concentration profile remains limited.

The rapid penetration of N and O atoms into the Zr matrix observed experimentally originates from the high solubilities of these light elements. The formation energies of N and O at the most stable octahedral interstitial site in α-Zr are as low as -3.73 eV and -5.62 eV, respectively, indicating that both species can dissolve into the Zr matrix in substantial quantities.

The combination of high solubility and an interstitial diffusion mechanism that requires no vacancy mediation enables N and O to penetrate the Zr matrix with extremely high flux under the driving force of the chemical potential gradient. This provides a quantitative rationale for the swift formation of the oxygen-rich α-Zr brittle phase in the UO2-Zr system [1] and for the extensive interfacial interdiffusion promoted by N in the UN-Zr system [4]. Our calculations quantitatively support this physical picture: the interstitial mechanism endows N and O with intrinsically high diffusion coefficients, while the high solubility ensures that a large number of atoms participate in the transport process, together giving rise to the fast fuel-cladding chemical interaction kinetics observed experimentally. From an accident-tolerant fuel design perspective, mitigating FCCI requires strategies beyond simply slowing the fastest diffuser. For UN-Zr and UO2-Zr, the combination of high solubility and interstitial mechanism suggests that barrier layers or solubility12

reducing dopants may be more effective than attempting to block diffusion paths. For U3Si2-Zr, the rapid diffusion of Si (fast interstitial diffuser with high solubility) is the primary concern, while U diffusion is inherently limited by its low solubility. These findings suggest that designing advanced nuclear fuels for compatibility with Zr-based cladding requires consideration of not only the diffusivity of individual elements but also their solid solubility and operative diffusion mechanisms.

4. Conclusion

In this work, we systematically investigated the diffusion mechanisms of N, O, Si, and U in hcp-Zr using first-principles calculations. Atomic size mismatch governs site preference: small N and O atoms spontaneously occupy octahedral interstitial sites with very low formation energies,

while larger Si and U prefer substitutional sites. N, O, and Si all diffuse via interstitial-dominated mechanisms. Interestingly, despite both being substitutional, Si exhibits near-random diffusion while U suffers from significant solute-vacancy binding (Eb = -0.19 eV) that drastically reduces its correlation factor. O exhibits both a lower migration barrier and a lower formation energy than N, leading to higher solubility and faster macroscopic diffusion. When thermal expansion and interstitial formation entropy are taken into account, interstitial diffusion becomes increasingly favorable at elevated temperatures; we therefore predict that U undergoes a transition from vacancy-mediated to interstitial-dominated diffusion at high temperatures. All solutes diffuse faster in the basal plane than along the c-axis. Mitigating FCCI requires not only slowing the fastest diffuser but also considering barrier layers or solubility-reducing dopants. These results demonstrate that both intrinsic mobility and solid solubility must be considered to predict FCCI kinetics, providing atomic-scale guidance for designing diffusion-resistant fuel-cladding interfaces by controlling solute site occupancy and solubility.

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Data availability Data will be made available on request.

Declarations Conflict of interest The authors declare that they have no conflict of interest.

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notation in brackets indicates the interstitial position occupied after relaxation.

Unstable

Unstable

−1.06

−3.73

−5.62

−2.22

−4.61

1000 K values of displacement S and correlation factor f for Si and U.

n (THz)

E m (eV)

S and f at 1000 K

n (THz)

E (eV)

S and f at 1000 K

Ebm' .

–3.30$×$10-14

–7.31$×$10-16

–5.41$×$10-6

–7.22$×$10-15

Ebm' .

–1.52$×$10-10

–2.97$×$10-13

–0.48

–5.81$×$10-11

in α-Zr. Interstitial site

1073 K

Solute

α-Zr.

In base

1.85 (Oct-Oct)

1.75 (Oct-Oct)

2.49 (Oct-H-Oct)

2.00 (Oct-H)

3.66 (Oct-Oct)

3.04 (Oct-Oct)

2.49 (Oct-H-Oct)

2.00 (Oct-H-Oct)

0.21 (Oct-Oct)

0.61 (BO-BOt)

0.60 (Oct-Oct)

0.97 (BO-BO)

On c-axis

Solvent

Solute

Vacancy

2 The schematic illustration of atomic jumps in an hcp lattice required for the eight-frequency model of Ghate [12].

Oct-Oct in base Oct-Oct on c-axis Oct-H-Oct

BO-BO in base BO-BO on c-axis

3 Schematic illustration of the dominant interstitial diffusion pathways in the hcp lattice. (a) For U atoms, the most stable interstitial site is the BO site; the dominant diffusion pathways are BO-BO jumps within the basal plane and along the c-axis direction. (b) For N, O, and Si atoms, the Oct site is the most stable interstitial configuration; the dominant diffusion pathways include direct Oct-Oct jumps in both the basal plane and along the c-axis. In addition, for N and O, the Oct-H-Oct pathway via H sites is also incorporated to accurately capture their diffusion kinetics.

(b) ||

Vcancy diffusers

Int_{Upper} bound

Int_{Best} estimate

Int Lower bound

4 Comparison of interstitial and vacancy-mediated activation energies for N, O, Si, and U in hcp Zr. (a) Perpendicular to the c-axis ( ), (b) parallel to the c-axis (||).

5 Comparison of vacancy-mediated diffusion coefficients for Si and U in hcp Zr (D perpendicular to the c-axis and D|| parallel to the c-axis) obtained from the eight-frequency model in this work, with those in bcc Fe from our previous work [44] calculated using the nine-frequency model. The diffusion coefficients of Si in hcp Zr are compared with previous DFT data [54], and those of U are in good agreement with the experimental values reported in Ref. [45].

(a) N

(b) O

6 Interstitial diffusion coefficients of (a) N and (b) O in hcp Zr perpendicular (D) and parallel (D||) to the c-axis. The present DFT results are compared with previous DFT calculations (Refs. [20, 48, 49] for O) and experimental data (Refs. [46, 47] for N; Refs. [50-53] for O).

7 Comparison of interstitial diffusion coefficients for N, O, Si, and U, along with vacancymediated diffusion coefficients for U in hcp Zr.

Note: Figure translations are in progress. See original paper for figures.

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