Stability of self-interstitial atoms in hcp-Zr

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ABSTRACT

This paper reports the relative stability of various configurations of self-interstitial atoms (SIAs) in hcp-Zr, based on density-functional-theory calculations. In contrast to literature reports of confusing and sometimes contradicting results based on smaller calculation cells, the results here are from calculation cells that contain more than 180 atoms, and provide the most accurate and reliable prediction of the relative stability of SIAs in hcp-Zr. At the most stable configuration of basal octahedral, the formation energy of SIA is 2.73 eV, which does not change with further increase of calculation cell size. The accurate determination of the stability sequence of different SIA configurations provides key material property knowledge in understanding the microstructure evolution of the zirconium-based cladding material in nuclear reactor systems, especially for the anisotropic diffusion of the radiation-induced point defects.

1. Introduction

Zirconium or its alloy (Zircaloy) is commonly used as the cladding of fuel rods in fission reactors, where the irradiation dose is extremely high. The mechanical properties are greatly affected by the radiation damage. It is well known that under irradiation, the volume conserved shape change occurs, due to the evolution of vacancies and interstitials, so called radiation growth [1–4]. Due to the large amount of the shape change, up to 150%, there is a safety issue in the operation of the nuclear reactors [5].

Self-interstitial atoms (SIAs) are point defects, contributing to mass transport in crystalline solids. Due to smaller formation energies, vacancies are more abundant than SIAs in metallic solids – reaching concentrations as high as 10^{-4} close to their melting point [6]. However, the concentration of SIAs can be high in solids under bombardment of energetic particles including energetic electrons, ions, and neutrons [7]. Large quantities of SIAs may dominate mass transport and more importantly the structure evolution of solids. In crowdion configuration, SIAs of body-centered-cubic solids diffuse in one dimension and trigger a range of unique structure evolutions [8]. However, the nature of the diffusion process depends on the relative stability of the SIAs in various configurations. In this paper we report the relative stability of SIAs in hcp-Zr.

There are eight symmetrical configurations for a SIA in hcp metal. Here we use the conventional notation for these eight configurations [9] – octahedral (O), split <0 0 0 1> dumbbell (S), crowdion (C), tetrahedral (T), basal octahedral (BO), basal split (BS), basal crowdion (BC), and basal tetrahedral (BT); shown in Fig. 1. The first four configurations are grouped as off-plane configurations since their positions are out of the basal plane. The other four are in-plane configurations, as the projections of off-plane counterparts onto the basal plane.

The knowledge of the properties of interstitials, especially the formation energy which determines the specific equilibrium defect concentration, is necessary for understanding the thermodynamic and kinetic behavior of metals and alloys [10,11]. The relative stabilities of the SIA configurations greatly affect their mobility, as well as the mechanism of solute diffusion. However, it is not a trivial task to determine the formation and migration energy of a single interstitial in the specific configurations. Both diffuse scattering experiments [12,13] and internal friction measurements [14] have failed to identify the most stable SIA configuration. This is because these quantities are affected by the local environment, including the presence of impurities around the defects. High purity samples are therefore expected to generate reliable results [15].

While a large number of publications have reported the stability of single SIAs, many of them are based on classical inter-atomic potentials and do not agree with each other [16–27]. This is because Zr is a transition metal with 4d electrons. As discussed by Zhang et al. [28], hcp transition metals are poorly described by empirical inter-atomic potentials as opposed to non-transition metals such as Mg.

Precise predictions rely on *ab initio* Density Functional Theory (DFT) calculations. Willaime [29] and Domain et al. [30–32] have studied SIA stability in hcp-Zr using DFT simulations. However, due to the small system size used, their study is inconclusive regarding the most stable SIA configurations. Interactions between the SIAs and their images introduced by the periodic boundary

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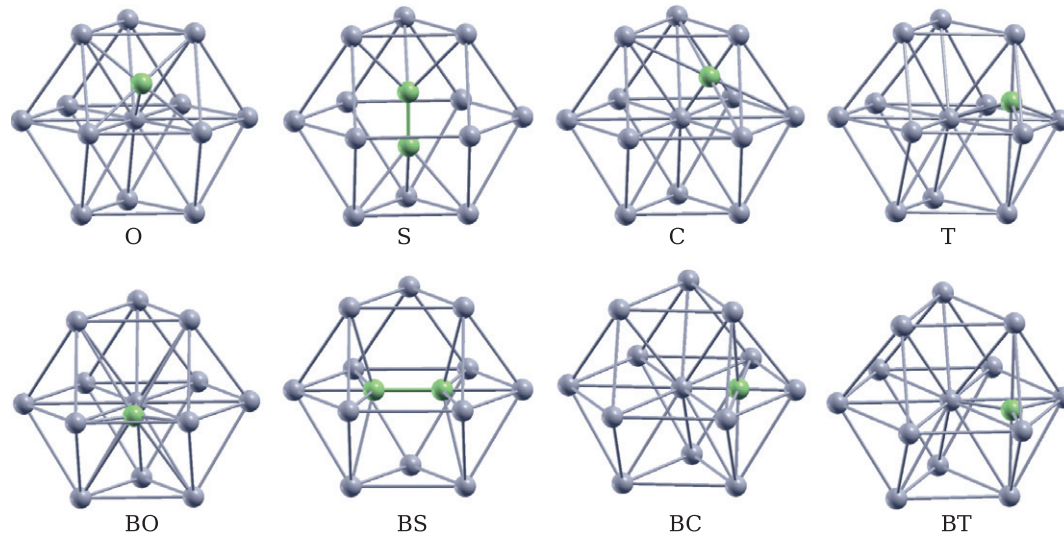E-mail address: qpeng.org@gmail.com (Q. Peng).

Fig. 1. Conventional eight configurations of SIA (green ball) in hcp metal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

conditions significantly influence formation energies and thus the stability of each SIA.

Our work aims to provide an accurate and reliable knowledge of SIA configurations in Zr from first-principles study. The ultimate goal is to investigate the fundamental mechanism of the radiation growth [2–4] in hcp-Zr. In this first work, we determine the most stable SIA configuration, which could provide the hint of the SIA diffusion path.

2. DFT calculations

In the present work, we studied the stabilities of self-interstitials by examining the formation energies of eight SIA configurations using *ab initio* Density Functional Theory (DFT) calculations with the super cell method [33,29,34]. Four super cells with N = 36, 96, 180, and 288 atoms plus one SIA are studied, which contains $3 \times 3 \times 2, 4 \times 4 \times 3, 5 \times 6 \times 3$ and $6 \times 6 \times 4$ primitive unit cells, respectively.

DFT calculations were carried out with the Vienna Ab-initio Simulation Package (VASP) [35–38] which is based on the Kohn–Sham Density Functional Theory (KS-DFT) [39,40] with the generalized gradient approximations as parameterized by Perdew, Burke and Ernzerhof (PBE) for exchange–correlation functions [41,42]. The pseudo-potential in this study has twelve electrons ($4s^2 4p^6 5s^2 4d^2$) explicitly included in pseudo-potentials as valence electrons. The core electrons are replaced by the projector augmented wave (PAW) and pseudo-potential approach [43,44].

The cutoff energy for the kinetic energy of wave-functions was carefully selected to be 400 eV after convergence tests. A Gamma-centered k-mesh is required to sample the irreducible Brillouin Zone in hcp structures to preserve the hcp symmetry. Here we used $7 \times 7 \times 7, 5 \times 5 \times 5, 3 \times 3 \times 3$ and $3 \times 3 \times 3$ Gamma-centered k-mesh for the four systems, respectively. The integration over eigenvalues is performed by the smearing technique using the Methfessel–Paxton function of order 1 and a smearing width of 0.05 eV [45], which results in a convergence of total energy of 2.0 meV/cell for the largest system in this study.

The formation energy is the energy cost of generating a defect configuration. SIA formation energies are calculated at rescaled constant volume conditions using the super cell method [33,29,34]:

$$E_{SIA}^f = E\left(N+1; \frac{N+1}{N}V\right) - \frac{N+1}{N}E(N;V), \qquad (1)$$

where $E(N;V)$ is the total energy of the perfect bulk with N atoms in volume V and $E(N+1; \frac{N+1}{N}V)$ is the total energy of the system with SIA, which has $N+1$ atoms and the volume is rescaled to $\frac{N+1}{N}V$.

With the initial atomic positions schematically shown in Fig. 1, the SIA structures are optimized with the conjugate gradient method. The criterion to stop the relaxation of the electronic degrees of freedom is set by total energy change to be smaller than 10^{-5} eV. The optimized atomic geometry was achieved through minimizing Hellmann–Feynman forces acting on each atom until the maximum forces on the ions were smaller than 0.03 eV/Å. The pressures of the systems after relaxation are less than 0.1 GPa. The parameters selected in this study ensure the convergence of formation energies within 0.05 eV/cell.

3. Results and analysis

The lattice constants of hcp-Zr are a = 3.238 Å and the c/a ratio 1.600, agreeing with experiments [46] of 3.23 Å and 1.593 respectively. The results of formation energies are summarized in Table 1, as well as the comparison with previous calculations [31,29].

At N = 36, the relative stabilities in descending order are O, BO, S, BS, C and BT. The BC configuration decays to BO, and configuration T decays to S during relaxation. The configuration O has the lowest formation energy of 3.05 eV. The order of the stability at this case agrees with previous calculations[30,31,29].

At N = 96, the stabilities of the eight SIA configurations, in descending order, are BO, O, BS, S, C, BT. The BC configuration decays to BO, and configuration T decays to S during relaxation. The formation energies are 2.97 eV and 2.98 eV for configuration O and BO respectively.

Table 1
Formation energies (in eV) of various SIA configurations of bulk hcp Zirconium from *ab initio* DFT calculations.

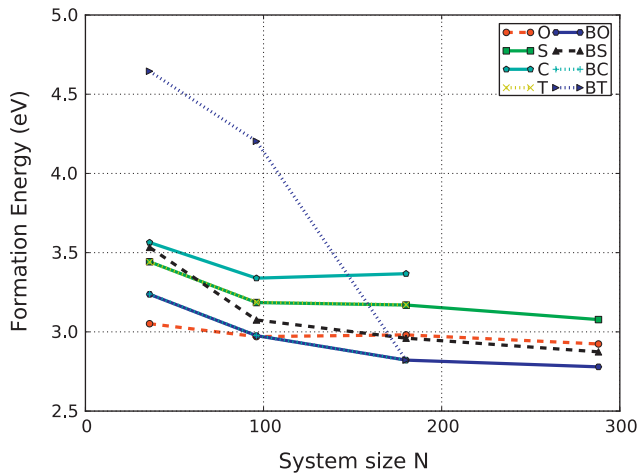|	N	O	S	C	T	BO	BS	BC	BT
Present	36	3.05	3.44	3.56	3.44	3.24	3.53	3.24	4.65
Present	96	2.97	3.19	3.34	3.19	2.98	3.08	2.98	4.23
Present	180	2.98	3.17	3.37	3.17	2.82	2.96	2.82	2.82
Present	288	2.92	3.08			2.78	2.87		
Ref. [31]	36	3.22	3.56	3.63		3.45		3.76	4.84
Ref. [31]	96	2.94	3.12	3.25		2.98		2.95	4.14
Ref. [29]	36	3.04	3.28	3.52		3.14	3.39		

Fig. 2. System size effects on the stabilities of SIAs in hcp-Zr.

At $N = 180$, the stabilities of the eight SIA configurations are, in descending order, BO, BS, O, S, C. Both BC and BT configurations decay to BO. Configuration T decays to S. The stablest configuration is BO, with a formation energy of 2.82 eV. The stability of configuration O is comparable to BS, with only 0.02 eV difference in formation energy. The basal configurations are more stable and favorable for self interstitials.

At $N = 288$, we only studied the four most stable SIA configurations at $N = 180$, i.e., BO, BS, O, S. The formation energies are 2.78, 2.87, 2.92, and 3.08 eV, respectively.

We found that the stability of each SIA configuration strongly depends on the system size. The general trend is that the formation energy decreases as the system size increases. For example, the formation energy of BS decreases from 3.53 eV to 2.87 eV, which is 0.66 eV or a change of 19% when N varied from 36 to 288. The BT configuration has the largest change of formation energy. With much higher formation energy than other SIAs at $N = 36$ and 96, BT decays to BO at $N = 180$ during relaxation.

The most stable SIA configuration also varies with the system size. As N increases, the most stable configuration changes from O at $N = 36$ to BO at $N \geqslant 180$. This could solve the long standing puzzle of why the most stable SIA structure changes from one system to another. Our results are in contrast to the confusing or contradicting results in the literature due to the use of insufficiently large calculation cells. (see Fig. 2)

Since the formation energy could be used as a rough estimate of the diffusion barrier, the small energy difference of BO, BS, BC and BT suggests one- or two-dimensional diffusion of SIAs in the basal plane.

The change of the formation energies of SIAs with respect to the system size is an artificial effect. It is well known that the presence of a defect in the system will introduce strain field which decays at r^{-2} with respect to the distance r to the defect [47]. The strain interactions are typically scaled as $O(\frac{1}{V}) = O(\frac{1}{N})$. Thus, a small system size N of a super cell strongly affects the formation energy of a defect, as a result of the strong interaction of the defect with its images due to the periodic boundary conditions applied. For example, the interactions between the self-images are particularly strong in the case of $N = 36$ atoms, where the distance between the defect and its images is very small (0.92 nm). It is the small supercell size limitation in the model of the first-principles calculations that leads to artificial effects on the stabilities of SIAs.

On the bright side, the artificial effects will fade out with respect to the system size. Our results show that the formation energies as well as relative formation energies converge at $N \geqslant 180$. We extrapolate our results to the ideal case of $N \rightarrow \infty$ by linear fitting the formation energies with respect to $1/N$. We predict that the formation energies of the lowest four SIA configurations BO, BS, O, and S are 2.73, 2.79, 2.93, and 3.05 eV respectively in an infinite large system.

One can use the formation energy of a SIA to estimate its concentration due to the thermal equilibrium at finite temperature T, as $\varrho = \exp(-E_{SIA}^f/k_B T)$, where k_B is the Boltzmann constant. For example, for $E_{SIA}^f = 2.8$ eV, the SIA concentrations are 9.2×10^{-48} at $T = 300$ K and 1.7×10^{-12} at $T = 1200$ K, far below the concentrations under irradiation.

Our result that the most energy favorite SIA configuration is BO sets a bias of the SIA's diffusion during the radiation damage. Considering a atom which is knocked out, forming a SIA, it will move to the BO configuration with the highest probability. This bias forms an anisotropy of the diffusion from off-plane configuration to in-plane configuration. Recall that the radiation growth is the expansion in the a direction and contraction in the c direction. The BO bias could play an important role in such mass transport. Our results provide a proof of the diffusion anisotropy difference [2,3] in hcp-Zr from energetics perspective. The bias of the BO configuration could assist the radiation growth [4] of Zr.

4. Conclusions

In summary, we studied the stability of SIAs in hcp-Zr using *ab initio* DFT calculations. We examined SIA configurations in four systems with system sizes $N = 36, 96, 180$ and 288. We found that the stability of SIA configurations is strongly affected by the system size. The O configuration is the most stable structure at $N = 36$ with $E_O^f = 3.05$ eV. At $N = 288$, BO configuration is the most stable one with $E_{BO}^f = 2.78$ eV. We predict that the formation energies of the lowest four SIA configurations BO, BS, O, and S are 2.73, 2.79, 2.93, and 3.05 eV respectively in an infinitely large system. The energy bias of the BO configuration provides an energy proof of the diffusion anisotropy difference and thus assists the radiation growth.

Acknowledgements

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