



Atomic self-diffusion anisotropy of HCP metals from first-principles calculations



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ABSTRACT

A plane wave pseudo-potential method based on density functional theory is employed to calculate the migration energy barrier for the atomic self-diffusion in HCP metals including Mg, Zn, Ti, Zr, and Hf. The influences of some key factors (plane-wave cutoff energy, k -mesh, supercell size, and geometric optimization scheme) on the calculated migration energy barrier and its anisotropy are systematically investigated. We show that the supercell size affects heavily the migration energy barrier and its anisotropy for the metals with valence d electrons (Ti, Zr, and Hf) but not for the ones with only valence s metals (Mg). In general, the anisotropy of the migration energy barrier reduces with increasing size of the supercell especially for Ti, Zr, and Hf. The optimization of the shape and volume of the supercell matters for the migration energy barrier calculated with the small size supercell but not for that calculated with the large supercell. With the calculated migration energy barrier, the self-diffusion coefficients are evaluated based on the transition state theory and compared with other first-principles calculations and the experimental measurements.

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1. Introduction

Atomic diffusion is involved in many processes (e.g., phase transition, dislocation climbing) in the engineering alloys. Thus, it is highly pertinent to the mechanical properties of the materials. For example, the creep of alloys at high temperature is directly determined by the atomic diffusion and the activation energy of the creep equals to the diffusion barrier of the atoms. Because of this, the atomic diffusion in materials has been a long-standing topic in material sciences.

Experimentally, the atomic diffusion coefficient is generally measured by using the radiotracers, from which, the activation energy of the diffusion may be determined by using the Arrhenius equation. However, the measured atomic diffusion coefficients of some metals were greatly scattered due to the inevitable impurity of the samples. For instance, the impurities such as Fe, Co, and Ni strongly reduce the diffusion activation energy and accelerate the self-diffusion in α -Ti and α -Zr [1–4]. Theoretically, the diffusion coefficient may be evaluated by using transition state theory with some of the parameters such as the atomic migration energy bar-

rier (ΔH), vacancy formation energy (ΔE_f), and the effective vibration frequencies ν calculated by using the first-principles methods based on density functional theory (DFT) [5,6]. The advantage of the first-principles calculations is that they may screen the influence of the impurities by constructing an ideally pure system.

Although first-principles methods have already been routinely employed to investigate the atomic diffusion in metals, there are still some problems to be addressed especially for the hexagonal-close-packed (HCP) metals such as Mg, Zn, Ti, Zr, and Hf. The primitive vectors along the c and a or b axes of HCP lattice are not equivalent to each other, which may make the in-basal-plane and out-basal-plane diffusions different. A literature survey shows that the diffusion anisotropies from different first-principles calculations may deviate significantly from each other. Table 1 summarize the atomic migration energy barriers of the HCP metals along different directions calculated by using first-principles method [6–13] in combination of the climbing image nudged elastic band (CI-NEB) approach [14,15]. For Ti, most of the first-principles calculations generated significant lower in-basal-plane migration barrier (ΔH_{in}) than the out-basal-plane one (ΔH_{out}) [7,8,11–13]. The difference may reach 0.15 eV, which should result in a high anisotropy of the in-basal-plane and out-basal plane self-diffusions of Ti. However, the calculations of Scotti et al. [9] predicted very close ΔH_{in}

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Table 1

Summary of the atomic migration energy barriers of the HCP metals calculated by using the first-principles methods.

Metals	Ref.	Supercell	GGA		LDA				
			ΔH_{in}	ΔH_{out}	ΔH_{in}	ΔH_{out}			
Mg	[6]	3 × 3 × 2	0.35	0.38	0.39	0.41			
	[7]	3 × 3 × 2	0.40	0.42					
Zn	[6]	3 × 3 × 2	0.27	0.17	0.35	0.30			
	[7]	3 × 3 × 2	0.34	0.20					
Ti	[8]	3 × 3 × 2	0.40	0.52	0.33	0.46			
	[7]	3 × 3 × 2	0.49	0.59					
	[9]	3 × 3 × 3	0.41	0.43					
	[10]	4 × 4 × 2	0.49	0.57					
	[11]	4 × 4 × 3	0.43	0.56					
	[12]	3 × 3 × 2	0.43	0.57					
	[13]	3 × 3 × 2	0.38	0.53					
	[13]	4 × 4 × 3	0.44	0.49					
	Zr	[7]	3 × 3 × 2	0.57			0.70	0.23	0.43
		[12]	3 × 3 × 2	0.51			0.67		
[13]		3 × 3 × 2	0.50	0.70					
[13]		4 × 4 × 3	0.67	0.71					
Hf	[7]	3 × 3 × 3	0.89	1.00					
	[12]	3 × 3 × 3	0.79	0.91					

and ΔH_{out} with difference of only about 0.02 eV such that the self-diffusion of Ti should behave very weak anisotropy. Similar situation occurs for Zr. The smallest difference between ΔH_{in} and ΔH_{out} predicted is about 0.04 eV whereas the largest one is 0.20 eV. Such discrepancy is obviously not acceptable and makes the comparison between experiments and theoretical calculations difficult. Therefore, a systematic investigation of the accuracy of the first-principles calculations is highly appreciable in order to obtain reliable atomic diffusion properties and clarify the discrepancy reported in literature.

In the present work, we calculate the migration energy barriers for the in-basal-plane and out-basal plane self-diffusions of the HCP metals including Mg, Zn, Ti, Zr, Hf by using a first-principles method. We choose these five HCP metals because of the following reasons: (1) These metals are engineeringly very important and found widespread applications in aerospace, marine, automobile, nuclear industry, medicine, etc. (2) Ti, Zr, and Hf have the same number of d electrons but locate in different periods of the periodic table of elements. Mg and Zn are simple metal elements without d electrons. Ti, Zr, Hf, and Mg have c/a close to the ideal value (1.63) whereas that of Zn is far from it. These differences may help us to understand the band filling and structure effects on the atomic diffusion in HCP metals. The influences of the calculation parameters such as the plane-wave cutoff energy, the k -point mesh, the exchange-correlation (XC) functionals, the supercell size, and the geometric relaxation scheme on the atomic migration energy barriers are systematically investigated on the equal footing. With the calculated migration energy barriers, the self-diffusion coefficients are evaluated and compared to the experiments. We will show that the discrepancy of the diffusion anisotropy reported in literature is mainly due to the supercell size effect.

This paper is arranged as follows. In Section 2, we introduce briefly the details of the first-principles calculations. In Section 3, the migration energy barriers calculated with different settings and the self-diffusion coefficients are presented. In Section 4, the effects of the supercell size and relaxation scheme on the migration energy barrier are discussed. Finally, we conclude our work in Section 5.

2. Calculation details

The calculations are performed by using a first-principles plane-wave pseudopotential method based on density functional theory (DFT), implemented in the Vienna Ab initio Simulation Package

(VASP) [16,17]. The projected augmented wave (PAW) [18,19] potentials is employed for the interaction between the nucleus and the electrons. The valence electron configurations of the PAW potentials are $3s^2 3d^1 04s^2$ for Mg and Zn, $4s^2 3p^6 3d^2$ for Ti, $4s^2 4p^6 5s^2 4d^2$, and $5s^2 5p^6 6s^2 5d^2$ for Zr and Hf, respectively. To evaluate the influence of the settings of the calculations on the results, the plane-wave cutoff energy, k -point mesh, exchange-correlation functionals [20,21], and supercell size as well as the geometric relaxation scheme are systematically tested. The convergence criterion is 1×10^{-5} eV for the electronic minimization and 0.01 eV/Å for the interatomic forces during the geometric optimization.

In general, the self-diffusion of the atoms occur through the vacancy mechanism, i.e., the exchange of position between the atom and vacancy. With the vacancy mechanism, the atomic diffusion coefficients may be calculated as

$$D_a = \frac{1}{2} C a^2 (3f_{Ax} \omega_A + f_{Bx} \omega_B) \quad (1)$$

and

$$D_c = \frac{3}{4} C c^2 3f_{Bz} \omega_B \quad (2)$$

where D_a and D_c are respectively the in-basal-plane and out-basal plane diffusion coefficients of the HCP metal. a and c are the lattice constants. ω_A and ω_B are respectively the jump frequencies of the in-basal plane and out-basal plane atomic migrations, which are calculated according to the Vineyard's transition state theory (TST) [22]

$$\omega = \nu^* \exp(-\Delta H/k_B T), \quad (3)$$

where ν^* is the effective vibrational frequency, calculated with

$$\nu^* = \frac{\prod_{i=1}^{i=n} \nu}{\prod_{i=1}^{i=n-1} \nu'}. \quad (4)$$

Here, ν denotes the vibrational frequency of the initial state and ν' for the transition state. The vibrational frequencies are calculated by using the finite displacement approach. The standard vibrational frequency calculation is time-consuming, and, therefore, we simply calculate the vibrational frequencies of the migrating atom: three branches for the initial state and two for the transition state with the imaginary frequency neglected. The migration energy barrier ΔH is evaluated as the energy difference between the transition

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