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Ab initio study of formation, migration and binding properties of helium–vacancy clusters in aluminum

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Abstract

Ab initio calculations based on density functional theory have been performed to study the dissolution and migration of helium, and the stability of small helium–vacancy clusters He_nV_m (n, $m = 0$–4) in aluminum. The results indicate that the octahedral configuration is more stable than the tetrahedral. Interstitial helium atoms are predicted to have attractive interactions and jump between two octahedral sites via an intermediate tetrahedral site with low migration energy. The binding energies of an interstitial He atom and an isolated vacancy to a He_nV_m cluster are also obtained from the calculated formation energies of the clusters. We find that the di- and tri-vacancy clusters are not stable, but He atoms can increase the stability of vacancy clusters.

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Keywords: Ab initio calculations; Helium; Aluminum; Cluster

1. Introduction

The creation of helium atoms in metals is considered with particular concern since their precipitation into bubbles can substantially deteriorate mechanical material properties, particularly in metals at high temperatures [1–3]. Over the past semicentury, various experimental techniques and theoretical methods have been used to investigate He effects in metals and alloys. Experimental results indicate that helium atoms tend to be trapped at defects within the crystal such as vacancies, dislocations and grain boundaries and precipitates into clusters or bubbles. For example, several experimental studies of the irradiated aluminum and aluminum alloys show the presence of He bubbles [4–6]. The formation of helium bubbles in materials can lead to void swelling and produces high temperature intergranular embrittlement, surface roughening and blistering [7,8]. However, the atomistic properties of helium in metals at the origin of these phenomena are difficult to identify from experiments. Computer simulations provide an important method to obtain insight into fundamental understanding of the complex atomic-level processes of defects controlling microstructural evolution in metals. Particularly, ab initio calculations [9,10], Molecular dynamics (MD) simulations [11,12] and kinetic Monte Carlo (KMC) methods [13] have been employed to investigate the properties of He defect and the dissolution and migration of He, as well as the formation and stability of helium–vacancy (He–V) clusters in bcc iron. Recently, ab initio calculations were used to investigate the properties of the intrinsic point defects and He in bcc tungsten [14]. Although MD methods were performed to calculate the formation energies of small He_nV_m clusters in aluminum using empirical potentials [15], which proved that the binding energies mainly depend on He–vacancy ratio of clusters rather than cluster size. The data about atomistic properties of helium in fcc aluminum

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are very small. Therefore, in this work, the energetics and mobility of helium in fcc Al, and the stability of small helium–vacancy clusters are studied using ab initio calculations.

2. Method of calculation

The present calculations were performed using the Vienna Ab initio Simulation Package VASP. In the calculations the interaction between ions and electrons was described by the projector-augmented wave (PAW) method [16,17]. Exchange and correlation functions were taken in a form proposed by Perdew and Wang (PW91) [18] within the generalized gradient approximation (GGA). The supercell approach with periodic boundary conditions was used to simulate point defects as well as pure phase and the supercell contains 108 atoms. The energy cutoff for the plane-wave basis set used throughout this work is 500 eV for relaxation of the atomic position and of the shape and size of the supercell. During the relaxation runs, the brillouin zone integration was achieved using a Methfessel–Paxton smearing of sigma = 0.2 eV, and once the relaxation was completed, accurate total-energy calculations were performed using the tetrahedron method with Blöchl corrections.

In this work, the migration energy calculations are performed at a fixed volume of the supercell using the following method: the atomic positions relative to the center of mass are constrained to relax in the hyperplane perpendicular to the vector connecting the initial and final positions. Furthermore, the formation energy of He_nV_m clusters that contains n He atoms and m vacancies is defined as

$$E_f(He_nV_m) = E_{tot}(He_nV_m) - n\varepsilon_{He} - (N-m)\varepsilon_{Al}, \quad (1)$$

where $E_{tot}(He_nV_m)$ is the calculated total energy of a computational cell containing a He_nV_m cluster, N denotes the number of perfect fcc lattice sites in the computational cell, ε_{Al} is the energy per Al atom in a perfect fcc Al lattice and ε_{He} is the energy of an isolated He atom. The binding energy of a defect (a vacancy or an interstitial He) to a He_nV_m cluster is calculated by

$$E_b(He) = E_f(He) + E_f(He_{n-1}V_m) - E_f(He_nV_m), \quad (2)$$

$$E_b(V) = E_f(V) + E_f(He_nV_{m-1}) - E_f(He_nV_m). \quad (3)$$

3. Results and discussion

3.1. Dissolution of He in Al

The vacancy formation energy and relative stabilities of the various helium insertion sites are determined with a 108-atoms supercell for various K points, as shown in Table 1. It is found that the energies weakly depend on the K points for the 108-atoms supercell. This indicates that a good estimate of He defect formation energies can be obtained within a 108-atoms supercell even if a poor K points is used. The formation energies of the He interstitials are larger than 3.0 eV. The present results differ significantly from those obtained with empirical potentials [15,21], which obtained the formation energy of interstitial He is only 1.25 and 1.32 eV, but almost consist with the Jing's result [22], i.e. 3.02 eV.

Table 1
Calculated and experimental values for vacancy formation energy ($E_f(V)$) and the He formation energies for the substitutional, the octahedral and the tetrahedral positions, where all energies are expressed in eV

	K points	$E_f(V)$	$E_f(He_{sub})$	$E_f(He_{tetra})$	$E_f(He_{octa})$
Full rel.	$3\times3\times3$	0.50	1.46	3.17	3.09
	$5\times5\times5$	0.55	1.55	3.29	3.23
	$7\times7\times7$	0.56	1.53	3.20	3.18
Other calc.				5.77 [20]	4.06 [20]
			2.69 [19]		1.25 [15]
		~0.65 [15]			
			0.77 [20]		1.32 [21]
					3.02 [22]
Expt.		0.66 [23,24]			

It is well known that the free volume of the octahedral defect is larger than that of the tetrahedral defect in fcc metal. Therefore, He is expected to occupy defect sites in order of largest free volume, namely, substitutional, octahedral and tetrahedral. The results of our ab initio calculations indicate that the ordering of the formation energies is $E_f(He_{sub}) < E_f(He_{octa}) < E_f(He_{tetra})$, however, the energy difference between the octahedral and tetrahedral positions is very small. We find that tetrahedral interstitial He induces strong relaxation in the Al lattice. For the tetrahedral interstitial He the relaxation increases the distance between it and its first-neighbor Al, while the He octahedral interstitial causes smaller lattice distortion. After relaxation, the volume around the tetrahedral position is almost same to that of the octahedral He interstitial. As a result, the He formation energies are nearly equal at the tetrahedral and octahedral positions.

3.2. Migration of interstitial He

Because helium atoms in a metal after He implantation or He production by transmutation may occupy either substitutional or interstitial lattice sites, the kinetics of these He defects in fcc aluminum are important. In this work, three possible paths for interstitial He migration were considered, as shown in Fig. 1. The first path is from one octahedral site to another octahedral site without passing the tetrahedral site, as shown in Fig. 1(a). The energy difference between the saddle point and the initial configurations equals the migration energy ($E_m^{0,0}$ (He_{int})), and we find that $E_m^{0,0}(He_{int}) = 0.16$ eV. Fig. 1(b) shows the second path from one octahedral site to another octahedral site with passing the tetrahedral site. The migration energy from the octahedral to the tetrahedral site is 0.10 eV, and it