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Diffusion mechanisms of vacancy and doped Si in Al_3Ti from first-principles calculations

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ABSTRACT

First-principles calculations were employed to study the migration of vacancy in clean and Si-doped Al_3Ti. The effect of Si doping on the formation of vacancy and the diffusion of doped-Si atom in the Al_3Ti were also investigated. It is found that, under Al-rich condition, the formation energies of Al vacancies in Al_3Ti with Si doping are decreased compared with those in clean Al_3Ti. The preferred migration paths of vacancies are not changed when Si occupies Al site, but the migration energy barriers for the majority of paths are decreased after Si doping. The doped-Si atom on Al site prefers to diffuse via the nearest Al vacancy.

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1. Introduction

Al–Si based alloys are important casting alloys in aluminum industry because of the high wear resistance, good weldability, good fluidity, and excellent mechanical properties. It is well known that Ti is an important additive for Al–Si alloy [1–3] and the $D0_{22}$–Al_3Ti phase can always be found [4,5]. Ti was added into Al–Si foundry alloys to investigate the influence of Ti addition on the wear properties and hardness, the results indicated that the formed $(Al,Si)_3Ti$ compounds can improve the hardness but it is harmful to wear resistance property [6,7]. Recently, Ti was also used to remove impurity Si by the removal of $(Al,Si)_3Ti$ compounds from Al alloys [8]. Previous research [9,10] indicated that up to 15% Al can be replaced by Si in $D0_{22}$–Al_3Ti, resulting in the formation of $(Al,Si)_3Ti$ phase with variable chemical composition and lattice parameter. The site preference of doped-Si atom and formation energies of vacancies in Al_3Ti have been investigated by using first-principles calculation [10,11]. However, up to now, the research on the diffusion behavior of vacancy and doped-Si atom, which is closely related to the intrinsic physical mechanism of Si substitution in Al_3Ti, is still lacking. The research will contribute to better understand the thermodynamics and kinetics of Si substitution, which plays an important role in improving the Si removal efficiency from molten Al.

$D0_{22}$–Al_3Ti has a similar site distribution with $L1_2$–Ni_3Al, and both $D0_{22}$ and $L1_2$ structures are the A_3B-type ordered structures based on the fcc lattice. The diffusion behaviors of vacancies and alloying elements in $L1_2$–Ni_3Al have been extensively investigated by using molecular dynamics simulations with empirical interatomic potential and first-principles calculation, where the first nearest neighbor diffusion mechanism, second nearest neighbor diffusion mechanism and sublattice diffusion mechanism have been discussed [12–15]. Moreover, other diffusion mechanisms have also been introduced in literatures. Höglund et al. [16] indicated that Zn in p-type GaP and InP diffuses by a substitutional–interstitial mechanism containing the dissociative mechanism and the kick-out mechanism. The six-jump cycle [17] and the triple defect mechanism [18,19] were also developed to enrich the vacancy migration mechanisms of intermetallic compounds.

In this paper, the migration mechanisms of vacancies and substitutional Si atom in $D0_{22}$–Al_3Ti have been investigated by first-principles calculations. The first nearest neighbor diffusion mechanism, the second nearest neighbor diffusion mechanism and sublattice diffusion mechanism were discussed to investigate the

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migration paths and energy barriers for vacancies, and a reasonable two-defect migration mechanism for Ti vacancy in Al_3Ti was proposed. Moreover, the effects of Si doping on the vacancy formation and migration were discussed, and the migration of doped-Si atom in Al_3Ti was also investigated.

2. Details of the calculations

2.1. Calculation method

The calculations presented in this paper were accomplished using the CASTEP code, which is based on density-functional theory (DFT), and a plane-wave basis set was employed for expansion of the electronic wave-function [20]. In this method, interactions of core–valence were represented by the ultra-soft pseudopotentials (USP) [21] and the exchange-correlation energy was treated by the generalized gradient approximation (GGA) of Perdew et al. (PW91) [22]. For a 32-atom Al_3Ti supercell, a $3 \times 3 \times 3$ Monkhorst–Pack *k*-point mesh was used for Brillouin zone integrations [23]. The crystal structures were fully optimized by independently modifying lattice parameters and internal atomic coordinates. The Broyden–Fletcher–Goldfarb–Shanno minimization scheme [24] was used to minimize the total energy and interatomic forces.

$D0_{22}$–Al_3Ti crystallizes in the I_4/mmm space group, having six Al atoms staying at two kinds of non-equivalent locations (denoted as Al1 and Al2) and two Ti atoms in one unit cell. The models of crystals with vacancy or containing doped-Si atom and vacancy simultaneously were built up by using $2 \times 2 \times 1$ supercells (containing 32 atoms). The defects were created in the center of the supercell and the concentration of vacancy or doped-Si atom is 3.125 at.%. The transition states were determined as stationary points that were energy maxima in the direction of the reaction coordinate and energy minima in all other directions. A generalized synchronous transit method was used for locating transition state structures or first-order saddle point [25]. The LST/QST algorithm combines the linear (LST) or quadratic synchronous transit (QST) methods with conjugate gradient (CG) refinements. Searching of the transition state began by performing an LST/optimization calculation, followed by a QST/maximization calculation. From the point thus obtained, CG minimization was performed to refine the saddle point geometry. The cycle was repeated until a stationary saddle point (transition state) was located [26]. The setting of calculation parameters and the convergence have been approved in our previous work [10]. Besides, considering that temperature has little influence on Si substitution behavior in Al_3Ti [10], the employed temperature in our calculations is 0 K. At last, the influence of interaction between defects in neighboring cells is evaluated and the difference of vacancy formation energy or vacancy migration energy between 128-atom Al_3Ti system and 32-atom Al_3Ti system is less than 0.02 eV, which indicated that 32-atom system is big enough to evaluate vacancy formation and migration energy in this research work.

2.2. Migration paths

The possible migration paths of Al1, Al2 and Ti vacancies are shown in Fig. 1. The first and second nearest neighbor hops as well as the inner sublattice hops were considered, and the migration distances are listed in Table 1. For Al1 vacancy (A1 in Fig. 1), there are four symmetry equivalent paths via which it hops to the nearest neighbor sites, e.g. A1 → A2 as shown in Fig. 1. The hops are also inner sublattice hops. There are two kinds of second nearest neighbor hops for A1 vacancy, A1 → B1 and A1 → T1, which have the same migration distance. Both A1 → B1 and A1 → T1 hops have four symmetry equivalent paths. The migration energy barriers of

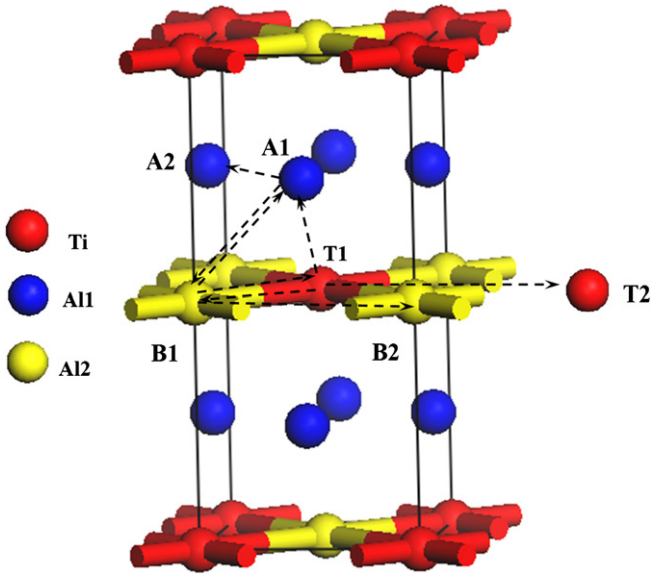

Fig. 1. Migration paths for the first nearest neighbor hop, the second nearest neighbor hop and the inner sublattice hop of Al1, Al2 and Ti vacancies in $D0_{22}$–Al_3Ti. The arrows represent the migration paths.

the two different hops were calculated, and the results indicate that the migration energy barrier of A1 → T1 hop is about two times higher than that of A1 → B1 hop. Therefore, the research was focused on this kind of A1 → B1 hop in second nearest neighbor hops which is obviously more possible to occur. For Al2 vacancy (B1 in Fig. 1), the first and second nearest neighbor hops are B1 → T1 hop and B1 → A1 hop, which have four and eight symmetry equivalent paths respectively. The migration distances of Al2 vacancy are the same as that of Al1 vacancy in the first and second nearest neighbor hops. Besides, the inner sublattice hops B1 → B2 for Al2 vacancy were also considered, which have four symmetry equivalent paths. Antisites are formed in both the first and second nearest neighbor hops of Ti vacancy (T1 in Fig. 1). The inner sublattice hop of Ti vacancy is shown in Fig. 1, and T2 atom is located at the neighboring unit cell. There are four, eight and four symmetry equivalent paths for T1 → B1, T1 → A1 and T1 → T2 hops respectively.

To study the effect of Si doping on the vacancy migration, we firstly placed a doped-Si atom on one of the lattice sites (Al1, Al2 or Ti), then a vacancy (Al1, Al2 or Ti) nearest to the doped atom was created. For the vacancies in the Si-doped Al_3Ti, we examined all possible first and second nearest neighbor hops as well as inner sublattice hops as done for clean Al_3Ti. Moreover, all migration paths via which Si hops to the nearest Al1, Al2 or Ti vacancy were calculated to reveal its diffusion behavior mediated by vacancies.

Table 1
Migration paths of Al1, Al2 and Ti vacancies and the migration distances (in Å) of vacancies in different hop behaviors. *a* (3.851 Å) and *c* (8.611 Å) are the lattice constants of Al_3Ti unit cell.

	First nearest neighbor hop		Second nearest neighbor hop		Inner sublattice hop	
	Migration path	Distance	Migration path	distance	Migration path	Distance
V_{Al1}	A1 → A2	$\frac{\sqrt{2}}{2}a$	A1 → B1	$\sqrt{\left(\frac{c}{4}\right)^2+\left(\frac{a}{2}\right)^2}$	A1 → A2	$\frac{\sqrt{2}}{2}a$
V_{Al2}	B1 → T1	$\frac{\sqrt{2}}{2}a$	B1 → A1	$\sqrt{\left(\frac{c}{4}\right)^2+\left(\frac{a}{2}\right)^2}$	B1 → B2	a
V_{Ti}	T1 → B1	$\frac{\sqrt{2}}{2}a$	T1 → A1	$\sqrt{\left(\frac{c}{4}\right)^2+\left(\frac{a}{2}\right)^2}$	T1 → T2	a

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