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Atomic diffusion mediated by vacancy defects in pure and transition element (TM)-doped (TM = Ti, Y, Zr or Hf) $L1_2$ Al_3Sc

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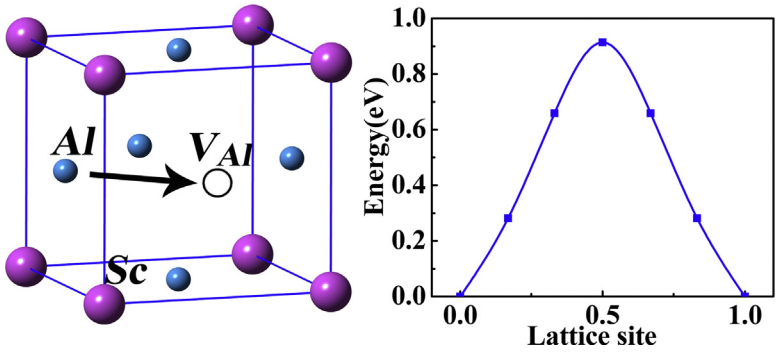
HIGHLIGHTS

- The point defects formation energies are determined in pure and doped Al_3Sc.
- The energy profiles for dominating diffusion paths are obtained using climbing image nudged elastic band method.
- Al atom nearest-neighbor jump mediated Al vacancy is most favorable for Al atom diffusion.
- Sc mainly diffuses by nearest-neighbor jump and antistructure sublattice mechanisms mediated by Al vacancy.
- The activation barriers increase with increasing atom size mismatch in transition metal-doped Al_3Sc.

GRAPHICAL ABSTRACT



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ABSTRACT

Atomic diffusion in pure and transition element (TM = Ti, Y, Zr or Hf)-doped Al_3Sc has been studied mainly along vacancy-mediated diffusion paths. After the point defect formation energies are determined, the energy profiles for dominant diffusion paths are obtained using climbing image nudged elastic band method. The energetic results show that Al atom diffusion through nearest-neighbor jump mediated by Al vacancy is most favorable due to the lowest activation barrier, the other diffusion processes would make very small contribution due to the high activation barrier or unstable final state. The dominant Sc atom diffusion mechanisms are the Al-vacancy mediated nearest-neighbor jump under Al-rich condition and antistructure sublattice mechanism under Sc-rich condition. The 6-jump cycle and next nearest-neighbor jump are greatly restricted with high activation barriers. Moreover, effect of typical transition element (Ti, Y, Zr or Hf) doping on atomic diffusion is further studied. The activation barriers for dominant diffusion mechanisms increase with increasing atom size mismatch in sequence of Zr < Hf < Ti < Y dopant.

1. Introduction

Al_3Sc has been attracting great attentions in high-temperature and high-strength technological applications in recent years [1–3]. The thermodynamic properties of Al_3Sc intermetallic have been studied from *ab initio* calculations [4], and mechanical properties [5] and electronic properties of Al—Sc intermetallics are also investigated [6]. Furthermore, the stabilities of low-index surfaces of $L1_2$–Al_3Sc intermetallic

Abbreviations: AS, antistructure sublattice mechanism; ASB, antistructure bridge mechanism; CI-NEB, climbing image nudged elastic band method; DFT, density functional theory; DOS, density of states; GGA, generalized gradient approximation; MEP, minimum energy paths; NNJ, nearest-neighbor jump; NNNJ, next nearest-neighbor jump; PAW, projector augmented wave; TDOSs, total density of states; TM, transition metal; VASP, Vienna *ab initio* simulation package; 6JC, 6-Jump cycle mechanism; V_{Al}, Al vacancy; V_{Sc}, Sc vacancy; Al_{Sc}, Al antisite; Sc_{Al}, Sc antisite.

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and surfaces electronic properties are reported in Ref. [7]. Thermal and constitutional point defects in $L1_2$ Al_3Sc have been further studied theoretically within local density functional theory framework [8].

Atomic diffusion is fundamental in formation, growth and property of material. The diffusion parameters are necessary for quantitative analysis of growth kinetics of materials and can be applied in optimum design of properties [9]. Particularly atomic diffusion mediated by vacancy and the activation energy play an important role in the simple Nabarro-Herring creep model and classic dislocation climb theory [10]. The nonequilibrium dynamics of diffusion-mediated plasticity and creep in high temperature structural materials is also a crucial subject [11]. Therefore, it is of great significance to study atomic diffusion based on vacancy.

Up to now, many experimental techniques are developed to study the atomic diffusion [12]. The radiotracer technique is used to measure the diffusion coefficients of ^{44}Ti and ^{63}Ni in slightly Ni-rich polycrystalline NiTi compound [13]. Operando XRD/MS experimental study on a nanocrystalline Pd(70%)Ag(30%) alloy suggests different diffusion mechanisms involving the Pd segregation [14]. Perturbed angular correlation (PAC) probe atoms have been used as tracers to study diffusion in L12 structure Lanthanide Indides [15]. Theoretical investigations are also performed extensively and various diffusion mechanisms are proposed [16]. In addition to the simple nearest-neighbor jump (NNJ) [17,18] and next-nearest-neighbor jump (NNNJ) [19], antistructure sublattice (AS) is emphatically discussed in $L1_2$ intermetallic compounds [20,21]. Antistructure bridge (ASB) and six-jump cycle (6JC) mechanisms are further investigated in B2 [13,17,22] and $L1_2$ [23–28] intermetallic compounds.

The investigations of atomic diffusions in $L1_2$ type Ni_3Al and Ni_3Ge [10,26,28–30] and Cu_3Au [24] had been conducted, in which several diffusion mechanisms for $L1_2$ type intermetallics were proposed. However, dominant diffusion mechanism for major element needs further verification, whereas diffusion mechanism for the minor element is far from complete understanding. For $L1_2$ Al_3Sc, study of atomic diffusion is very scarce, detailed atomic diffusion mechanisms and activation barriers have not been reported. Therefore, it is necessary and valuable to gain more insight into atomic diffusion in pure and doped Al_3Sc. The present work is valuable to advance understanding of atomic diffusion in $L1_2$ type intermetallics, to design and control the proper heat-treatment process, and to further improve mechanical behavior especially diffusion-mediated properties such as creep, plasticity and so on.

Further, to improve mechanical [31–33] and other properties [34–36], and to decrease cost of alloy, doping the third elements into Al_3Sc has been studied. Theoretical calculation results indicate that elements Ti, Zr, Y and Ta tend to substitute for Sc in Al_3Sc, while Ni and Si prefer to substitute for Al [3]. By addition of the transition metal (TM) elements (Ti, Zr or Hf), the positive effects of Al_3Sc phase in Al—Sc alloys can be promoted [37], and Ti is found to be very effective for retarding the coarsening kinetics of the Al_3Sc precipitates [38]. Mechanical properties of doped Al_3Sc have also been studied in our previous study [39,40]. What's more, doping third element has obvious effect on atomic diffusion [19,41]. Creep property, which is limited by diffusion, is studied experimentally in transition metals doped intermetallics $Al_3(Sc_{0.74}X_{0.26})$ (X = Ti, Y, Zr or Hf). The results show that ternary $Al_3(Sc_{0.74}X_{0.26})$ exhibits a decreased creep rate by about one order of magnitude for Zr and Hf and by about two orders of magnitude for Ti and Y [42]. So it is also significant to investigate the effect of doping on atomic diffusion of $L1_2$ type Al_3Sc phase.

The present work is focused on study of atomic diffusion in Al_3Sc intermetallic. After calculating the relative stability of point defects, the possible atomic diffusion model and migration details are analyzed. Then the climbing image nudged elastic band (CI-NEB) method [43] is employed to compute the energy profiles along possible diffusion paths, and migration and activation barriers of atomic diffusions are further determined. Moreover, effect of TM dopants on activation barriers of dominant mechanism is also studied. The aims of this study are to identify the dominant atomic diffusion mechanism in pure Al_3Sc, to reveal the effect of transition metal (Ti, Zr, Hf or Y) on atomic diffusion, and to provide theoretical guideline for further design and improvement of the crucial mechanical properties of Al_3Sc.

2. Calculation methods

The present density functional theory (DFT) calculations were based on generalized gradient approximation (GGA) and projector augmented wave (PAW) [44] basis, as implemented in Vienna *ab initio* simulation package (VASP) [45]. The cut-off energy for plane wave basis set is 320 eV and Brillouin zone sampling was performed by the Monkhorst-Pack scheme with a k-point $4 \times 4 \times 4$ mesh [46]. The total energy was calculated using the linear tetrahedron method with the Blöchl correction until the total energy was converged to 10^{-4} eV/atom.

64-atom and 108-atom supercells are used to test calculation accuracy by computing excitation energies [47] (also called raw energy [8]) of the point defects. With 64-atom supercell, the excitation energies of point defects for V_{Al}, V_{Sc}, Al_{Sc} and Sc_{Al} are respectively 5.011, 8.423, 5.075 and −1.824 eV, being in reasonable agreement with the other theoretical calculations using ultrasoft pseudopotential within local density functional theory framework [8], which generally underestimates the lattice constant and overestimates the bonding energy compared to GGA [48]. The excitation energies of point defects with 108-atom supercell are respectively 4.978, 8.373, 4.977 and −1.856 eV for V_{Al}, V_{Sc}, Al_{Sc} and Sc_{Al}, being lower than that with 64-atom supercell, implying a 64-atom supercell is not large enough due to the interaction between point defect and its period image. To diminish this interaction and obtain reliable accuracy, a $3 \times 3 \times 3$ supercell with 108-atoms was used in present calculations.

The point defect plays a crucial role in mechanical properties [49,50]. Especially, atoms diffusion mediated by vacancy is performed by atom-vacancy exchange [22], in which diffusive atom moves from the initial state to the final state recreating a new vacancy. So formation energy of point defect is calculated to study the stability. To calculate the energy profile and gain migration barrier, the CI-NEB method [43] was employed, in which a series of images are constructed by interpolating the atomic positions between the initial and final states, and connected by an elastic band [23]. The band of images is then relaxed until the force threshold on the images is 10^{-2} eV/Å. Based on possible diffusion paths in Al_3Sc, the effect of TM doping on atomic diffusion was further studied, in which the dopant was located at the site nearest from minimum energy path for atomic diffusion.

The computed lattice constant is 4.104 Å, which is in good agreement with experimental value of 4.103 Å [37] and other theoretical results of 4.108 Å [51] and 4.103 Å [52]. The obtained formation enthalpy is −0.457 eV/atom, agreeing well with experimental results of −0.451 eV/atom [53], and theoretical value of −0.457 eV/atom [51] and −0.464 eV/atom [54], showing that our calculations are reliable enough.

3. Results and discussion

3.1. Point defects

Point defects are important mediums for atomic diffusion, so are firstly studied here. Al_3Sc unit cell contains only two sublattices, Al atom sublattice occupies Wyckoff position 3c (0, 1/2, 1/2), and Sc atom sublattice is at 1a (0, 0, 0). So there are four types of native point defects in Al_3Sc: Al antisite (Al_{Sc}) and Sc antisite (Sc_{Al}), Al vacancy (V_{Al}) and Sc vacancy (V_{Sc}).