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A curved pathway for oxygen interstitial diffusion in aluminum

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ABSTRACT

The diffusion of interstitial oxygen (O) in fcc aluminum (Al) has been studied using first-principles and the diffusion coefficient has been calculated. Whereas interstitial atoms in fcc systems are typically found to hop directly between interstitial centres, the diffusion pathway for interstitial O in fcc Al was calculated to have a curved minimum energy pathway with an energy barrier of 0.95 eV. The barrier was found to be off-centre of a neighboring octahedral site. Also unlike the majority of fcc metals, O prefers to sit in the tetrahedral interstitial site as opposed to the octahedral site. The calculated O diffusion coefficient is on the same order of magnitude of the diffusion coefficient of O in other fcc metals. The preferred interstitial site, diffusion pathway and vacancy binding energy were found to be related to the bond length of O with neighboring Al atoms.

1. Introduction

During the oxidation of fcc aluminum (Al), oxygen (O) chemisorbs onto the Al surface and then, after some time, is absorbed into preferable sub-surface sites, and eventually forms a thin oxide layer, typically Al_2O_3, on its surface (a process which is rapid even at low temperatures [1,2]). Due to the technological importance of Al_2O_3, this oxidation process has been studied extensively. Most studies focused on the chemisorption process and the subsequent absorption into sublayers. It was found that when O is absorbed into the sublayers, it occupies the tetrahedral interstices [3–5]. Little work is available with respect to the diffusion of O in Al. This is due to the characteristics of oxidation of Al at any given temperature range. At low temperatures, oxidation is controlled by Al diffusion through the oxide lattice or grain boundaries, and at high temperatures it is controlled by both O and Al diffusion through the oxide [2,6]. In either case little experimental information can be obtained regarding the O diffusion in the Al lattice due to the rapid establishment of the surface oxide. The tendency of O and Al to form Al_2O_3 is so strong that this oxide is often formed as an internal precipitate in the alloy upon oxidation. During steady state oxidation, O will diffuse only through the base metal after Al has been consumed to create Al-rich oxides [7]. However, it has been suggested that during internal oxidation a supersaturation of O will occur before reacting with Al [8,9]. As a first approximation, it is possible to simulate this effect as a function of Al concentration so long as O diffusion in pure Al is defined [10]. Unfortunately this information is not available in the literature. Given the scarcity of this information and the possible implications for oxidation of other alloys, the present work focuses on calculating the diffusion of O in bulk fcc Al.

Statistical analysis of the lowest energy state and the saddle point state of a chemical reaction led to the development of transition state theory (TST), by Eyring [11], which determines the rate of a given reaction process based on the energy difference between these states. Vinyard extended this theory to account for the vibrational lattice contributions [12]. The work by Vinyard and Eyring provided the methodology for calculating diffusion coefficients of species in solids at finite temperatures. This methodology has been successfully used to determine the diffusion coefficient of substitutional and interstitial elements in various solids from first-principles, using density functional theory (DFT) [13–15]. To calculate the diffusion coefficient, the minimum energy pathway (MEP) and the associated saddle points for the O atom are obtained in the present work by using the climbing image nudged elastic band method (CI-NEB) [16]. Finite-temperature thermodynamic properties for O atom energy barriers are obtained using the phonon supercell method [17,18] and the Debye model [19,20]. Given its importance in other systems such as Ni [21] and Fe [22], the effect of a lattice vacancy on O atom diffusion is evaluated. The preferred pathway for O atom diffusion as calculated by these methods is discussed.

Bonding between metallic atoms and O atoms is typically ionic with the electrons localized near the O atom. This type of strong localized bonding falls under the prevue of bond valence theory [23], which only requires the measure of metal-O bond lengths to provide information about the overall valence of an atom [23,24]. Hence it is possible to give a simple estimate the valence

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of the O atom in its interstitial sites and its transition states. In addition, recent efforts have made it possible to carry out bonding analysis on local environments by using a projected crystal orbital Hamilton population (pCOHP) [25–27]. The pCOHP and its integrated value (IpCOHP) are both discussed in the present paper in terms of the local bonding between the O atom and the surrounding fcc Al atoms along with the diffusion pathway and the relative stability of O atom interstitial sites.

2. Computational methodology

Diffusion of O atoms in the transition elements of bcc Fe [22], fcc Ni [21] and H atoms in fcc Ni [13] has been studied from first-principles calculations. In those cases, the lowest energy interstitial site for the O or H atom is the larger octahedral site. Diffusion takes place through atomic jumps between these sites. Through analysis of interstitial atomic jumps between the closely-packed planes, Wert and Zener constructed a relation for the diffusion coefficient of an interstitial atom [28]:

$$D = n\beta d^2\Gamma \tag{1}$$

where n is the number of the nearest neighbor jumps, β is the probability that the interstitial atom jumps to a new plane, d is the jump distance between planes and has a value of $a/2$ where a is the lattice parameter, and Γ is the frequency of an interstitial jump. In the current system the lowest energy site for O was calculated to be the tetrahedral site instead of the expected octahedral site. An interstitial atom in the fcc tetrahedral site can make six jumps to neighboring tetrahedral sites. Of these jumps, two jumps leave the plane, making $\beta = 1/6$. Based on TST, the frequency, Γ, can be given by [11,13,29]

$$\Gamma = \frac{kT}{h}\frac{Z_{TS}}{Z_0}e^{-\Delta E/kT} \tag{2}$$

where k is the Boltzmann's constant, T is the temperature, h is Plank's constant, ΔE is the difference in energy between the transition and initial states, and Z_0 and Z_{TS} represent the partition functions for the initial states and the transition states, respectively. Building on the work by Vineyard [12] and Eyring [11], Wimmer et al. derived an expression for Γ in terms of the free energy difference for the system of interest [13]:

$$\Gamma = \frac{kT}{h}e^{-\Delta G_m/KT} \tag{3}$$

where ΔG_m is the molar Gibbs energy difference between the final and initial state. The Gibbs energy can be calculated using DFT from the Helmholtz energy when the pressure of the system is zero. For a system at volume V and temperature T, the Helmholtz energy is [19,30]

$$F(V,T) = E_{0K}(V) + F_{vib}(V,T) + F_{el}(V,T) \tag{4}$$

where $E_{0K}(V)$ is the static energy at 0 K without vibrational contributions, $F_{vib}(V,T)$ is the vibrational contribution, and $F_{el}(V,T)$ is the electronic contributions to the Helmholtz energy. $F_{vib}(V,T)$ can be calculated either using the Debye model or the phonon method [31]. The Debye model needs only the Debye temperature as a function of the equilibrium volume, bulk modulus and the first derivative of the bulk modulus with respect to pressure [20,32]. These can be obtained from equation of state (EOS) fittings of first-principles energy-volume (E-V) calculations where the energy of a structure with several volumes expanded around its equilibrium volume is calculated [31,33]. The phonon method requires inputs from the phonon density of states (PDOS), and $F_{el}(V,T)$ can be determined by the electronic density of states (EDOS) [19,20,30].

In the present work, first-principles calculations were calculated via the Vienna Ab Initio Package (VASP) version 5.2 [34,35] using the generalized gradient approximation parameterized by Perdew-Burke-Ernzerhof (PBE) [36] to treat the exchange–correlation. Electron-ion interactions were accounted for using the projector augmented wave (PAW) method [37]. Calculations were carried on $2 \times 2 \times 2$ supercells of fcc Al with a single interstitial O atom. In addition, calculations were performed on $2 \times 2 \times 1$ supercells to compare the energy of O in the substitutional lattice site with the energy of those structures where O occupied an interstitial site. The first nearest neighbor lattice vacancy to O was placed on the $2 \times 2 \times 2$ supercells of the fcc Al lattice so as to assess its possible effect on diffusion. Select calculations were also carried out with the local density approximation (LDA) [38]. This was for comparison of the site occupation of O calculated between PBE and LDA and because LDA produces more accurate description of the internal vacancy surface due to a cancelation effect [39,40]. The Monkhorst-Pack method [41] was used for Brillion zone sampling, and a k-point mesh of $9 \times 9 \times 9$ was used for relaxations followed by a $12 \times 12 \times 12$ k-point mesh for the final static calculations [41]. A plane wave cut-off energy of 520 eV was used along with a convergence criteria of 10^{-6} eV/atom for the electronic self-consistent iterations.

The minimum energy pathway and transition state configurations were obtained using the CI-NEB method, which relaxes a number of configurations (images) along a reaction path connected by a spring force between adjacent images. Three images between the initial and final structure and a spring force of -5 eV Å^2 between images in all CI-NEB calculations were set. PDOS were calculated with the ATAT software package using the supercell method [42] where force constants were obtained from VASP and analyzed using the code YPHON [17,18].

Bonding analysis was carried out through the use of pCOHP analysis between interstitial O atoms and neighboring Al lattice atoms using the code LOBSTER [25–27]. Crystal orbital Hamilton populations (COHP) separate the energy of the band-structure by contributions of orbital-pairs. The product of the density of states matrix of two neighboring atoms with their corresponding Hamiltonian matrix element produces this COHP [25]. The COHP, in turn, allows one to evaluate the bonding strength since contributions will either make the band-structure energy more positive or negative corresponding to bonding and anti-bonding, respectively. However, because the COHP is based on orbital pairs this puts the COHP in a local basis which is unsuitable for direct analysis from plane wave functions such as those used in DFT. To adapt a formulation of COHP to DFT, Deringer et al. developed a method for projecting the density matrix and Hamiltonian matrix elements to a local atomic basis set [26,27]. This projection produces the pCOHP and yields similar information to the COHP. For the current analysis additional static calculations are performed on the $2 \times 2 \times 2$ fcc Al supercells to obtain vasp wave function outputs needed for analysis by LOBSTER. Since there must be at least as many bands in a calculation as there are orbitals for the analysis performed by LOBSTER, the number bands in each VASP calculation was set to 132. Additionally, symmetry conditions were turned off because the version of LOBSTER used in this work did not have the capability to deal with k-point symmetry. Only a k-point mesh of $7 \times 7 \times 7$ was small enough for each of these static calculations due to memory restrictions.

3. Results and discussion

The occupancies of O in the interstitial octahedral and tetrahedral sites and the substitutional lattice site were considered. Four parameter Birch-Murnaghan EOS fittings of E-V calculations