



Study of vacancy-(H,B,C,N,O) clusters in Al using DFT and statistical approaches: Consequences on solubility of solutes

Damien Connétable*, Matthieu David

CIRIMAT UMR 5085, CNRS-INP-UPS, ENSIACET 4, allée Émile Monso, BP 44362, F-31030, Toulouse Cedex 4, France

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ABSTRACT

This article is a study of the solubility of interstitial atoms in aluminum using a multi-scale approach. We focused on hydrogen, boron, carbon, nitrogen and oxygen atoms (labeled X). We studied isolated atoms as well as the possible formation of clusters with and without vacancies (V), i.e., X_m , VX_m and V_2X_m ($m \geq 0$). Formation and segregation energies are first obtained using first-principles calculations, subsequently, a statistical approach is employed in order to evaluate the concentration of impurities and defects according to the temperature. For instance, we find that, in solute solution, H, N and O atoms prefer to be located in tetrahedral sites, and C and B atoms in octahedral sites. The chemical and energetic interactions between the interstitials, the metal and the vacancies are consequently presented and analyzed in detail. Results show that certain species prefer to interact with themselves, thus forming X_m clusters, and others with vacancies, thus forming stable VX_m clusters in the metal. Using a statistical approach, we finally discuss the formation of clusters according to the temperature and the X concentration. At low and intermediate temperatures (below 600 K), we found that the atoms prefer to form clusters rather than stay isolated in aluminum. We show that H and B atoms are the only elements likely to increase vacancy concentration.

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1. Introduction

It has been shown in earlier works [1–5] that the presence of interstitials, even in undetectable quantities, can have a significant impact on the concentration of defects (clusters, cavities, etc.) present in metals, especially on vacancy concentration. Therefore, the concentration of interstitial elements and point defects can be significantly different from what is expected with conventional laws (like Sieverts' law [6]). For instance, in the case of nickel [1,7], it has been shown that O and H atoms can form high concentrations of clusters (V_nX_m , composed of n V vacancies and m X atoms), especially at low and intermediate temperatures. In the case of iron, Schuler et al. [4] have shown that C atoms can form V_2C_2 clusters in a non-negligible concentration. The use of relevant multi-scale approaches has also clearly proved [1,4,8] that DFT simulations alone are not able to analyze and interpret these mechanisms. It has been shown that the energy associated with cluster formation in the metal can strongly reduce the formation of vacancies, thus

increasing the concentration of defects in the system, consequently enhancing the processes of diffusion of all species in the metal.

In the present work, we discuss the insertion of five interstitial elements in fcc-Al: hydrogen, boron, carbon, oxygen and nitrogen. Their interactions with vacancies and their capacity to form clusters in aluminum are thus discussed. The formation of H and He clusters in aluminum has been partly discussed in the literature: either only VX_m clusters were considered [5,8–10], or the multi-scale approach was not aimed at discussing the actual influence of cluster concentration on vacancy concentration [11]. In a recent work [12], diffusion mechanisms of interstitial elements were presented without discussing the interactions between Al and interstitials. This manuscript is aimed at filling these gaps as well as studying the case of other interstitials.

From an experimental standpoint, studies show that the maximum solubility of interstitial species in aluminum strongly depends on experimental conditions as well as on the specie. It has been shown that the limit of solubility is low in the case of H, C, N, O and B atoms, even at high temperature. The content of nitrogen dissolved in the Al matrix is thus probably low. But according to Wriedt's [13] observations, this experimental data has little credibility. The exact N concentration is therefore unknown but can be

* Corresponding author.

E-mail addresses: damien.connetable@ensiacet.fr (D. Connétable), matthieu.david@ensiacet.fr (M. David).

considered relatively low. When the fugacity of N₂ becomes too “high” (10^{−20} Pa at 933 K [13]), an AlN phase, with a wurtzite type structure, is formed. As for nitrogen, the Al–O phase diagram [14] is composed of only one intermediate structure between Al–fcc and O₂ gas: alumina α-Al₂O₃ (with many additional allotropic structures). The O content in the metal is likewise supposed very low. The solid solubility of C atoms is also low, it is estimated at 400–800 appm [15]. However, Okamoto [16] explains that this concentration value is probably overestimated by at least one order of magnitude. In the case of hydrogen, the study of Al–H system [17] also shows that hydrogen barely dissolves in aluminum: 15–20 appm near the melting point. Finally, the boron concentration is also low: a maximum solid solubility of 45 appm of B in Al has been measured at 933 K, see the Al–B system [18]. In summary, the concentration of interstitial elements can be considered ranging from 10 to 100 appm.

This work aims at evaluating solubility energies of these species and identifying the forms under which they are dissolved in the metal as a function of the temperature (T). The mechanisms of diffusion and the thermodynamics should vary depending on whether they are free or form clusters. As a first-order approximation, we used a multi-physics approach coupling first-principles simulations and a statistical model. At the atomic scale, simulations allow modeling free species (X) and different types of clusters (X_m, VX_m and V₂X_m) in the metal. It is not an exhaustive study, not all configurations were considered. However, the current work provides a broad overview of the interactions between X atoms and Al. We calculated the formation energies of these clusters and analyzed their chemical properties. Subsequently, by using these accurate values in the statistical model, we computed the distribution and concentration of the different clusters as a function of T and the total concentration of interstitials in the metal.

The remainder of this paper is organized as follows. Section 2 summarizes the DFT parameters and briefly describes the model that was used. In part 3, we discuss the insertion of the five species in the light of DFT results. The formation of different types of clusters is then presented (sections 4–6). We will conclude (section 7) with a discussion on the concentration and fraction of clusters in the metal using a statistical approach.

2. Computational details

First-principles calculations were performed with the density functional theory (DFT) using VASP (Vienna *ab initio* simulation package [19]). We used the Perdew–Burke–Ernzerhof (PBE [20]) functional. Projector augmented wave (PAW) pseudo-potentials [21] were employed to describe atoms. As aluminum is not magnetic, the magnetic moment was not taken into account. In Appendix A, we report some results about several stable structures used hereinafter, especially reference states. Experimental structures are remarkably well reproduced by the DFT.

To study V_nX_m clusters, simulations were carried out on a large super-cell (3 × 3 × 3, that which corresponds to 108 atoms per unit-cell) with full periodic boundary conditions. The inter-atomic forces were fully relaxed and all calculations were performed at zero pressure. We made sure that atomic forces were always smaller than 0.01 eV/Å on the atoms. The plane-wave cut-off energy was set to 600 eV, and 8 × 8 × 8 Monkhorst–Pack mesh grids [22] were used to sample the first-Brillouin zones. With these criteria we obtain converged formation and segregation energies (<2–3 meV). To compute frequencies, we used the finite displacement method on super-cells. As a first-order approximation, only frequencies of X atoms were computed, we thus neglect the effects of the insertion on Al frequencies (values reported in tables). However, due to the

strong coupling between Al and X frequencies, we calculated the full inter-atomic force constants on 2 × 2 × 2 super-cells, displacing only non-equivalent atoms along non-equivalent directions according to the symmetry of the system. The *phonopy* package [23] was used to generate finite displacements according to the symmetry of each structure, it was then used to analyze, plot vibrational properties (phonon dispersion curves and density of states, not shown here) and compute vibrational free energies.

To evaluate the distribution and concentration of clusters, we used an approach similar to the one described by Dome et al. [1]. For each type of cluster *i* of V_pX_m composed of *m* X atoms and *p* vacancies, its concentration (C_i[V_pX_m]) is related to its formation energy (H_fⁱ[V_pX_m]) and its number of equivalent configuration (Z_i[V_pX_m]):

$$C_i[V_pX_m] \approx Z_i[V_pX_m] \exp\left(-H_f^i[V_pX_m]/k_B T\right) \quad (1)$$

The general formulation of the formation energy (H_f) of each V_pX_m cluster is expressed by:

$$H_f^i[V_pX_m] = E_o[(M-p) \cdot Al + m \cdot X] - E_o[M \cdot Al] + p \cdot \mu[Al] - m \cdot \mu[X] \quad (2)$$

where E_o[(M-p)·Al + m·X] and E_o[M·Al] are the DFT energies of the system with and without a cluster (composed of *M* Al atoms), respectively. The chemical potentials (μ) were taken equal to the energy per atom either of the perfect structure for Al (E_o[M·Al]/*M*) or of the reference state of X. In the tables, H_f values were computed using μ[X] = E_o[ref] (see Appendix A). To compute concentrations, the temperature (T) and the chemical potential −μ[X] − (or the total concentration, C_{tot}[X]) are the free parameters of the equations.

The total vacancy concentration, C_{tot}[V] and C_{tot}[X] are thus given by:

$$\begin{cases} C_{tot}[V] = \sum_{p,m,j} p \cdot C_j[V_pX_m] \\ C_{tot}[X] = \sum_{p,m,j} m \cdot C_j[V_pX_m] \end{cases} \quad (3)$$

In the following discussions, we will also use the segregation energy of X in V_pX_m (E_{seg}[V_pX_m]) expressed by:

$$E_{seg}[V_pX_m] = E_o[(M-p) \cdot Al + m \cdot X] + E_o[M \cdot Al] - E_o[(M-p) \cdot Al + (m-1) \cdot X] - E_o[M \cdot Al + X] \quad (4)$$

where E_o[(M-p)·Al + m·X] and E_o[(M-p)·Al + (m-1)·X] are the DFT energies of the V_pX_m and V_pX_{m−1} clusters, respectively. Segregation energy, not directly used in the thermodynamic model presented above, nevertheless allows us to provide information on atomic-scale processes. Indeed, it gives an idea of the affinity between a defect (here V_pX_{n−1}) and an isolated atom (X), and the possibility that it is trapped. We will therefore give this quantity in addition to the formation energy.

3. Ideal solubility

From first-principles calculations, we first discuss the formation energies of X in fcc-Al in the dilute limit, and analyze their relative stability. Three configurations were considered: the substituted, the tetrahedral (*t*, in 8c Wyckoff position) and the octahedral sites (*o*, 4b). The formation energies and the zero-point energies (ZPE)

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