



Review

Segregation of hydrogen to defects in nickel using first-principles calculations: The case of self-interstitials and cavities

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ABSTRACT

A detailed first-principles study of the interactions of hydrogen with different point defects in Ni is presented. In particular we discuss the trapping of multiple hydrogen atoms in monovacancies, divacancies and at the self-interstitial (dumbbell). We show that, contrary to the previous theoretical works, the dumbbell cannot trap H atoms. In the case of a single vacancy, the segregation energy is found approximately equal to -0.26 eV, in excellent agreement with implantation anneal experiments and thermal desorption spectra in the literature. This segregation energy is obtained for the relaxed octahedral (labeled O_1) and tetrahedral (T_1) positions inside the vacancy, with a slight site preference for O_1 . Outside the vacancy, the binding energy becomes lower than 20 meV after the second shell of octahedral sites (O_2). The H_2 molecules are never stable inside the small vacancy clusters. Therefore, VH_n clusters show a maximum trapping capacity of six H atoms. In the case of the divacancy, the H segregation energy can be as low as -0.4 eV. This reconciles theory and experiments by attributing the deepest trap energies to multiple vacancies.

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1. Introduction

Hydrogen (H) embrittlement of metals is a major concern because it is involved in most practical cases of aqueous stress corrosion cracking and fatigue. Despite considerable experimental efforts, the microscopic mechanisms are still debated with three competing mechanisms: decohesion [1], hydrogen enhanced localized plasticity [2] and local hydrides stabilized by stress [3,4]. Although decohesion is observed experimentally, at least for intergranular propagation (in Ni [5], in Al [6], for example), its quantitative modeling is not completed, as discussed in the review by Birnbaum et al. [7], because of two main weaknesses: the configurations for the calculation of the work of separation are usually limited to simple crystallographic planes, which is over-simplistic, and where the driving force for H localization is limited to the effect of the hydrostatic stress. This is not enough, by several orders of magnitude, to reach high local concentrations. This gave room for an additional mechanism where H-stabilized vacancies can slowly diffuse, cluster and form crack nuclei that coalesce with the main crack (see [8] and references therein) [9,10]. This mechanism is supported by the observation by Fukai that multiple H occupancy of the vacancy can result in extremely high concentrations of vacancies [11]. It has been specifically observed in Ni [12], although at high temperature and high H pressure, but also in electrodeposited Ni [13]. At room temperature, it has been proposed that out of equilibrium vacancies, stabilized by H, could be produced by localized plasticity [10].

A critical evaluation of this mechanism requires a systematic quantification of the H-vacancy cluster' properties (VH_n): stability as a function of H concentration and T, mobility, clustering and segregation to other crystalline defects. The subject of the present paper is the first step where a detailed calculation of the energetics is made (segregation energies of the isolated H and formation energy of the clusters containing several H). In line with what was recently done for other metals [14–16], we apply Density Functional Theory (DFT) to H in Ni and carefully compare our results with what was previously predicted by the semi-quantitative Effective Medium Theory (EMT) [17–20] and implantation-annealing experiments [21,22]. Three characteristic segregation energies were found. An incoherency has been recently pointed out between the interpretation based on EMT and Thermal Desorption Spectra (TDS) (see [11] p. 222). In EMT, the segregation of an isolated H atom is high and goes down when several H occupy the vacancy because of H–H repulsive interactions. On the contrary, TDS shows that the low segregation energy (in absolute value) is observed in the dilute limit. We will show that our calculations reconcile experiments with theory and give a clear microscopic picture of trapping by single and multiple vacancies. They also constitute a reliable database upon which statistical models for VH_n stability and mobility can be built.

The paper is organized as follows. In the first section, the method is exposed. Then, preliminary calculations are performed with two goals: prepare configurations for H segregation (single/divacancy), and study H in solution in the perfect bulk, since it is the reference state for segregation and several interstitial sites are in competition. The objective is also to reproduce some key quantities that appeared in the literature to firmly establish the coherency between our DFT calculations and those done in the past. As a side, we study the self interstitial because it is useful to interpret the implantation experiments. In the fourth section, comprehensive calculations of *m* H atoms (*m* ≤ 13) in a vacancy are presented where we specifically investigate the H–H interactions inside the vacancy and the possibility to form H₂ molecules. The goal is to establish the maximum trapping capacity of the vacancy and to extract the typical segregation energy range that can be compared to experiments. In the last section, we extend

the same approach to divacancies. Finally, the results are summarized and a simple picture of trapping, coherent with experiments, is established.

2. Methods

Calculations were performed using the Vienna *ab initio* simulation package (VASP) [23–25]. The Kohn–Sham equations were solved by using the projector augmented wave (PAW) method [26] to describe the electron-ion interactions and using the Perdew–Wang (PW91) approximation [27] for the exchange and correlation functionals. The magnetic moments taken into account in all calculations were necessary to avoid errors even at high temperature (see discussion page 5 in Ref. [28] on the differences between para- and ferromagnetic calculations).

The plane-wave cut-off energy was set to 400 eV and 8 × 8 × 8 Monkhorst–Pack mesh grids [29] were used to sample the Brillouin zone for the large supercells (3 × 3 × 3, i.e., 108 Ni atoms), which produced energy of segregation values converged to within 10 meV. These criteria have been validated in previous works [30,28]. Within these criteria, the ground states properties of fcc nickel (the lattice parameter, the cohesive energy and the magnetism are equal to 3.52 Å, 4.89 eV/atom and 0.62 μ_B, respectively) agree with the previous DFT calculations [31] and the experimental values [32].

Lattice relaxations were introduced by means of a conjugate-gradient algorithm. The ions and the lattice parameters were allowed to relax. We ensure that the atomic forces were smaller than 0.01 eV/Å on the H and Ni atoms. It will be shown that, in most cases, the final configurations are symmetric even if the symmetry of the initial configurations is perturbed by random displacements of the H atoms prior to minimization.

3. Preliminary calculations

In this section, we briefly present the main properties of the defects that will be used later to trap H atom (vacancies and self-interstitials). H in solution, in the perfect bulk, is also reviewed.

3.1. Single and divacancies

First, single and divacancies are studied. The formation enthalpy of an *n*-vacancy (H_{nv}^f , where *n* = 1 or 2) is calculated. As the supercell is relaxed (the pressure on the supercell is equal to zero), the formation enthalpy is equal to the formation energy (E_{nv}^f) in our approach. The E_{nv}^f values were calculated as follows:

$$E_{nv}^f = E_o[(N - n) \cdot Ni, \Omega_n] - \frac{N - n}{N} E_o[N \cdot Ni, \Omega_o] \quad (1)$$

where $E_o[(N - n) \cdot Ni, \Omega_n]$ and $E_o[N \cdot Ni, \Omega_o]$ correspond to the internal energy of the relaxed supercell of a system with *n*-vacancies and that of the relaxed supercell of a system without any vacancies (i.e., *N* nickel atoms). The formation volume (Ω_{nv}^f) of the defect is given by

$$\Omega_{nv}^f = \frac{V[(N - n) \cdot Ni] - (N - n) \cdot V_{at}[Ni]}{V_{at}[Ni]} \quad (2)$$

Table 1

Formation energies (E_{nv}^f , in units of eV) and volumes of formation (Ω_{nv}^f , in atomic volume) of a single vacancy and first nearest neighbor (1NN) and second nearest neighbor (2NN) divacancies (per vacancy).

		E_{nv}^f/n		Ω_{nv}^f/n	
		Our work		Our work	
V ₁		1.40	1.45/1.70 [37,38]	0.76	0.82–0.97 [33]
V ₂	1NN	1.37	1.49/1.73 [33]	0.64	0.79 [33]
	2NN	1.42	–	0.65	–

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