

Binding of multiple H atoms to solute atoms in bcc Fe using first principles

W. Counts^{a,*}, C. Wolverton^a, R. Gibala^b

^a Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA

^b Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA

Received 16 March 2011; received in revised form 27 May 2011; accepted 29 May 2011

Available online 27 June 2011

Abstract

We previously performed a series of density functional theory calculations to investigate the interaction between single H atoms and point defects in body-centered cubic (bcc) Fe (Counts W, Wolverton C, Gibala R. *Acta Mater* 2010;58:4730). Here, we extend that work to a systematic study of binding between multiple H atoms and solute atoms in bcc Fe. We investigate the binding of multiple H atoms to one another, to interstitial C and to substitutional solutes. Our study shows the following: (i) H–H interactions are weak. The maximum attractive H–H binding energy is around 0.03 eV, which agrees with experimental values. (ii) The maximum attractive incremental binding energy of a second H atom to a C–H defect pair is 0.07 eV. (iii) We investigate the ability of 3d transition metal solutes to bind up to five H atoms. The binding energy of the second H to a 3d transition metal solute is attractive with a value ~ 0.03 eV greater than binding of energy of the first, independent of solute. The binding energies of the third to fifth H atoms vary but are generally positive. Based on a stability analysis of the H binding energies, we find that the largest H–solute defect complex for V, Cr, Co, Ni and Zn contains two H atoms, while for Sc, Ti, Mn, and Cu the largest defect complex contains four H atoms.

© 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Density functional; Hydrogen embrittlement; Ferritic steels; Iron

1. Introduction

Hydrogen embrittlement (HE) of body-centered cubic (bcc) iron (α -Fe) is a well-known but still not well understood phenomenon. A number of different HE mechanisms have been proposed, including decohesion [1,2], hydrogen-enhanced localized plasticity [3,4], and the hydrogen-enhanced strain-induced vacancy [5,6] models. While these mechanisms are all distinct, each of them requires that H accumulates within the material to form a high H concentration region that enables the respective HE mechanism. Such HE-susceptible regions form as a result of H diffusion, making each of these different HE mechanisms dependent on H diffusion.

H readily diffuses through α -Fe [7], but lattice defects impede the motion of H [8]. However, experiments are less clear concerning the strength of the H–defect interactions because it is not possible to directly measure the H–defect binding energy. In the literature, H–defect binding energies have been probed using a variety of different experimental techniques: magnetic relaxation [9], H permeation [10], thermal detrapping [11,12] and internal friction [13] among others. The magnitude of the H–defect interaction in each of the aforementioned experiments is then determined with the aid of a model that includes a binding energy term. Using this general approach, experimental H–point defect interactions like H–H self-interactions [9], as well as H–C [9], H–Ti [10] and H–□ binding [11,12] in bcc Fe have been quantified (□ = vacancy). Experiments are often also unable to extract details about the geometry of the H–point defect cluster. In one case, Meyers et al. [11] used ion-channeling to obtain additional information about the

* Corresponding author.

E-mail address: waccounts@gmail.com (W. Counts).

position of the D atom. They showed that D atoms occupied a position displaced 0.4 Å from the octahedral site (o-site). However, this technique did not explicitly identify the lattice defect that had bound D.

Theoretical and computational investigations into H–point defect interactions are an important complement to experimental studies because they can provide information to validate and interpret experimental results and can also provide details that are difficult to access experimentally. Computational approaches, if sufficiently accurate, are valuable because they can directly quantify the binding energy of H with a particular point defect in a given configuration. One example where insight from theory was valuable is the D–□ defect pair. Initially, experiments and theory both revealed strong D–□ binding in bcc Fe. Results from an effective medium theory (EMT) based study by Besenbacher et al. [12] revealed that the D–□ binding energy for one to six D atoms was favorable. Guided by these theoretical results, the authors of Ref. [12] were able to explain the emergence of a second plateau region in their detrapping data at higher D concentrations. They argued that when the concentration of D is larger than that of vacancies, vacancies bind multiple D atoms. Thus, the second detrapping plateau observed in the experiment was due to multiple D atoms binding to the vacancy. Both EMT and a diffusion model were then used to qualitatively determine that the incremental vacancy binding energy for the first two D atoms is 0.63 eV,¹ and 0.43 eV¹ for the subsequent (3–6) D atoms.

Density functional theory (DFT) has been successfully used to model □–point defect interactions in a variety of systems. There is good agreement between available experimental data and DFT concerning □–solute interactions in Al [14,15], Mg [16], bcc Fe [17,18] and face-centered cubic (fcc) Fe [19]. DFT has also shown that vacancies are effective H traps in various metal systems. DFT has shown that it is energetically favorable for a vacancy to bind up to between 10 [20] and 12 [21] H atoms in fcc Al, up to 9 H atom in hcp Mg [20], and up to 6 H atoms in bcc Fe [22]. In the case of bcc Fe, the DFT-based binding energies agree well both qualitatively and quantitatively with the experimental results of Besenbacher et al. [12].

It should be noted that binding energies alone are not enough to determine how many H atoms a defect will bind because the defect configuration depends on both the binding energies and defect concentrations. For example, the H–□ binding energy in Al is ~0.35 eV,¹ and the binding energy of a second H to the vacancy is also positive, around 0.30 eV.¹ In cases when the concentration of H (c_H) is much larger than the concentration of vacancies (c_\square), there is a large probability that H atoms will find vacancies along their diffusion path. These H atoms will

bind to the vacancy and form H–□ defects because the H–□ binding energy is positive. The excess H atoms will find these H–□ defects and form defect clusters containing a vacancy and two H atoms defects (2H–□) because the binding energy of a second H to the vacancy is also positive. In cases when $c_\square \gg c_H$, it is far more likely that a H atom will encounter a vacancy rather than a H–□ defect. Thus it is more likely in this case to form H–□ defects over 2H–□ defect clusters even though the binding energy of a second H is positive.

A number of studies have used a thermodynamic formalism to account for this defect concentration effect. All of these thermodynamic evaluations use DFT binding energies as input. As mentioned earlier, DFT calculated binding energies indicate that it is energetically favorable for a vacancy to bind 10–12 H atom in Al and 9 H atoms in Mg. Based on an analytical thermodynamic analysis, Ismer et al. [20] found that vacancies trap multiple H atoms in fcc Al only when the H₂ gas pressure is of the order of 10 GPa and in hexagonal close-packed (hcp) Mg when the H₂ gas pressure is nearly 1 GPa. Gunaydin et al. [23] used Born–Oppenheimer molecular dynamics to probe the effect of defect concentrations on H–□ in Al. In spite of the fact that the H–□ binding energies reveal that it is energetically favorable for a vacancy to bind up to 12 H atoms, they observed that only H–□ defect complexes with 1, 2 or 6 H atoms formed depending on c_H .

While a number of the aforementioned DFT studies have focused on □–point defect (including □–H) interactions, there are fewer theoretical studies focused on H–solute interactions. Monasterio et al. [24] explored the interplay of binding processes when H, C and vacancies are present in bcc Fe. Using DFT, they calculated the H–C binding energy to be 0.02 eV, and the binding energy of a second H to a pre-existing H–C defect to be –0.05 eV.¹ In a previous study, we investigated binding of a single H to a number of different solutes [25]. We found that the maximum H–solute binding energies ranged from 0.00 to 0.25 eV.¹ The fact that these binding energies are positive indicates that H–solute defects are stable.

An open question concerning H–solute interactions is the following: can solute atoms, like vacancies, bind multiple H atoms? Solutes that bind multiple H atoms can have a greater effect on the H diffusion rate than solutes that can bind only a single H atom and thus may also play larger role in HE. Furthermore, the vacancy formation energy in bcc Fe is quite large, of the order of 2 eV [25,26], making the equilibrium vacancy concentration low. In bcc Fe-based steels, the concentration of alloying elements is normally much larger than that of vacancies. Therefore, it is important to fully understand character of H–solute interactions. In this paper, we use first-principles DFT calculations to quantify the binding energy of multiple H atoms to various solute atoms in bcc Fe. We investigate the binding of multiple H atoms to one another, to interstitial C and to substitutional solutes.

¹ A positive binding energy refers to an attractive interaction, and negative value refers to a repulsive interaction between defects.

Download English Version:

<https://daneshyari.com/en/article/1447324>

Download Persian Version:

<https://daneshyari.com/article/1447324>

[Daneshyari.com](https://daneshyari.com)