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First-principles assessment of hydrogen absorption into FeAl and Fe_3Si: Towards prevention of steel embrittlement

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Abstract

We characterize the ability of two potential surface alloys, FeAl and Fe_3Si, to prevent H incorporation into steel, with a view toward inhibiting steel embrittlement. Periodic density functional theory calculations within the generalized gradient approximation are used to evaluate H dissolution energetics and the kinetics of H diffusion into and through FeAl and Fe_3Si. We predict increased dissolution endothermicities and diffusion barriers in both alloys compared to bulk Fe. Fe_3Si is predicted to be the most effective at inhibiting H incorporation, with a 1.91 eV [0.97 eV] surface-to-subsurface diffusion barrier on the (1 1 0) surface [(1 0 0 surface)] and a 0.79 eV endothermicity to bulk dissolution, compared to a 1.02 eV [0.38 eV] barrier and 0.20 eV dissolution energy in pure Fe [37]. We therefore propose that a thin layer of Fe_3Si may provide protection against H embrittlement of the underlying steel.

Keywords: Density functional; Kinetics; Hydrogen absorption; Hydrogen diffusion; Iron alloys

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1. Introduction

Materials failure is a universal problem, especially for situations in which materials are exposed to high temperature, high pressure or corrosive environments. For example, steel is frequently degraded by dissociative adsorption of H-containing gases, such as H_2, H_2O, and H_2S, which produce adsorbed H atoms on the steel surface that subsequently penetrate into the bulk. Increased H concentration significantly alters the mechanical properties of steel, typically leading to hydrogen embrittlement (HE) and structural failure [1–5]. Hydrogen may become a practical clean fuel in the future and the potential use of steel in storage and distribution systems makes HE of these components a critical concern. Economic and safety concerns associated with mechanical failure prompt the development of new coatings to protect steel from such embrittlement, thereby increasing the service lifetimes of such materials.

Many research investigations have been aimed specifically at understanding how H affects the mechanical properties of iron and steel. Due to its high mobility in an array of host materials, H tends to diffuse quickly to regions of high tensile stress, becoming trapped near dislocation cores or microcracks [6,7]. As H builds up in these critical regions, the bulk mechanical properties change via various mechanisms [3]. In iron, a combination of H-enhanced decohesion (HED) [8–10] and H-enhanced localized plasticity (HELP) [11–13] are thought to operate in concert to embrittle Fe, leading to secondary phenomena such as crack propagation [14], intergranular fracture [15] and blistering [16].

Many experiments have provided meaningful insight into these corrosion mechanisms as well as the process of H uptake into bulk Fe. Dissociative adsorption of H on low-index Fe surfaces is exothermic [17–20]. Dissolution of H into tetrahedral interstitial sites in bulk Fe is sug-

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gested by indirect evidence [2]. Measurements of H diffusion through bulk Fe indicate high diffusivity, $\sim 1.0 \times 10^{-8}\ m^2\ s^{-1}$ at room temperature [21]. Due to recent interest in Fe–Al-based alloys, there have been several recent experimental and theoretical investigations aimed at understanding H behavior in these bulk alloys. H diffusivity in Fe_3Al [22,23] and Fe–40Al (40 at.% Al) [24] alloys is lower than in pure Fe, and electrochemical permeation techniques [25–28] found that H diffusivity in Fe–Al alloys decreases with increasing Al content. Previous density functional theory (DFT)–local density approximation (LDA) calculations predicted that H sits at tetrahedral sites in the bulk FeAl lattice [29]; more recent DFT calculations using the B3LYP exchange–correlation functional predicted that H sits at a displaced octahedral site [30]; however, the latter prediction should be viewed with caution since the B3LYP exchange–correlation functional introduces Hartree–Fock exchange which is not well-founded for metals [31].

Corrosion resistance for steel is typically achieved by applying a thin protective coating of, e.g., Zn or Cr. Although such surface treatments are effective under ambient conditions, they are not robust to chemical attack, high temperature and associated thermal cycling stresses in some environments. Galvanized steel (a Zn coating) is not stable at high temperatures and Cr coatings contain inherent microcracks formed upon initial electrodeposition. Corrosive gases easily penetrate the microcracks and degrade the Cr/Fe interface, eventually causing erosion of the coating and the steel [32]. A new coating is desired that possesses the thermal stability of a high melting point coating like Cr but one that also resists chemical corrosion.

Two interesting candidates to act as protective surface coatings are FeAl and Fe_3Si. These alloys are stable up to 1300 °C and form protective oxide scales in air. Additionally, Al and Si are not known to embrittle steel. In reducing environments, where an oxide scale might not be present, the alloy surfaces might be directly exposed to deleterious gases such as H_2S, e.g., in high-pressure oil recovery vessels or military tank guns. As a first step in determining whether such alloys might inhibit reactions with various corrosive gases, Jiang and Carter used periodic DFT within the generalized gradient approximation (GGA) to investigate the dissociation of H_2S and CO on FeAl, Fe_3Si and pure Fe surfaces [33–36]. They ultimately concluded that neither alloy would effectively inhibit dissociation of H_2S on its surfaces, which is of particular concern for the HE problem. Nevertheless, although dissociative chemisorption is not inhibited by these alloys, it is possible they could still act as protective coatings depending on how difficult it is for surface H to penetrate into the subsurface of these alloys.

Experiments and first-principles calculations of H in pure Fe offer another set of useful benchmarks. In ferromagnetic (FM) body-centered-cubic (bcc) iron, H diffusion occurs rapidly between tetrahedral sites [21,37]. Previous DFT–GGA calculations of H dissociation on Fe surfaces [37–39] found exothermic dissociative adsorption, endothermic absorption and significant energy barriers for surface-to-subsurface diffusion. Barriers are predicted to be smaller for diffusion from the subsurface to the next layer, and once H penetrates past the second layer, the diffusion barriers are similar to the very small values found in bulk Fe [39].

While H on Fe surfaces has been studied extensively, less information is available regarding H on Fe alloy surfaces. Thermal desorption experiments for deuterium on FeAl revealed two D_2 desorption peaks attributed to adsorbed D recombination at the surface ($\sim$500 K) and D release from trapping sites followed by surface recombination ($\sim$820 K) [40]. Experiments of H desorbing from $Fe_{0.6}Al_{0.4}$ were used to estimate H diffusivity in the alloy ($10^{-9}\ cm^2\ s^{-1}$) and the measured desorption peaks were similar to those for D_2 [24]. Recent DFT–GGA calculations using the projector augmented wave (PAW) method [41] predicted that H should readily dissociate on the surface of FeCo(1 1 0). H is predicted by DFT–GGA to preferentially adsorb on threefold hollow sites on both FeAl (1 1 0) and Fe_3Si (1 1 0) alloy surfaces [33], similar to low-energy electron diffraction (LEED) [42] measurements and DFT–GGA predictions [38] of the preferred adsorption site on pure Fe (1 1 0). By contrast, H is predicted to adsorb on top of Al or Si atoms on the FeAl (1 0 0) and Fe_3Si (1 0 0) alloy surfaces. This low coordination is quite different from the fourfold adsite preferred by H on pure Fe (1 0 0), as deduced from high-resolution electron energy loss spectroscopy (HREELS) [17] and predicted by DFT–GGA calculations [37].

In the present work, we investigate whether these Fe alloys can inhibit H uptake into the bulk material despite facile H adsorption onto their surfaces. Specifically, we use PAW–DFT–GGA to evaluate subsurface absorption energies and barriers/rate constants for surface-to-subsurface diffusion of hydrogen from FeAl and Fe_3Si surfaces, to assess the energetics and kinetics associated with the first step of H incorporation. Bulk dissolution energies and equilibrium constants, as well as barriers and associated rate constants for H diffusion through bulk alloys are then considered.

The organization of the paper is as follows. Section 2 provides calculational details for the results presented in Section 3. Section 4 offers a comparison of the predicted dissolution and diffusion behavior to analogous processes in pure Fe, in order to assess how use of these alloying elements in a possible surface pretreatment might affect H incorporation into steel. Our results, in conjunction with other work examining carbon interacting with the same alloys (D.F. Johnson and E.A. Carter, 2009, submitted), suggest that applying Fe_3Si as a protective coating should greatly inhibit uptake of both H and C in steel.

2. Calculational details

We perform Kohn–Sham DFT calculations within the Vienna Ab initio Simulation Package (VASP) [43,44].