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Short Communication

Effect of hydrogen on the surface energy of ferrite and austenite

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ABSTRACT

Calculations indicate that the introduction of hydrogen into the body-centred cubic and face-centred cubic allotropes of iron in both cases reduces the {100} surface energy. The reduction is rather small in magnitude so this mechanism cannot present the major cause of the well-known hydrogen embrittlement phenomenon. Consistent with the theory of grain boundary embrittlement in iron, carbon is confirmed to increase the surface energy, thereby rendering cleavage fracture less likely assuming that other factors governing fracture are maintained constant.

1. Motivation

The embrittlement that occurs when small concentrations of hydrogen are introduced into body-centred cubic iron was first noted in 1875 [1]. The mechanisms postulated to explain this phenomenon include the internal pressure theory [2] where diffusible hydrogen accumulates at critical defects, combines to form molecular hydrogen and the resulting pressure helps initiate fracture. The second may involve a reduction in the cohesive energy of iron, thus making it easier to cleave [3]. In the localised plasticity model, hydrogen promotes dislocation mobility and if this happens in a localised region then it can result in a shear instability which in turn stimulates further failure modes such as cleavage [4].

Recently, Takano [5] investigated the cohesive energy in cleavage fracture on the {100} (cleavage) planes of single crystal α-iron with hydrogen occupying octahedral interstices. The fracture in the method was simulated by monitoring the energy change as the displacement of a {100} surface relative to the underlying plane is increased. Decohesion is said to occur when the energy no longer changes with displacement. However, those calculations did not consider the lattice expansion due to the hydrogen addition into the octahedral interstices of ferrite; this can be seen from the fact that there was no increase in energy as the separation of {100} planes increased from 0 to 0.06 nm. So in this case, the energy reduction due to the hydrogen is overestimated. It was found that hydrogen reduced the cohesive energy, with the conclusion that it therefore assists crack initiation.

It is important to assess this conclusion again, taking account of the issues highlighted above, and in addition, accounting for the fact that hydrogen can occupy both the tetrahedral and octahedral interstices. The calculations have been conducted for austenite in addition to ferrite in order to provide a basis for comparison, and the role of carbon in influencing the surface energy is also examined. In the present work, the calculations were carried out for the case of hydrogen atoms; molecular hydrogen is not addressed, and neither is intergranular failure, which has been the subject of previous investigations [6 for example].

2. Calculation procedure

Density functional theory (DFT) [7,8] calculations were carried out with the Vienna ab initio simulation package commonly referred to as VASP [9–11] using the projector augmented wave basis set [12] and the generalized gradient approximation (GGA) of the Perdew, Burke, and Ernzerhof (PBE) form for electron exchange and correlation [13]. An energy cutoff of 450 eV was used for all calculations.

The ferrite was simulated using a $2 \times 2 \times 4$ supercell of conventional body-centred cubic structure with $6 \times 6 \times 3$ *k*-point sampling. For the austenite the supercell was $2 \times 2 \times 4$ of the conventional face-centred cubic structure with $8 \times 8 \times 4$ *k*-point sampling. Spin-polarised calculations were performed for ferrite and non-spin-polarised calculations in the case of austenite. Both cell shape and atomic positions were allowed to relax for bulk calculations. Lattice parameters of 2.84 and 3.45 Å were obtained with ferrite and austenite, respectively. The reference hydrogen was assumed to be an H_2 molecule and the total energy of the hydrogen molecule was calculated by putting H_2 in a cubic box

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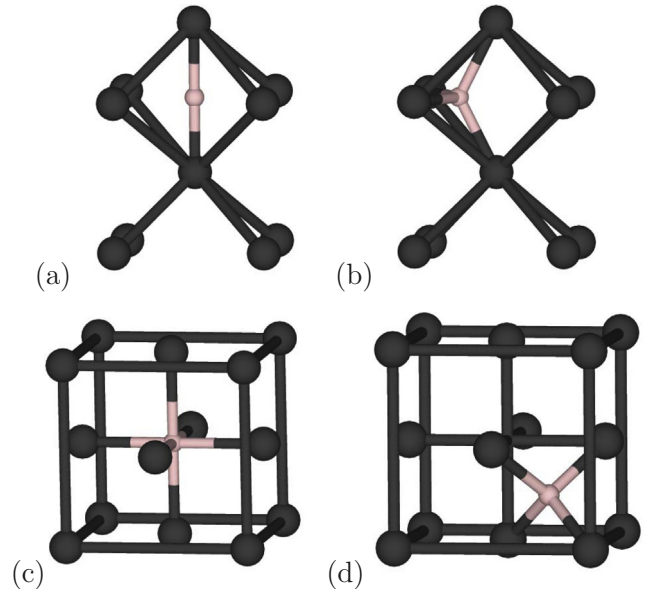

Fig. 1. Atomic structure for dissolution of hydrogen in (a) ferrite, octahedral (b) ferrite, tetrahedral (c) austenite, octahedral and (d) austenite, tetrahedral site, respectively.

Table 1
Dissolution energy of hydrogen (eV) in ferromagnetic ferrite and non-magnetic austenite. The values in parenthesis are zero point energy corrected values.

Phase	Sites	Present work	Published calculated data	Measured data
Ferrite	Octahedral	0.34	0.32 [15], 0.34 [16]	–
	Tetrahedral	0.19	0.19 (0.30) [15], 0.21 (0.30) [16]	0.30
Austenite	Octahedral	0.07	–	0.28
	Tetrahedral	0.51	–	–

Table 2
Dissolution energy (eV) of hydrogen in ferrite and austenite as a function of the separation of two H atoms in units of the number of separating (100) planes.

Phase	Single H atom	0 Layer	1 Layer	3 Layers
Ferrite	0.19	0.24	0.20	0.19
Austenite	0.07	0.11	0.09	0.07

with 10 Å sides and carrying out a Γ-point calculation. A bond length of 0.75 Å was obtained for H_2.

For modelling the surface, the lattice parameters obtained from relaxed bulk Fe_n and Fe_nH were fixed and then the thickness of 0.2–10 Å vacuum layer was inserted. Only the atoms located in the top

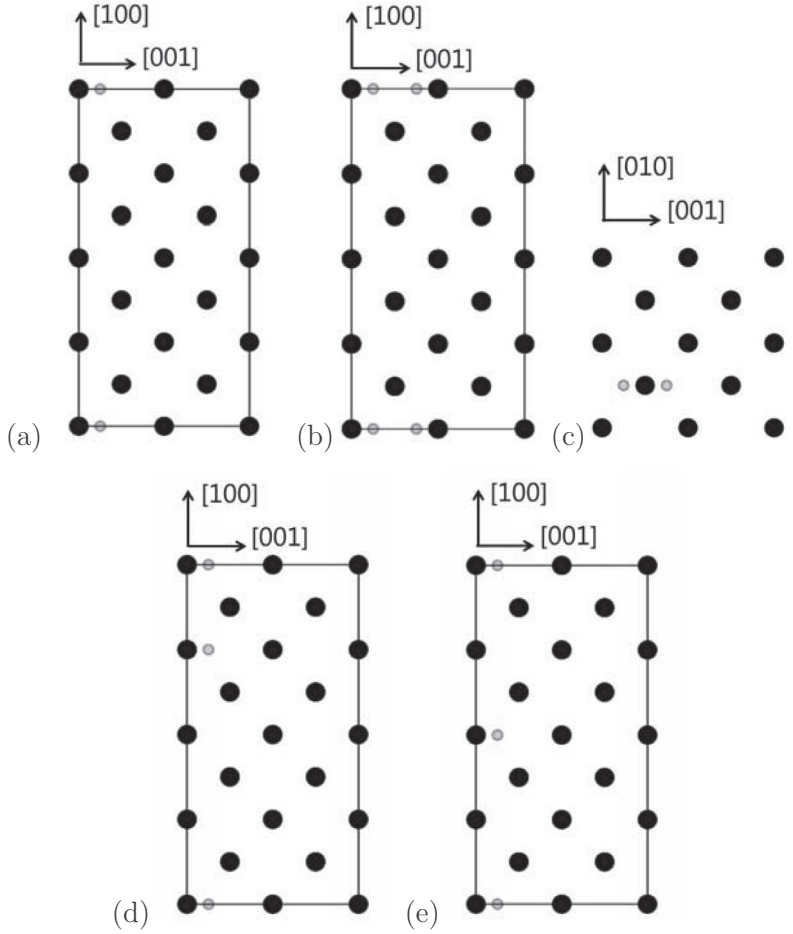

Fig. 2. Atomic structures for H–H interaction with different intermediate layers in ferrite (a) an atom, (b) two atoms with less than 1 intermediate layer (indicated as 0 intermediate layer in Table 2), (c) hydrogen configuration on (100) in the system (b), (d) 1 intermediate layer and (e) 3 intermediate layers.