Modelling Hydrogen-Dislocation Interactions With the Tight Binding Approximation

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Introduction

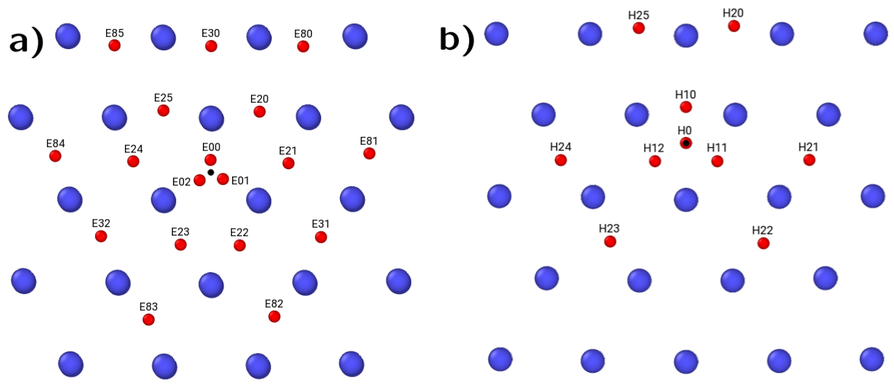
Hydrogen embrittlement is an umbrella term referring to the deleterious effects of hydrogen in the lattice, resulting in degradation of mechanical properties such as strength, ductility and toughness. One mechanism that is commonly proposed is the defactant concept[1]: it is based on a thermodynamic consideration of the segregation of solutes to defects, resulting in a reduction of the defect formation energy. This is particularly important when considering plasticity in BCC materials at finite temperatures and low stresses, which is primarily dependent on the screw component of dislocations, and the mobility of screw dislocations will be mediated by the thermal activation of kink-pairs. With increasing hydrogen concentration this theory predicts that the effect in BCC metals will first be macroscopic softening, as the hydrogen reduces the kink-pair formation energy, and then hardening, as the excess concentration of hydrogen results in drag on the migrating kinks.

The goal of the present work was to investigate the changing interaction between hydrogen atoms and screw dislocations in iron with applied tensile and compressive strain, in order to approximate the high local stress fields surrounding a crack-tip. This data will form input for a future kinetic Monte Carlo model of screw dislocation motion in the presence of hydrogen, in order to model the effect of hydrogen in the region where failure is most likely to occur.

Hydrogen Binding Energy

The binding energies of hydrogen to several of the trap sites surrounding a screw dislocation were calculated for isolated dislocations of hard and easy core configuration. This is calculated as the difference in dissolution energies between each site and a bulk tetrahedral site, including a correction for the zero point energy (ZPE). Results are shown in the table, the figures in brackets are the equivalent binding energies calculated with GGA-DFT by Itakura *et al.*[2]

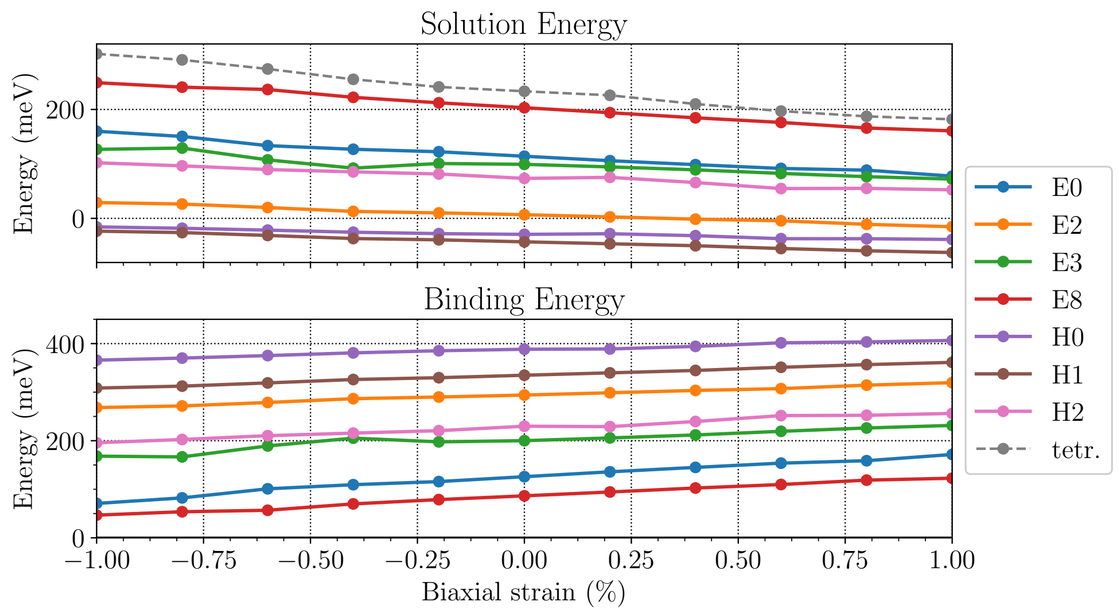
$$E_s = E_{d+nH} - E_d - \frac{n}{2}E_{H_2}$$



Site	E_b (meV)
E0	126 (99)
E2	294 (256)
E3	200 (201)
E8	86 (77)
H0	388 (390)
H1	335 (322)
H2	230 (189)

Application of Strain

The cells were then strained incrementally, in units of 0.1%, with biaxial tension and compression in the plane normal to the dislocation line. The solution energies and ZPE corrections were recalculated at each applied strain.



The concentration of hydrogen in a site of binding energy E_b at temperature T with bulk concentration C_0 may be estimated from McLean's isotherm:

$$C_b = \frac{(C_0/3)\exp(E_b/k_BT)}{1 + (C_0/3)\exp(E_b/k_BT)}$$

Estimating the Effect on Kink Mobility

Hydrogen in the E2 site behind the dislocation line will be moved relative to the dislocation core into the weaker E8 site when a kink passes by, defining a stress-dependent trap energy $E_t(\sigma)$ from the change in binding energy. The average velocity at which kinks travel past hydrogen may be estimated from the rate at which kinks escape these traps:

$$P_H = f_k \exp\left(-\frac{E_t(\sigma)}{k_BT}\right)$$

but this must be modified by the chance for the kink to jump back into the trap, which may be estimated from the forward and backward jump frequencies of the kink from the position immediately after the hydrogen trap[3]:

$$J_k^+ = f_k \exp\left(\frac{\sigma b^2 h}{k_BT}\right) \qquad J_k^- = f_k \exp\left(\frac{E_t(\sigma) - \sigma b^2 h}{k_BT}\right)$$

$$P_H^+ = P_H \frac{J_k^+}{J_k^+ + J_k^-}$$

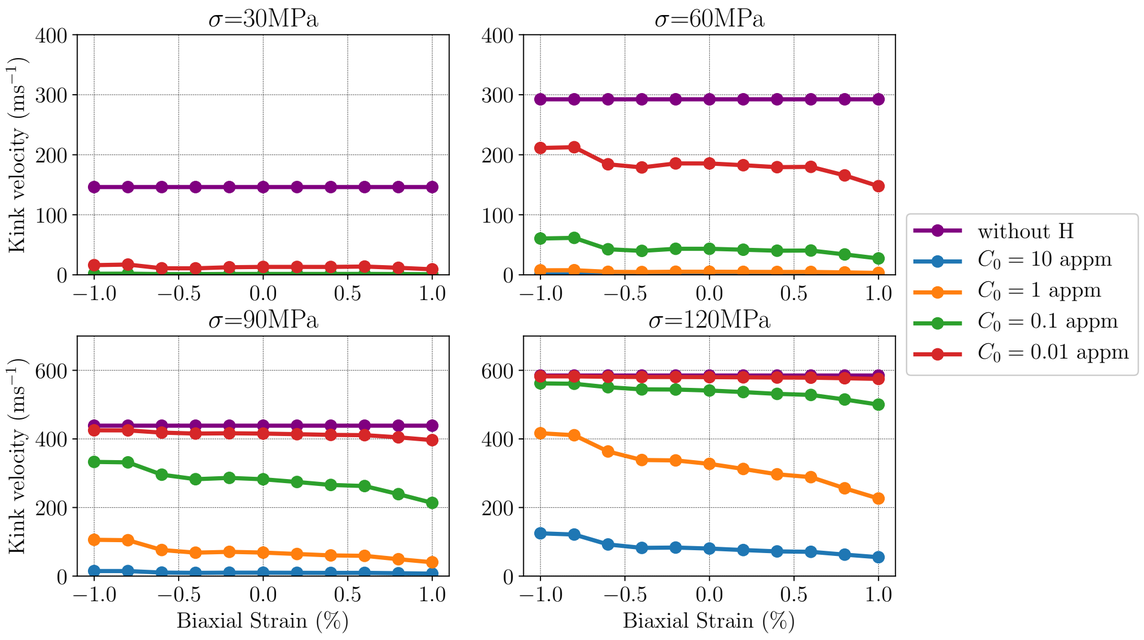
Where f_k represents the attempt frequency, b the Burgers vector and h the kink height. Finally this may be employed to obtain the hydrogen-bypass velocity. Kink velocity v_k without hydrogen will be dependent on the phonon drag, which may be represented with a fitted coefficient $B_k(T)$. Together they yield an estimate for the hydrogen-reduced kink velocity:

$$v_k^H = \frac{\sigma b h}{k_BT} b^2 P_H^+ \qquad v_k = \frac{\sigma b}{B_k(T)}$$

$$v_k' = C_b v_k^H + (1 - C_b) v_k$$

Kink Velocities

The resultant kink velocities at 300K for several applied stresses and hydrogen bulk concentrations, across the range of strain, are shown below.



However, unless kink movement and annihilation is the rate-limiting step for dislocation movement, kink velocity will not directly determine the screw dislocation mobility. Kink-pair formation is a rare event, and newly nucleated pair will frequently come together and annihilate. A hardening effect that may be more likely is the formation of pinning-points on the screw dislocations by the collision of kinks on different glide planes. This event will become more likely as the kink-pair nucleation rate is enhanced and the kink velocity reduced.

Pinning-Point Formation

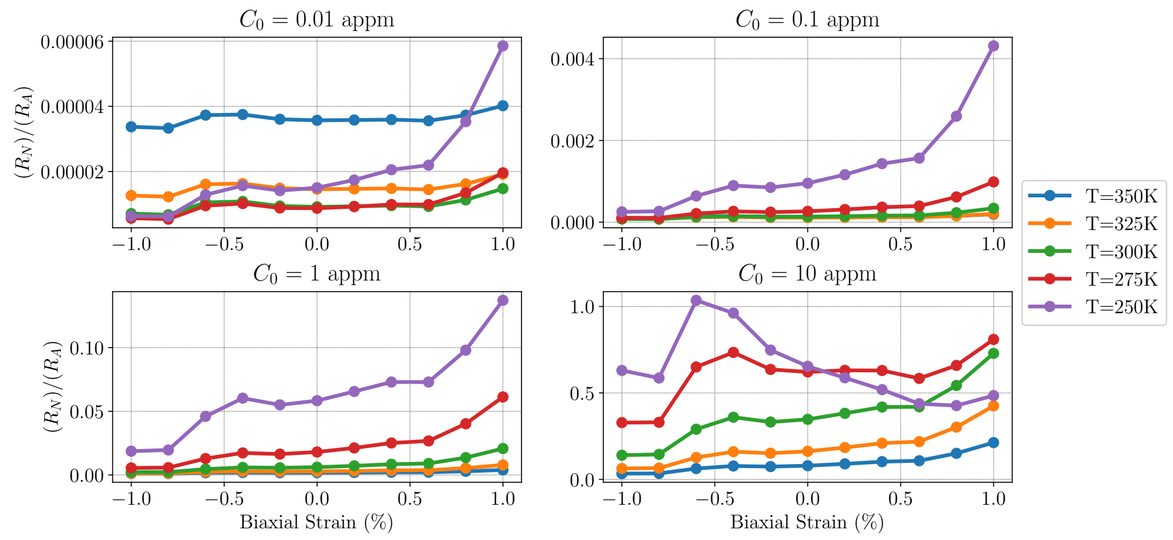
The rate of kink-pair nucleation without hydrogen may be estimated from the dislocation length N_d, the formation enthalpy E_k and an attempt frequency D_d, chosen to reproduce experimental results.

$$R_N = D_d N_d \exp\left(-\frac{E_k}{k_BT}\right)$$

Hydrogen in the binding site front of a nucleating kink-pair will reduce the enthalpy by ΔE_k, leading to an enhancement of this rate by a factor F_N:

$$F_N = 1 + C_b W_k \{\exp(\Delta E_k / K_BT) - 1\}$$

A rough estimate of the chance of pinning-point formation may then be calculated as the enhanced nucleation rate over the rate at which the kinks travel the dislocation line R_A.



References

[1] Kirchheim, Reiner. "Solid solution softening and hardening by mobile solute atoms with special focus on hydrogen." Scripta Materialia 67.9 (2012): 767-770.

[2] Itakura, M., et al. "The effect of hydrogen atoms on the screw dislocation mobility in bcc iron: A first-principles study." Acta Materialia 61.18 (2013): 6857-6867.

[3] Katzarov, Ivaylo H., Dimitar L. Pashov, and Anthony T. Paxton. "Hydrogen embrittlement I. Analysis of hydrogen-enhanced localized plasticity: Effect of hydrogen on the velocity of screw dislocations in α-Fe." Physical Review Materials 1.3 (2017): 033602.

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