

Semiempirical, Quantum Mechanical Calculation of Hydrogen Embrittlement in Metals

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A new, semiempirical model of metals and impurities (embedded atom method) makes possible a static treatment of the brittle fracture of a transition metal in the presence of hydrogen. Results indicate that hydrogen can reduce the fracture stress in nickel.

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The ability of hydrogen to alter the mechanical properties of metals to the point of rendering them unreliable is an outstanding technological problem.¹⁻³ One mode of degradation is hydrogen-assisted cracking, in which crack initiation and propagation are controlled by a combination of stress and the presence of hydrogen. There is a relationship between the requisite stress and hydrogen concentration: More hydrogen can reduce the failure stress. Some models of this effect propose that fracture occurs by brittle means, others propose that plastic processes involving dislocations are dominant. A fundamental understanding of the atomistic processes involved in hydrogen embrittlement has been impossible, largely because of difficulties in the theory of such complicated systems. Even with modern computers, *ab initio* techniques are incapable of handling the large numbers of atoms required to represent fracture. Even the capacity of one-electron methods⁴ falls far short of the number of atoms required to simulate fracture. The use of a pairwise interaction greatly increases the number of atoms that can be treated,^{5,6} but requires a volume-dependent term to represent the bulk compressibility of the electron gas.⁷ Volume dependence restricts the use of pair potentials to situations where the volume is definable; it is not during fracture. The theoretical investigation of hydrogen embrittlement requires a new approach.

We report here a static calculation of the brittle fracture of a transition metal in the presence of hydrogen. The calculation is made possible by the development of a new model of metals and impurities. We find that hydrogen can cause decohesion of the metal bonds in nickel in the absence of plasticity. We do not yet know what will be the interaction between the plasticity and the hydrogen.

The quasiautom theory^{8,9} has been used successfully to calculate the characteristics of hydrogen in metals.¹⁰ We generalize that theory to treat

all atoms in a unified way. We call this scheme the embedded atom method, because it views each atom as embedded in a host lattice consisting of all other atoms. Such a view permits calculations employing an electron density, which is always definable, and allows realistic treatment of impurities in structures that include cracks and surfaces. The generalized method is not significantly more complicated to use than pair potentials, and yet is capable of describing more complex situations, such as hydrogen embrittlement.

Solution of the Schrödinger equation yields the electron density established by a given potential, and the energy is a functional of that potential. Hohenberg and Kohn¹¹ show the converse: that the energy is a functional of the density, and the potential is determined to within an additive constant by its electron density. Stott and Zaremba⁸ proved a useful corollary, that the energy of an impurity in a host is a functional of the electron density of the unperturbed (i.e., without impurity) host. That is, $E = \mathcal{F}_{Z,R}[\rho_H]$, where $\rho_H(r)$ is the unperturbed host electron density, and Z and R are the type and position of the impurity. The Stott-Zaremba corollary is to be distinguished from the Hohenberg-Kohn theorem, which states that the total energy is a functional of the total electron density. Rather, the new statement is that the embedding energy of an impurity is determined by the electron density of the host before the impurity is added. We make use of this by viewing each atom in a system as an impurity in the host consisting of all other atoms.

The functional \mathcal{F} is universal, independent of host. Its form is unknown, and probably complicated. A simple approximation would be to assume that the embedding energy depends only on the environment immediately around the impurity,⁹ or equivalently that the impurity experiences a locally uniform electron density.⁸ This can be viewed either as a local approximation, or as the lowest-order term involving successive

TABLE I. Quantities used for determination of the functions and their fitted values: lattice parameter a_0 ; elastic constants C_{11} , C_{12} , and C_{44} ; sublimation energy E_s ; vacancy formation energy E_{1V}^F ; the energy difference between bcc and fcc phases for Ni; and the hydrogen heat of solution and migration energy in Ni.

| | Experiment | Fit |
|--|--------------------|-------|
| a_0 (Å) | 3.52 ^a | 3.52 |
| C_{11} (10^{12} dynes/cm ²) | 2.465 ^b | 2.452 |
| C_{12} (10^{12} dynes/cm ²) | 1.473 ^b | 1.452 |
| C_{44} (10^{12} dynes/cm ²) | 1.247 ^b | 1.233 |
| E_s (eV) | 4.45 ^c | 4.45 |
| E_{1V}^F (eV) | 1.4 ^d | 1.43 |
| $(E_{\text{bcc}} - E_{\text{fcc}})$ (eV) | 0.06 ^e | 0.14 |
| H heat of solution (eV) | 0.16 ^f | 0.22 |
| H migration energy (eV) | 0.41 ^g | 0.41 |

^aRef. 13.

^bRef. 14.

^cRef. 15.

^dRef. 16.

^eRef. 17.

^fRef. 18.

^gRef. 19.

gradients of the density. Then the functional \mathfrak{F} is approximated by a function of the electron density at the impurity site plus an electrostatic interaction, and the energy is $E = F_i(\rho_i(R_i))$

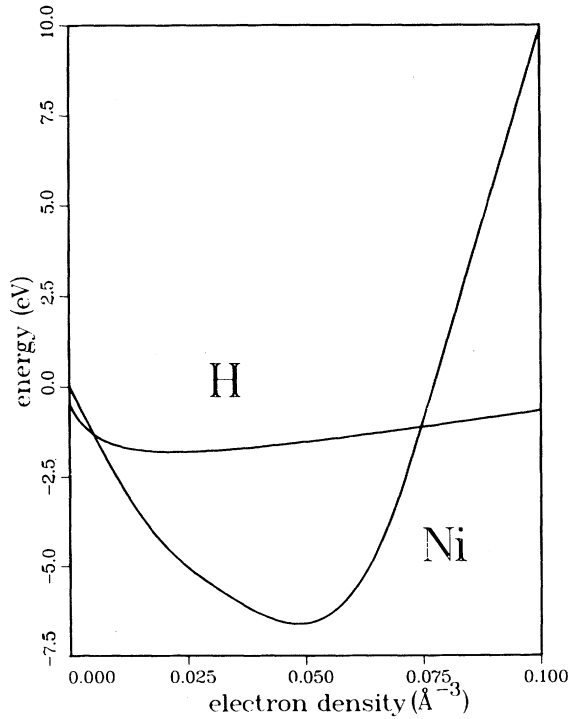


FIG. 1. Embedding energies of H and Ni as functions of background electron density. The function for H is taken from Ref. 20. That for Ni is deduced in this work.

$+\frac{1}{2}\sum_j\varphi(R_{ij})$, where ρ_i is the electron density of the host without atom i , and φ is a short-range electrostatic pair potential. The total energy is a sum over all individual contributions:

$$E_{\text{tot}} = \sum_i F_i(\rho_i(R_i)) + \frac{1}{2} \sum_{i,j} \varphi(R_{ij}). \quad (1)$$

Corrections can be included for involving gradients of the density⁸; these do not modify the form of Eq. (1).⁹ We make a further simplification by assuming that the electron density is given by a linear superposition of the electron densities of the constituent atoms.¹²

Ground-state properties of the solid can be calculated from Eq. (1) in a straightforward way. But because the functions F and φ are not known in general, we have used experimental data, listed in Table I, to determine the functions, shown in Figs. 1 and 2. (We found that both functions F and φ are required to fit the elastic properties, such as the Cauchy discrepancy.) The function $F(\rho)$ for hydrogen was taken from electron gas computations by Puska, Nieminen, and Manninen.²⁰ The $\varphi(r)$ for H-Ni was established by using the experimental heat of solution and the migration energy of H in Ni. $\varphi_{\text{H-H}}$ was next fixed by assuming that $\varphi_{\text{H-Ni}}$ was the geometrical mean of $\varphi_{\text{H-H}}$ and $\varphi_{\text{Ni-Ni}}$.

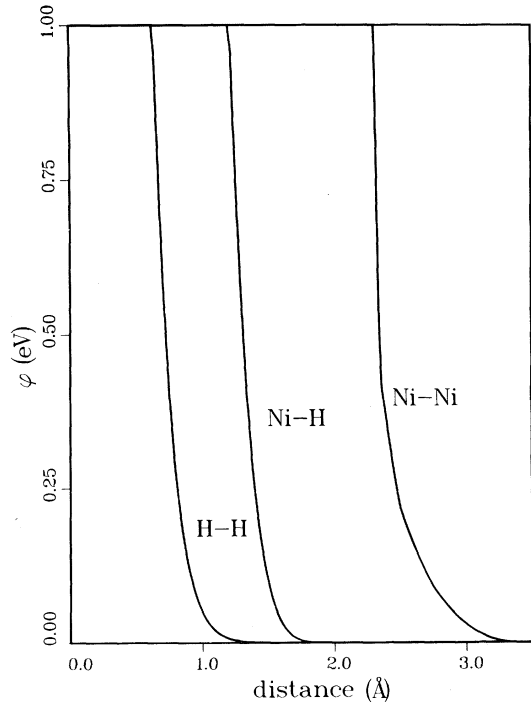


FIG. 2. Short-ranged electrostatic pair potentials for Ni-Ni, Ni-H, and H-H.

We use Eq. (1) to calculate the energy of a semi-infinite slab of Ni, illustrated in Fig. 3. The slab is 17 layers thick in the $[111]$ direction, with a free surface on each side. Periodic bounds are imposed in the $[1\bar{1}0]$ and $[11\bar{2}]$ directions. The unit cell consists of four primitive cells of the slab, so that there are eight atoms in each of the layers and a total of 136 atoms in the unit cell. The total energy is minimized with respect to the coordinates of all atoms while enforcing the periodic bounds. External stresses are applied to the free surfaces, resulting in an expansion of the lattice along the $[111]$ direction. For small external stresses, the slab expands to minimize the energy, and the strain calculated with the present method agrees with the one computed from continuum elasticity theory. This agreement is to be expected because the functions in Eq. (1) are established by fitting to the elastic constants of the solid. The perfect crystal re-

sponds to increased stress by further expansion because there is nothing to break the symmetry of the lattice. However, any defects or perturbations in the lattice will cause the slab to break in response to a critical applied stress, creating two additional (111) surfaces in the center. Specifically, we model cracks by removing four of the eight atoms in the center layer of the unit cell, as shown in Fig. 3(a). These four vacancies are mapped by the periodic bounds into an array of cracks in the midplane and oriented along the $[11\bar{2}]$ direction.

We found that a stress of $0.13 \text{ eV}/\text{\AA}^3$ applied to the external surfaces is sufficient to cause the slab with four vacancies to break apart at the midplane, the vacancies serving as a nucleation site. However, a stress of $0.11 \text{ eV}/\text{\AA}^3$ or less is insufficient to cause cracking, as shown in Fig. 3(a). Here the lattice expands slightly, with some small amount of bowing in the structure around the vacancies. Thus the largest stress that the lattice can provide in resistance to the applied stress is about $0.13 \text{ eV}/\text{\AA}^3$. We calculate the binding energy of hydrogen to the interstitial sites next to the midplane (there are four inequivalent sites) and find that the hydrogen is bound to these sites relative to the bulk by $0.01\text{--}0.35 \text{ eV}$, depending on site and applied stress. It is plausible therefore to suggest that the hydrogen makes its way to the midplane and binds there. Furthermore, when a hydrogen atom occupies any interstitial site adjacent to the midplane of the slab, we find that the stress that could not break the slab ($0.11 \text{ eV}/\text{\AA}^3$) becomes sufficient to do so, as seen in Fig. 3(b). [We repeat that the present calculations are not dynamic. The configuration in Fig. 3(a) is at a minimum in the energy, but Fig. 3(b) is an intermediate configuration that has not converged. Further iterations change Fig. 3(b) by separating the two halves completely.] Thus we have shown that a single hydrogen atom per unit cell can weaken the metallic bonds between the halves of the slab enough to lower the fracture stress by 15%.

We have observed also that a higher hydrogen concentration near the crack results in a further lowering of the fracture stress. Eight hydrogen atoms in the bridge can lower the critical breaking stress to less than $0.09 \text{ eV}/\text{\AA}^3$, a 30% reduction. Hydrogen therefore reduces the resistive force that the lattice can give in response to applied stresses.

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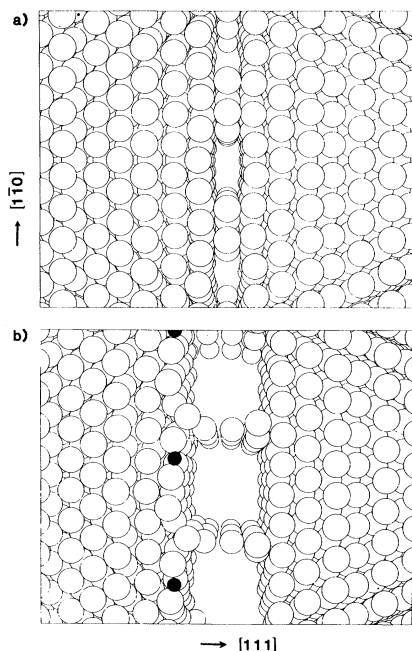


FIG. 3. Cross-sectional views of a Ni slab with defects, showing the effects of hydrogen and stress. Crystallographic directions are indicated. Open circles represent Ni atoms. Three unit cells in the vertical direction are shown, and three in the direction perpendicular to the page. (a) Four Ni atoms in each cell have been removed from the midplane and an artificial stress of $0.11 \text{ eV}/\text{\AA}^3$ applied to the outer surfaces. No fracture occurs. (b) Same slab with the addition of one H atom (solid circles) per unit cell. The energy in (b) is not converged, and further iterations show the halves to be completely separated.

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