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Editor's Choice

Interatomic Fe-H potential for irradiation and embrittlement simulations

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ABSTRACT

The behavior of hydrogen in iron and iron alloys is of interest in many fields of physics and materials science. To enable large-scale molecular dynamics simulations of systems with Fe-H interactions, we develop, based on density-functional theory calculations, an interatomic Fe-H potential in the Tersoff–Brenner formalism. The obtained analytical potential is suitable for simulations of H in bulk Fe as well as for modeling small FeH molecules, and it can be directly combined with our previously constructed potential for the stainless steel Fe–Cr–C system. This will allow simulations of, e.g., hydrocarbon molecule chemistry on steel surfaces. In the current work, we apply the potential to simulating hydrogen-induced embrittlement in monocrystalline bulk Fe and in an Fe bicrystal with a grain boundary. In both cases, hydrogen is found to soften the material.

1. Introduction

Hydrogen, although not soluble in iron in equilibrium, can be introduced into it by irradiation, nuclear decay, or chemical processes. Hydrogen is well known to cause embrittlement in iron and steel [1–8], which is a serious issue in, e.g., the automotive and nuclear industries. In the former, the high mechanical resistance desired from the body steels must often be traded off against their increased susceptibility to hydrogen embrittlement [9–12], while the nuclear processes in the latter will, on long time scales, induce hydrogen buildup in the reactor steels [13–16]. Moreover, the recent changes in the design of the ITER fusion reactor are to render some of its steel components directly exposed to the fusion plasma [17], making it important to study how the energetic H isotopes escaping from the plasma interact with Fe.

Atomic-level molecular dynamics (MD) simulations have proven to be a good tool for examining irradiation effects [18,19], mechanical properties of materials [20–22], and plasma–wall interactions [23,24]. The key physical input for MD is the interatomic potential. Since steels by definition contain Fe and C [25], simulations of H effects in steels require, at a minimum, a potential that can describe all interactions in the ternary Fe–C–H system.

In this work, we develop a potential for Fe-H interactions in the same reactive Tersoff–Brenner formalism [26–28] we used previously to construct a potential for the stainless steel Fe–Cr–C system [29]. The potential is fitted to a database of properties of FeH molecules and H in bulk Fe, obtained from literature and our own density functional theory (DFT) calculations. By using already available C–H parameters [27,30], the potentials can be directly combined to model the entire ternary Fe–C–H system. The potential allows simulating H in bulk Fe as well as ion irradiation and chemical reactivity of H at Fe and Fe–C surfaces. We demonstrate its use in simulating hydrogen-induced softening in bulk Fe and in Fe grain boundaries.

Fe-H potentials have been already devised using the embedded-atom method [31,32]. However, its associated functional form cannot realistically describe the C–H bonding chemistry [27]. Since our aim is to obtain a potential for the entire Fe–C–H system, we choose to develop the Fe-H potential in the Tersoff–Brenner formalism which allows combining the Fe-H part with both Fe and C interactions, similar to what was done earlier for the W–C–H system [30].

The remainder of this article is organized as follows. In Section 2, we summarize the Tersoff–Brenner potential formalism and describe our fitting procedure. Section 3 presents the obtained Fe-H potential and evaluates its performance against experimental

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and *ab initio* data. In Section 4, we employ the potential in tensile-test simulations of hydrogen-containing iron. We discuss the implications and limitations of the study in Section 5. Finally, Section 6 concludes the article with a brief summary.

2. Potential formalism and fitting procedure

The reactive Tersoff–Brenner formalism [26–28] used in this work originates from the concept of bond order proposed by Pauling [33], and it has been shown [34] to resemble both the tight-binding scheme [35] and the embedded-atom method [36,37]. Since the formalism has been described extensively elsewhere [34,38,39], we will give here only a brief overview.

The total cohesive energy E_c of the system is written as a sum of individual bond energies:

$$E_c = \sum_{i<j} \sum f^c_{ij}(r_{ij}) \left[V^R_{ij}(r_{ij}) - \frac{b_{ij}+b_{ji}}{2} V^A_{ij}(r_{ij}) \right], \tag{1}$$

where r_{ij} is the distance between atoms i and j, f^c is a cutoff function for the pair interaction, V^R is a repulsive and V^A an attractive pair potential, and b_{ij} is a bond-order term that describes three-body interactions and angularity. The pair potentials are of the Morse-like form

$$V^R_{ij}(r) = \frac{D_{0,ij}}{S_{ij}-1} \exp\left[-\sqrt{2S_{ij}}\beta_{ij}(r - r_{0,ij}) \right], \tag{2}$$

$$V^A_{ij}(r) = \frac{S_{ij}D_{0,ij}}{S_{ij}-1} \exp\left[-\frac{\sqrt{2}\beta_{ij}}{\sqrt{S_{ij}}}(r - r_{0,ij}) \right], \tag{3}$$

where D_0 and r_0 are the bond energy and length of the dimer molecule, respectively. The parameter β is related to the ground-state vibrational frequency ω and the reduced mass μ of the dimer according to

$$\beta_{ij} = \frac{\sqrt{2\mu_{ij}}\pi\omega_{ij}}{\sqrt{D_{0,ij}}}. \tag{4}$$

The bond-order term is given by

$$b_{ij} = \frac{1}{\sqrt{1+\chi_{ij}}}, \tag{5}$$

where

$$\chi_{ij} = \sum_{k(\neq i,j)} f^c_{ij}(r_{ij}) g_{ik}(\theta_{ijk}) \exp\left[\alpha_{ijk}(r_{ij} - r_{ik}) \right]. \tag{6}$$

Here θ_{ijk} is the angle between the vectors $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{r}_{ik}$, and the angular function is defined as

$$g_{ik}(\theta_{ijk}) = \gamma_{ik}\left[1 + \frac{c^2_{ik}}{d^2_{ik}} - \frac{c^2_{ik}}{d^2_{ik} + (h_{ik} + \cos\theta_{ijk})^2} \right], \tag{7}$$

where γ, c, d, and h are adjustable parameters. The range of the interaction is restricted to the next-neighbor sphere by the cutoff function

$$f^c_{ij}(r) = \begin{cases} 1, & r \leqslant R_{ij} - D_{ij}, \\ \frac{1}{2} - \frac{1}{2}\sin\frac{\pi(r - R_{ij})}{2D_{ij}}, & |r - R_{ij}| \leqslant D_{ij}, \\ 0, & r \geqslant R_{ij} + D_{ij}, \end{cases} \tag{8}$$

where R and D determine the locus and width of the cutoff interval.

If the analytical potential is used for modeling nonequilibrium phenomena involving short-distance interactions, such as high-energy particle irradiation processes or melting, the short-range part of the potential must be adjusted to include a strong repulsive core that follows, i.a., from the Coulomb repulsion between the positively charged nuclei. To this end, the potential is modified in the manner already used for other Tersoff-like many-body potentials [34,40]: The total potential V_{tot} is constructed by joining the universal Ziegler–Biersack–Littmark potential V_{ZBL} [41] with the equilibirium potential V_{eq} using

$$V_{tot}(r) = V_{ZBL}(r)[1 - F(r)] + V_{eq}(r)F(r), \tag{9}$$

where V_{eq} is the potential implied by Eq. (1) and F is the Fermi function $F(r) = \{1 + \exp[-b_F(r - r_F)]\}^{-1}$. The values of the parameters b_F and r_F are chosen manually such that the potential is essentially unmodified at equilibrium and longer bonding distances and that a smooth fit at short separations with no spurious minima is obtained for all realistic coordination numbers.

In order to devise a well-performing Fe-H potential in the Tersoff–Brenner formalism, we use the following fitting procedure: The parameter sets for the H–H and Fe–Fe interactions are taken unchanged from Refs. [27,42], respectively, so that only the parameter set for the Fe-H interactions is fitted. From the outset, we fix the parameters pertaining to the properties of the dimer FeH—i.e., D_0, r_0, and β—according to their experimentally observed values. To avoid unwanted side effects, we set the three-index parameters α_{ijk} to zero. The values of the remaining seven parameters (S, γ, c, d, h, R, and D) are then fitted to a structural database comprising the molecules FeH_2 and FeH_3, the stoichiometric FeH with the rock-salt crystal structure, and the energies of the lowest-lying hydrogen point defects in body-centered cubic (bcc) iron. The fitting is formulated as a nonlinear least-squares minimization problem, which we solve using the trust-region-reflective algorithm [43–45] implemented in MATLAB [46].

3. Obtained potential

The optimized parameter values for the analytical Fe-H potential are given in Table 1. We also show the parameter values used for the H–H and Fe–Fe potentials; it should be noted, however, that during the fitting process, H–H and Fe–Fe interactions play a role only in the evaluation of the hydrogen point-defect energies.

Table 2 presents the fitting database together with the results from the analytical potential. The potential exactly reproduces the experimentally observed dimer properties that are also in good agreement with all the *ab initio* calculations. For the linear trimer FeH_2, the experimentally measured bond lengths in Refs. [47,48] are, respectively, 1.1% and 2.1% greater than the analytical prediction, while differing from each other by roughly the same relative amount. The analytical potential yields a bond length for the trigonal planar FeH_3 molecule that falls between the values given by the different *ab initio* calculations. The lattice constant a, bulk mod-

Table 1
Tersoff–Brenner parameters [Eqs. (1)–(9)] for the Fe-H system. The H–H potential is taken from Ref. [27] and the Fe–Fe potential from Ref. [42]; the Fe-H potential is derived in this work. The parameters α_{ijk} are zero in all cases. In Section 4, we use $R = 3.5$ Å for the Fe–Fe interactions instead of 3.15 Å.

		H–H	Fe–Fe	Fe-H
D_0	(eV)	4.7509	1.5	1.630
r_0	(Å)	0.7414	2.29	1.589
β	(1/Å)	1.9436	1.4	1.875
S		2.3432	2.0693	4.000
γ		12.33	0.01158	0.01332
c		0.0	1.2899	424.5
d		1.0	0.3413	7.282
h		1.0	−0.26	−0.1091
R	(Å)	1.40	3.15	2.497
D	(Å)	0.30	0.2	0.1996
b_F	(1/Å)	15.0	2.9	16.0
r_F	(Å)	0.35	0.95	1.0