THE EFFECT OF INTERSTITIAL N ON GRAIN BOUNDARY COHESIVE STRENGTH IN Fe

Miyoung Kim[1], Clint B. Geller[2], and A. J. Freeman[1]
[1]Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208
[2]Bechtel Bettis, Inc., West Mifflin, PA 15122

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[1]Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208
[2]Bechtel Bettis Laboratory. West Mifflin, PA 15122

Keywords: Ab-inito calculation; Grain Boundaries; Embrittlement; Composition Fe steel; FLAPW

Abstract

The effect of interstitial N on the cohesion of an Fe Σ3[110](111) grain boundary (GB) was investigated by ab-initio electronic structure calculations to reveal that free interstitial N produces a large strengthening energy, reduces the magnetic moments of the GB Fe atoms and is embrittling at the GB's.

Introduction

Increased nitrogen levels have been correlated with decreased ductility and elevated ductile-to-brittle transition temperature in pressure vessel steels [1]. However, the exact role played by nitrogen in the embrittlement of steels remains unclear. Miller and Burke have reported atom probe ion microscopy findings from neutron-irradiated low-alloy pressure vessel steel showing the presence of a 1 to 2 ruonolayer thick film of Mo, N, and C at prior austenitic grain boundaries (GB's) [2], suggesting a role for nitrogen as an intergranular embrittler. It is of interest for the development of mitigation strategies whether nitrogen must combine with other impurities to form nitride precipitates in order to exert an embrittling effect. Briant et al [1] have associated the embrittling effect of N in steels exclusively with intergranular nitride formation. This association suggests that high nitrogen levels may be acceptable if nitride precipitation at grain boundaries is suppressed. To address whether precipitate formation is indeed essential to the N embrittlement process in pressure vessel steel, a computational study was undertaken to ascertain whether the presence of interstitial nitrogen alone could embrittle an Fe GB. If so, nitrogen in any form must be kept completely away from the grain boundaries, if not out of the material altogether.

Computational Method

The theoretical basis for the present study is due to Rice and Wang [3]. In this thermodynamic theory, a quantity called the "strengthening energy," ΔE_{SE}, is defined, that is the amount of energy per unit area of GB by which the work required to separate the GB into free surfaces is changed by the presence of an impurity. ΔE_{SE} is evaluated via Equations 1,2 and 3:

$$\text{Eq.1} \quad \Delta E_{SE} = \Delta E_b - \Delta E_{s,}$$

$$\text{Eq.2} \quad \Delta E_b = E(GB) - E(I/GB) + E(I)$$

$$\text{Eq.3} \quad \Delta E_s = 1/2[E(FS) - E(I/FS)] + E(I)$$

In the above, E(GB) is the energy of the clean GB, E(I/GB) is the energy of the GB with an interstitial impurity, E(FS) is the energy of the clean free surface, and E(I) is the energy of an isolated impurity. A positive value for ΔESE denotes an embrittler and a negative value denotes a cohesion enhancer. The ability of this methodology to predict the qualitative effects of specific interstitial and substitutional impurities in Fe and in Ni grain boundaries is well established [4-9]. Figure 1 shows the starting geometry for the GB and FS computational cells.

All calculations herein reported were performed using the parallelized version of the full-potential linearized augmented plane wave (FLAPW) [10,11] code at the generalized-gradient approximation (GGA) level [12] of density functional theory. The final calculated geometries of the GB and free surfaces are fully relaxed. The 2D Brillouin Zones of the computational cells were sampled at 30 k-points in the irreducible part of the zone to accurately determine the energy minima and resulting forces.

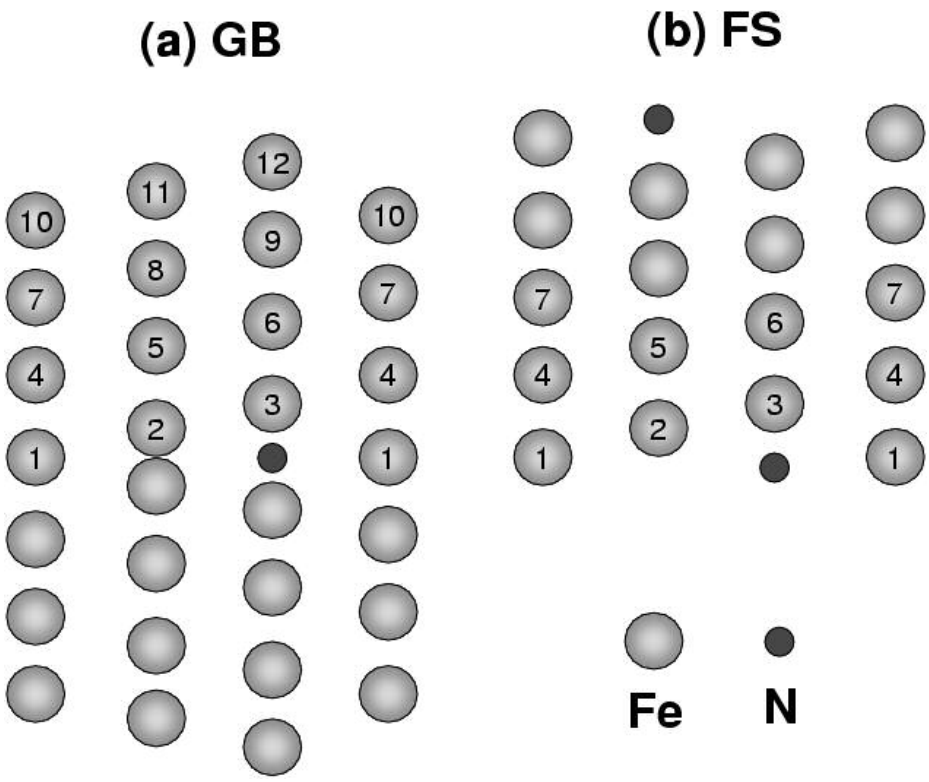

Figure 1. (a) GB and (b) FS computational cells – starting atomic positions before relaxation.

Results and Discussion

The strengthening energy for any particular impurity/GB combination may be viewed as the sum of three contributions: the strain energy associated with the presence of the impurity; the change in the electronic energy density associated with the impurity; and, for magnetic materials like Fe, the change in the magnetic energy density due to the impurity. The first contribution always reduces cohesiveness, and may also depend strongly on the GB geometry. The third contribution is usually negative for nonmagnetic impurities, whereas the second contribution may be positive or negative depending on whether chemical bonding is enhanced or diminished due to the impurity.

Charge density and magnetization density difference plots are shown in Figs. 2 and 3, respectively, for both the GB and the free surface with the impurity. Contours were obtained by subtracting the superimposed charge (or spin) densities of a free N monolayer and the reference system (i. e. the GB or FS with the same geometry as in the fully relaxed systems considered but without impurity adatoms) from the charge (or spin) density of the corresponding systems. Therefore, in Fig. 2 (Fig. 3), the contours corresponding to net charge (spin) depletions are shown as dashed lines, whereas contours in areas of charge (spin) accumulation are shown as solid lines. Figure 2 shows that N is predicted not to establish strong chemical bonds with any of the adjacent Fe atoms, as evidenced by the presence of charge depletion zones between the N atom and each of its Fe neighbors. Thus, the net chemical effect of the presence of the N atom appears to be to disrupt the chemical bonds between surrounding Fe atoms that would exist in its absence. Similarly, Fig. 3 shows that the N atom depresses the magnetic energy density in its vicinity, which does not appear to be offset by increases in any other area. Both of these factors contribute to a large strengthening energy.

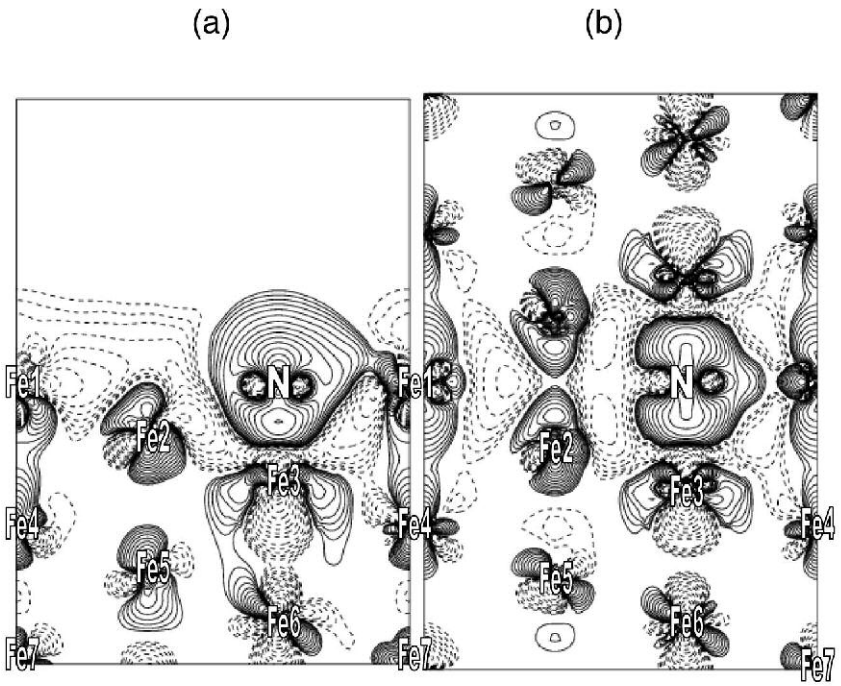

Figure 2. Charge density difference plots for the (a) Fe free surface and (b) GB. Dashed contours indicate regions of charge depletion. Solid contours indicate regions of charge accumulation.

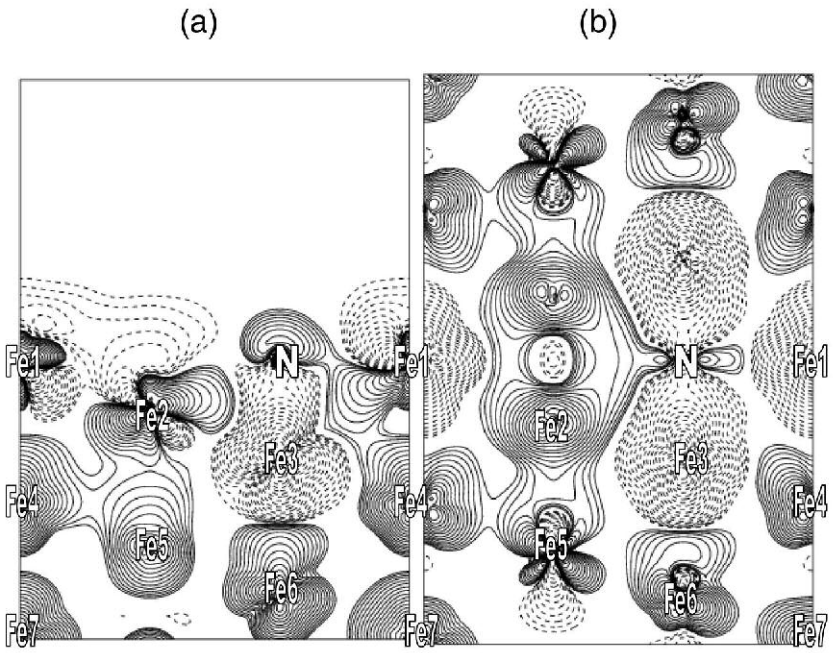

Figure 3. Magnetization density difference plots for the (a) Fe free surface and (b) GB. Dashed contours indicate regions of decreased magnetization. Solid contours indicate regions of increased magnetization.

The current and previously reported FLAPW strengthening energy results for N, P, B and C in Fe are summarized in Table 1. The previously reported results for P, B, and C are in qualitative accord with the known effects of these impurities and provide a basis for confidence in the results for N. It is expected that the strengthening energy for higher index tilt GB's would likely be even larger (more embrittling) than that for the Σ3 GB, considering the reduced volume of the interstitial site.

Table 1. Calculated Σ3[110](111) coincident-site tilt GB strengthening energies (eV per adatom) in ferromagnetic Fe for selected impurities

Impurity	Strengthening Energy	Reference
N	+7.80 (embrittler)	This report
P	+7.40 (embrittler)	[4]
P	+7.37 (embrittler)	[8]
B	0.00 (neutral)	[8]
C	- 8.80 (strengthener)	[5]

Summary

The effect of interstitial N on the cohesion of an Fe Σ3[110](111) GB has been evaluated based on ab initio calculations of the strengthening energy. The results indicate that free interstitial N is embrittling at Fe GB's, in agreement with literature observations. N acts to disrupt chemical bonds between neighboring Fe atoms in the GB, and also reduces the local magnetic energy density. These factors, together with the strain energy contribution, produce a large strengthening energy. The current computational results suggest that suppression of nitride formation at prior austenitic grain boundaries in steel may not alone eliminate the deleterious effects of elevated nitrogen levels, but that absolute nitrogen levels may need to be reduced.

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