Computational Materials Science 152 (2018) 308–323

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Effect of solutes on the lattice parameters and elastic stiffness coefficients of body-centered tetragonal Fe

Michael R. Fellinger[a,*], Louis G. Hector Jr.[b], Dallas R. Trinkle[a]

[a] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[b] General Motors Global R&D Center, 30500 Mound Road, Warren, MI 48092, USA

ARTICLE INFO

Keywords:
Lattice parameters
Elastic constants
Solutes
Iron
Steel
Martensite
Ab initio

ABSTRACT

We compute changes in the lattice parameters and elastic stiffness coefficients C_{ij} of body-centered tetragonal (bct) Fe due to Al, B, C, Cu, Mn, Si, and N solutes. Solute strain misfit tensors determine changes in the lattice parameters as well as strain contributions to the changes in the C_{ij}. We also compute chemical contributions to the changes in the C_{ij}, and show that the sum of the strain and chemical contributions agree with more computationally expensive direct calculations that simultaneously incorporate both contributions. Octahedral interstitial solutes, with C being the most important addition in steels, must be present to stabilize the bct phase over the body-centered cubic phase. We therefore compute the effects of interactions between interstitial C solutes and substitutional solutes on the bct lattice parameters and C_{ij} for all possible solute configurations in the dilute limit, and thermally average the results to obtain effective changes in properties due to each solute. The computed data can be used to estimate solute-induced changes in mechanical properties such as strength and ductility, and can be directly incorporated into mesoscale simulations of multiphase steels to model solute effects on the bct martensite phase.

1. Introduction

Solutes play a critical role in determining the properties of steel alloys, and steel chemistries are tuned to help achieve desired mechanical properties for numerous applications [1,2]. Solutes interact with defects like dislocations, grain boundaries, stacking faults, and point defects, each of which contributes to the macroscopic response of a material to loading [3]. Isolated solutes induce lattice strain and alter the local bonding environment, which changes the structural parameters and the deformation properties of the host crystal [4–6]. These changes affect the single-crystal mechanical response, and ultimately the mechanical properties of the polycrystalline material [7]. Technologically important steels are multi-phase alloys [1,2,8] which can include the body-centered cubic (bcc) ferrite phase, the face-centered cubic (fcc) austenite phase, and strengthening phases such as bainite and body-centered tetragonal (bct) martensite. The bct phase is metastable in steels and forms from the fcc phase via a diffusionless martensitic phase transformation, and the tetragonality of the bct phase is maintained by interstitial solutes preferentially occupying one of three symmetry-equivalent types of octahedral interstitial sites in the bct lattice [1,2,9,10]. The bct martensite phase is characterized by high strength and hardness [11], and is the key strengthening phase in many advanced high-strength steels [1,2,10,11]. Therefore, a detailed understanding of the impact of solutes on the single-crystal lattice parameters and elastic stiffness coefficients C_{ij} of bct Fe can increase the accuracy of mesoscale models for the mechanical behavior of steel alloys containing martensite.

Experimental studies have measured solute-induced changes in the polycrystalline elastic moduli of steels [4,12] and the effects of C and N on the single-crystal lattice parameters [13] and C_{ij} [14] of bct Fe, and a theoretical study [15] has computed the dependence of the bct Fe lattice parameters and C_{ij} on the concentration of C and N solutes. However, none of these studies determined the separate strain and chemical contributions from solutes to the changes in the bct C_{ij} nor the effects of interactions between interstitial C and substitutional solutes on the lattice parameters and C_{ij}. We generalize the density functional theory (DFT)-based methodology we developed in Ref. [6] to compute the effects of substitutional Al, B, Cu, Mn, and Si solutes and octahedral interstitial B, C, and N on the lattice parameters and C_{ij} of bct Fe. Ref. [6] uses the solute strain misfit tensor which determines general solute-induced changes in the lattice parameters of a crystal structure to account for changes in both the size and shape of a crystal due to the strain induced by solute additions. The solute strain misfit tensor is a generalization of the solute size misfit [16] which only accounts for

---

[*] Corresponding author.
E-mail address: mfelling@illinois.edu (M.R. Fellinger).

https://doi.org/10.1016/j.commatsci.2018.05.021
Received 4 March 2018; Accepted 13 May 2018

solute-induced changes in the size of a crystal. Solutes change the elastic stiffness coefficients C_{ij} of crystals by inducing lattice strain and by changing the local electronic structure and hence chemical bonding around the solute. Previously, we computed these two contributions to the changes in the C_{ij} of bcc Fe, where only solute-induced volumetric lattice strains that preserve the cubic symmetry of the bcc crystal were considered [6]. We apply a similar methodology here for bct Fe, but generalize the approach to account for independent changes in the two bct lattice parameters. Octahedral C is the most important interstitial solute in steels since it increases the strength, toughness, and hardenability of Fe and stabilizes the martensite phase [1,2]. Hence, we also compute the effects of interactions between C and substitutional solutes on the lattice parameters and C_{ij}. The computed datasets can be used to estimate solute-induced changes in mechanical properties like strength and ductility, and also can serve as inputs to mesoscale methods such as crystal plasticity simulations [17].

This paper is organized as follows. Section 2 discusses our methodology for computing solute effects on the lattice parameters and the C_{ij} of single-crystal bct Fe. We give the details of our DFT calculations, discuss the computational geometries used in this study, and present our models for the lattice parameters and the C_{ij} as functions of solute concentrations. Section 3 presents the computed data and assesses its accuracy through comparisons with available DFT calculations and experimental data from other studies. Section 4 summarizes our computational models and results and provides conclusions. The Appendix presents the derivatives of the Voigt, Reuss, and Voigt-Reuss-Hill average polycrystalline elastic Young's and shear moduli with respect to solute concentrations in terms of the derivatives of the single-crystal bct elastic stiffness coefficients.

2. Computational methods

We compute the lattice parameters and C_{ij} of bct Fe as functions of the concentration of Al, B, C, Cu, Mn, N, and Si solutes. It is well-known that Al, Cu, Mn, and Si are substitutional solutes, and C and N are octahedral interstitial solutes in ferrite and martensite [2]. Experimental data [18,19] supported by recent DFT calculations [20–22] suggest that B is a substitutional solute in bcc and bct Fe at low temperature, but the DFT-computed 0 K formation energy in the octahedral interstitial sites is only slightly larger. However, the octahedral site formation energy becomes lower than the substitutional site formation energy upon volumetric expansion of $\sim 0.3\%$ or greater[21]. We therefore present data on changes in the lattice parameters and C_{ij} of bct Fe due to B in both substitutional and octahedral interstitial sites.

The bct structure of Fe is stabilized over the ground-state bcc structure by interstitial solutes preferentially occupying one of three symmetry-equivalent types of octahedral sites [10]. For example, [001]-oriented octahedral interstitials induce a different stress along the [001]-direction than along the [100]- and [010]-directions. The lattice strains to relieve these stresses, producing a bct variant with lattice parameter a_1 along the [100]- and [010]-directions and a_3 along the [001]-direction. To simplify the discussion and to avoid possible confusion later in the text, from now on we refer to both the bct and bcc structures as bct and distinguish between them by their axial ratio [23] a_3/a_1. The bcc structures have an axial ratio of 1, and the bct structures have an axial ratio value c/a that depends on the concentration of interstitial octahedral solutes and the interactions between C and the substitutional solutes. We refer to pure bcc Fe as "ideal" bct Fe. The value c/a smoothly goes to 1 as the concentrations of interstitial octahedral solutes go to zero, and the lattice parameters and C_{ij} of bct Fe reduce to the ideal bct Fe values a_0 and C_{ij}^0 as the concentrations of all the solutes go to zero.

In this study we use DFT to compute the lattice parameters and C_{ij} of bct Fe as functions of the concentrations of octahedral interstitial B, C, and N. We combine these results with our previously calculated data on substitutional Al, B, Cu, Mn, and Si solutes in bct Fe from Ref. [6] (which was referred to as bcc Fe in that work since substitutional solutes preserve cubic symmetry), and the effects of interactions between C and substitutional solutes computed in this study to model the full dilute-limit solute dependence of the bct Fe lattice parameters and C_{ij}. Nitrogen is a trace impurity in many steels [24] and B has low solubility in Fe phases [1,2], so we treat interstitial N and interstitial B as isolated solutes. In the remainder of this paper we refer to the DFT approximations of physical quantities X as $\widetilde{X}$.

2.1. DFT calculation details

We use the plane-wave basis code VASP [25] to perform all of our DFT calculations. The PBE generalized gradient approximation (GGA) functional [26] accounts for electron exchange and correlation energy, and a projector augmented wave (PAW) potential [27] with electronic configuration [Ar]$3d^7 4s^1$ generated by Kresse and Joubert [28] models the Fe nuclei and core electrons. The solutes Al, B, Cu, Mn, Si, C, and N are modeled using PAW potentials [28] with respective electronic configurations [Ne]$3s^2 3p^1$, [He]$2s^2 2p^1$, [Ar]$3d^{10} 4s^1$, [Kr]$3d^6 4s^1$, [Ne]$3s^2 3p^2$, [He]$2s^2 2p^2$, and [He]$2s^2 2p^3$. The calculations require a plane-wave energy cutoff of 550 eV to converge the energies to less than 1 meV/atom. A conjugate gradient method relaxes the atoms until all of the atomic forces are less than 5 meV/Å, and the energy tolerance for the electronic self-consistency loop is 10^{-8} eV. All of the calculations are spin polarized to model the ferromagnetism of the bct phase. We use standard stress-strain calculations to compute the C_{ij} [6,29,30], and standard finite difference formulas to compute derivatives of the C_{ij} with respect to lattice parameters or solute concentrations [6,31].

Energies, lattice parameters, C_{ij}, and derivatives of C_{ij} converge slowly for bct lattices using standard Γ-centered or shifted Monkhorst-Pack k-point meshes [6], so we use improved k-point meshes based on the simple tetragonal lattice in reciprocal space [6,32]. The reciprocal lattice of the bct structure is face-centered tetragonal (fct), and even Γ-centered and shifted Monkhorst-Pack k-point meshes are fct meshes of points in reciprocal space. Combining these meshes forms a simple tetragonal k-point mesh which leads to faster convergence of bct properties. Our primitive cell calculations use k-point meshes generated by combining $34 \times 34 \times 34$ Γ-point-centered and shifted Monkhorst-Pack meshes, and our $3 \times 3 \times 3$ supercell calculations use k-point meshes generated by combining $8 \times 8 \times 8$ Γ-point-centered and shifted Monkhorst-Pack meshes. We use order-one Methfessel-Paxton smearing [33] to ensure accurate forces and stresses for structural relaxations and C_{ij} calculations. We choose a smearing energy width of 0.2 eV for our chosen k-point density to ensure close agreement between the smeared electronic density of states near the Fermi energy with the electronic density of states computed using the linear tetrahedron method with Blöchl corrections [34].

2.2. Computational geometries

All of our DFT calculations use supercell geometries with periodic boundary conditions. The effects of substitutional solutes on the lattice parameters and C_{ij} are given in Table 1 in our previous work [6] (and presented here in Table 3 for completeness), determined using linear fits to data from cubic $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercell calculations. In this study, we compute the effects of interstitial B, C, and N using cubic $3 \times 3 \times 3$ supercells containing 54 Fe atoms and a single solute in a [001]-oriented octahedral site. This supercell size corresponds to an interstitial concentration of $1/54 \approx 1.85$ at.%. This concentration is higher than concentrations in many steels, but we find that calculations using larger $4 \times 4 \times 4$ supercells with an interstitial concentration of $1/128 \approx 0.78$ at.% give similar results for solute strain misfits and derivatives of the C_{ij} with respect to interstitial solute concentration (see Figs. 3 and 4 in Ref. [6]). We also compute the effects of interactions between C and the substitutional solutes using $3 \times 3 \times 3$ supercells that contain a [001]-oriented octahedral C interstitial and a single