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First-principles study on the dilute Si in bcc Fe: Electronic and elastic properties up to 12.5 at.%Si

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ABSTRACT

In order to understand the effect of Si on various properties in bcc Fe, first-principles calculations are employed to investigate the elastic, electronic, and bond characteristic of Fe–Si system with the main focus on dilute Si up to 12.5 at.%Si concentrations based on electronic structure calculations. The stress–strain method for elasticity are performed to obtain the elastic constants of dilute Si in bcc Fe at 0, 2.4, 5.6, 8.3, 10.9, and 12.5 at.%Si. The calculated elastic properties show significantly change beyond 8.3 at.%Si. The bulk to shear modulus ratio indicate the ductile to brittle transition as the Si content increases beyond 8.3 at.%. Electronic density of states, local magnetic moment, and force constants results indicate different Fe–Si bond characteristic between above and below 8.3 at.%Si concentrations which can be taken as the combined effect of the magnetic property and the ordering tendency from bcc solid solution to partial ordering of $D0_3$ around 10.9 at.%Si.

1. Introduction

Silicon steel (Si dilute Fe–Si alloys) has excellent magnetic and mechanical properties. Depending on compositions and manufacturing processes, wide range of properties can be achieved such as small hysteresis, high permeability, or nearly zero magnetostriction constant [1–4]. Thus, it is widely used in transformers, motors, magnetic coils, and structural materials due to better corrosion resistance than carbon steel. Phase diagram of Fe–Si system [5] shows that, as Si content increases, there are three bcc-based structures from a disordered bcc (A2) to two ordered bcc (B2 and $D0_3$). At high temperature and low Si contents, A2 structure is presented. As the Si contents increase B2 becomes stable and $D0_3$ appears. Typical silicon steel has silicon content from 2 up to 6.5 wt.%. Increasing the Si content from 2–3 to 5–6 wt.% improves yield stress without decreasing ductility. However, at Si concentration beyond 4.5 wt.%, the ductility decreases significantly [6]. It is become more difficult to form, i.e. cold roll into thin sheet, for the high Si content steel. Several processing techniques have been investigated [7–12] to produce higher Si content for Fe–Si alloys but mostly are not suitable for industrial scale. Poor ductility at higher Si concentration inhibits further development for this alloy for an industrial applications. Understanding the behavior, mechanism, or origin of the decreasing ductility might be enabling a further development of higher Si content steel.

The present work aims at investigating the behavior of dilute bcc Fe as the Si concentrations increase up to 12.5 at.% through the first-principles calculations. The goal is to explain the Si concentration dependence of the ductility and figure out the main factors which dominant the phenomenon. Section 2 details the first-principles calculations used in this work. Elastic constants and force constants procedures are also provided. In Section 3, we present the results of our calculations from elastic, electronic, and force constant data for different Si concentration of dilute bcc Fe up to 12.5 at.%Si. The concentrations dependent elastic properties such as elastic stiffness, bulk modulus, shear modulus, and Young's modulus will be discussed. The effect of Si to the ground state electronic properties of dilute bcc Fe will be investigated. Force constants between different types of atoms will also presented. From various properties discussed in Section 3, we try to figure out the main reason behind the lower ductility in silicon steel at higher silicon concentration.

2. Methodology

2.1. First-principles calculations

All the calculations in this study are based on density functional theory (DFT) which implemented in the Vienna Ab-initio Simulation Package (VASP) [13,14]. Projector augmented wave (PAW) method is used to describe the electron–ion interactions [15].

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The exchange and correlation are treated using generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [16]. The PAW potential set comprised of a $3d^7 4s^1$ valence configurations for Fe and $3s^2 3p^2$ for Si. Spin polarized calculations are included for all calculations. During the structure relaxation, the total energies from VASP are calculated by integration over a Monkhorst–Pack [17] mesh of k-points in the Brillouin zone integration using Methfessel–Paxton order 1 smearing method [18] for smearing electronic occupation. The final self-consistent static calculation with the linear tetrahedron method including Blöchl correction [19] are performed after the structure relaxation. A 350 eV cutoff energy and k-points meshes are adopted to provide the convergence of electronic energies to a least 0.1 meV per formula unit for all calculations.

2.2. Elastic constants calculations

Elastic constants (c_{ij}) are calculated from completely relaxed structures using stress–strain approach based on the Le Page and Saxe [20]. A set of strains ($\varepsilon = \varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5$, and ε_6) are applied to the completely relaxed structures via the following equation:

$$\overline{R} = R \begin{pmatrix} 1+\varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & 1+\varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_6/2 & 1+\varepsilon_3 \end{pmatrix} \tag{1}$$

where $\overline{R}$ and R are deformed and fully relaxed structure, respectively, ε_1, ε_2, ε_3 refer to normal strains and ε_4, ε_5, ε_6 refer to shear strains. For the $Im\bar{3}m$ symmetry, one set of strains is sufficiently to determine the elastic constants. Because of Si atom is replaced one of the Fe atom, the total of twelve independent strains (six independent negative and six independent positive) are used for each structure to obtain the elastic constant. The corresponding stresses ($\sigma = \sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5$, and σ_6) are obtained from VASP. From twelve set of independent strains and twelve set of stresses (σ), elastic constants are calculated by solving the following equation:

$$c_{ij} = \varepsilon_{ij}^{-1} \sigma_{ij} \tag{2}$$

where c_{ij} are elastic stiffness, ε_{ij} and σ_{ij} are strains and stresses, respectively. Due to the symmetry of bcc lattice, only c_{11}, c_{12}, and c_{44} are independent. The bulk (B), shear (G), and Young's modulus (E) are calculated using Voigt's method [21]:

$$B = \frac{\overline{C}_{11} + 2\overline{C}_{12}}{3} \tag{3}$$

$$G = \frac{\overline{C}_{11} - \overline{C}_{12} + 3\overline{C}_{44}}{5} \tag{4}$$

$$E = \frac{9BG}{G+3B} \tag{5}$$

where

$$\overline{C}_{11} = \frac{c_{11} + c_{22} + c_{33}}{3} \tag{6}$$

$$\overline{C}_{12} = \frac{c_{12} + c_{13} + c_{23}}{3} \tag{7}$$

$$\overline{C}_{44} = \frac{c_{44} + c_{55} + c_{66}}{3} \tag{8}$$

2.3. Force constant calculations

Force constants are obtained from the component in Hessian matrix calculated using density functional perturbation theory implemented in VASP. Force constant between atoms i and j ($\Phi_{i,j}$) is defined from the following equation:

$$\Phi_{i,j} = \frac{\partial^2 E}{\partial \mu_i \partial \mu_j} \tag{9}$$

where E is the total energy, μ_i and μ_j are displacements of the atom i and j. Two different types of force constants (stretching and bending) are calculated. Stretching is respected to the displacement of atom along the bond while bending is respected to the bond angle.

3. Results and discussions

Different concentrations of Si in the bcc lattice are achieved through supercells of standard bcc primitive cell [22]. By changing supercell size and substituting one Si atoms in the supercell, different Si concentrations from 2.7 up to 8.3 at.%Si can be achieved. Fig. 1a–c illustrates the supercell represented different Si concentrations from 2.7 up to 8.3 at.%Si. For the Si concentration higher than 8.3%, 64 atoms supercell that also based on the bcc primitive cell was used which 7 and 8 Fe atoms inside the supercell are replaced by Si atoms in order to achieve the Si concentration of 10.9 and 12.5 at.% respectively. Fig. 1d illustrate 64 atoms supercell that represented 10.9 at.%Si. For 12.5 at.%Si, Si atoms are distributed evenly to achieve the maximum distances among Si atoms. Fig. 2a–e shows different Si configurations for supercell tested for 12.5 at.% case to ensure that the most stable configuration is realized. First-principles calculations on a supercell of $D0_3$ (Fe_3Si) structure with half of Si atom replaced with Fe atom is also carried out to compare with the 64 atom supercell at 12.5 at.%. Fig. 2f shows the $D0_3$ structure representing 25.0 at.%Si. Based on $D0_3$ structure, 32 atoms supercell with half of Si atoms replaced by Fe atoms are used to represent the $D0_3$ structure at 12.5 at.%Si concentration.

Fig. 3 shows calculated elastic properties including c_{11}, c_{12}, c_{44}, bulk modulus (B), shear modulus (G), and Young's modulus (E) at different Si concentrations. The mechanical stability of the structure at each concentration can be judged from calculated elastic stiffnesses. According to Born's criteria [23], bcc structure is mechanical stable when the following conditions are met:

$$\begin{aligned} c_{11} - |c_{12}| &> 0 \\ c_{11} + 2c_{12} &> 0 \\ c_{44} &> 0 \end{aligned} \tag{10}$$

For all calculated structures ranging from 0 to 12.5 at.%Si, all of the calculated values from Eq. (10) are greater than zero. This mean that all of the calculated structures in this work should be mechanically stable at 0 K. The values of $c_{11} - |c_{12}|$ are decreased and extrapolated to negative around 25 at.%Si. Experimental data [24] also show the decreasing in $c_{11} - |c_{12}|$ value. Meanwhile, the thermodynamic stability of these dilute solid solutions can be also investigated by the calculated formation energies for each system with respect to the Fe-bcc and Si-diamond as reference states, as shown in Fig. 4. It can be seen that perfect ordered $D0_3$ structure have formation energy about −31.5 kJ/mol-atom. Drawing a tie line between pure Fe and $D0_3$ energy which stands for the segregation limit of Fe-bcc and $D0_3$ structure, once can see that all the calculated systems are located slightly up the line. which indicating that none of the solid solution are stable in this low Si range compared to separation to pure Fe and $D0_3$ at 0 K. Meanwhile, the very small energy differences of these solid solution structures to the lie line suggest that as the temperature increases, entropy contribution from the mixing between Fe and Si atoms will lower the free energies of the solid solution structures to enable their presence stable states. Furthermore, at 12.5 at.%Si, it is noticed a lower energy of the partial ordering $D0_3$ than all energies of disordered configurations at this concentration, predicting the possibility of appearance of $D0_3$ ordering. Ohnuma et al. [25] calculated phase diagram of the