Fusion Engineering and Design 137 (2018) 22–29

Contents lists available at ScienceDirect

Fusion Engineering and Design

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

Effects of interstitial atoms (N/O) in bcc Fe from first-principle calculations

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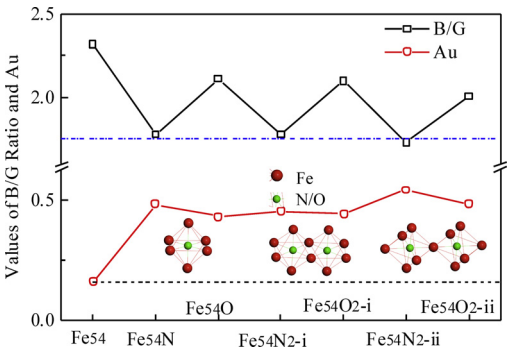
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Interstitial atoms
Structural characters
Mechanical properties
Magnetic properties
First principles

ABSTRACT

Based on the supercell structures of bcc-Fe alloys, the structural, electronic, and magnetic properties of bcc Fe with N/O atoms in octahedral interstices were investigated using first-principle calculations. Structural models with double atoms in the near neighbor sites were built; their combined action and the interactions between them were also analyzed. The effects of pressure on the properties of bcc Fe with one N (or O) atom or double N (or O) atoms in the octahedral sites were discussed. After N (O) solid solution, lattice distortion occurs in the bcc-Fe supercells. Interstitial N and O atoms increase the stability of the bcc-Fe supercells. The valence character and ionic character exist in the Fe—N and Fe—O bonds. The magnetic moments of the supercells increase after N/O dissolution. The ratios of B/G for Fe_{54} with N reduce more obviously than that for Fe_{54} with O. The interstitial atoms (N/O) increase the anisotropy of the mechanical properties of bcc Fe. The magnetic moments of the bcc-Fe supercells decrease with increasing pressure.

1. Introduction

High strength Fe-based alloys of bcc phase have been used in a huge variety of practical applications, as one of the most common structural materials [1–3]. In some specialized service environments, e.g. nuclear power plants, there are many gaseous elements (H, He, O, N etc.) [3–7]. To safely use Fe-based alloys in these environments, it is crucial to know how they are affected by these elements. When a foreign atom inserts in bcc Fe, it will occupy one of three possible positions: the substitutional, octahedral, and tetrahedral sites. Generally, atoms with smaller radii (than Fe), such as H, C, He, B, N, and O, are apt to occupy the interstitial sites, while atoms with larger radii (similar to or larger than Fe) prefer to occupy the substitutional sites [3–11].

Recently, the effects and interactions of solid solution atoms in bcc

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https://doi.org/10.1016/j.fusengdes.2018.08.004
Received 21 May 2018; Received in revised form 2 August 2018; Accepted 12 August 2018

Fe have been investigated using theoretical calculation methods [3–6]. Zhang et al. [3] investigated the energetics and clustering trends of noble gas atoms (He, Ne, and Ar) in bcc Fe using first-principle calculations, and found that interstitial noble gas atoms tend to stay with each other by self-trapping. Interstitial He atoms and small He interstitial clusters are highly mobile in the lattice, while Ar and Xe atoms prefer to occupy substitutional sites [4,5]. La atoms also occupy substitutional sites, where anti-bonding states build up between La and Fe atoms, and a strong repulsive interaction builds up between La and C/N atoms within the bcc lattice parameter; the introduction of the La atom causes increased C/N—Fe bond populations [6].

The diffusion and segregation of solid solution atoms (H, He, O, P, Cu, Mn, Cr, Si etc.) in bcc Fe have also been calculated [7–11]. The effective diffusivity of H is decreased due to the vacancy trap effect; the trapped H atoms hardly contribute to hydrogen diffusivity because of the difficulty in detrapping and the low mobility of the vacancy-H complex [7]. O atoms in octahedral interstices are always energetically favorable (minimum energy) with and without vacancies, and vacancies possess an extremely high affinity for O in bcc Fe, dramatically increasing the energy barrier for O migration [8]. There is a considerable synergetic effect in the case of self-interstitial atoms, which have been found to bind strongly with Mn—Si pairs, and the presence of point defects near the weakly attractive Mn—Si pairs significantly enhances the solute–solute binding [9]. He atoms always remain confined to the grain boundary (GB) region while diffusing; He diffusion is highly anisotropic along the GBs, and the GB diffusion of an interstitial He atom is always faster than its bulk diffusion [10]. P atoms strongly bind to GBs and free surfaces; segregation of P, and of Cu, lead to GB embrittlement [11]. The diffusion coefficients of solute rare earth Y are lower than that of Fe self-diffusion above 970 K, and higher than the latter below 970 K. The diffusivity of solute La is about one order of magnitude less than that of Y [12].

To our knowledge, research into the effects of interstitial N or O atoms on the electronic and magnetic properties of bcc Fe, especially double solution atoms, has rarely been reported. This work aims to investigate the roles of gaseous atoms N/O in octahedral interstices on the phase stability, the electronic and magnetic properties of bcc Fe. In particular, structural models of double atoms in the near neighbor sites will be built; their combined action, and the interactions between them, will also be analyzed. The effects of pressure on bcc Fe with single or double N (or O) atoms in the octahedral sites will be discussed.

2. Calculation details and structural models

The first-principle calculations are based on density functional theory (DFT) and carried out with CASTEP code [13]. The ion–electron interaction is modeled by ultrasoft pseudopotentials of the Vanderbilt type [14].

The exchange-correlation potential was evaluated using the generalized gradient approximation (GGA) of Perdew et al. [15,16]. The Kohn–Sham one-electron states were expanded in a plane wave basis set up to 450 eV. The energy calculations in the first irreducible Brillouin zone were made using a $3 \times 3 \times 3$ k-point grid of Monkhorst–Pack scheme [17]. The convergence criteria for structure optimization and energy calculation were set to ultra-fine quality; the tolerance for the stress concentration factor (SCF), energy, maximum force, and maximum displacement were set to: 10^{-6} eV/atom, 10^{-5} eV/atom, 0.1 eV/nm, and 5×10^{-5} nm respectively. After getting the equilibrium geometry, the elastic constants were also calculated using the stress–strain method [18].

Supercells of $3 \times 3 \times 3$ bcc unit cells (containing 54 Fe atoms) were used in our models, based on the results of You's calculations [6]. The structural models with (a) one N (or O) atom in an octahedral site and (b,c) double N (or O) atoms in two octahedral sites are shown in Fig. 1. $Fe_{54}N$ ($Fe_{54}O$) is one N (O) atom dissolving in the octahedral sites; $Fe_{54}N_2$-i ($Fe_{54}O_2$-i) is double N (O) atoms in the first nearest neighbor sites; and $Fe_{54}N_2$-ii ($Fe_{54}N_2$-ii) is double N (O) atoms in the second nearest neighbor sites. According to the symmetry relationship between iron atoms and interstitial atoms, the iron atomic sites are labeled for convenience in the structural models (see Fig. 1).

3. Results and discussion

3.1. Structural and phase stability

The ground state properties of the 54-atom supercells and the cells with solute N or O atoms in the octahedral sites are analyzed through the total energy, which is calculated as a function of volume. The equilibrium atomic positions, bond lengths, and lattice constants can be calculated using the Birch–Murnaghan equation of state [19,20]. After N (O) solution, the lattice constants of the supercell change and the cell volumes increase slightly (see Table 1 and Fig. 2). After N (O) solid solution, lattice distortion occurs in the bcc-Fe supercells. The $Fe_{54}N$ ($Fe_{54}O$) and $Fe_{54}N_2$-ii ($Fe_{54}O_2$-ii) supercells become tetragonal crystal structures ($a = b \neq c$), and the $Fe_{54}N_2$-i ($Fe_{54}O_2$-i) supercell becomes an orthorhombic crystal ($a \neq b \neq c$) (see Table 1).

The volume of the supercell (Vc) and the octahedral volume (Vo) were shown in Fig. 2. The octahedral volumes are the volumes of Fe_6N or Fe_6O in the supercell, as shown in Fig. 1. The octahedron is the nearest neighbor shell around solutes (N/O). The volume of the supercells increases below 4% after N and O added. With one oxygen atom dissolved in the supercell (Fe54), the volume of the supercell increases slightly (below 1%). The volume increase of the supercell with N solid solution is greater than that with O solid solution, while the volume increase of the octahedron with N is less than that with O. With one atom dissolved, the octahedral volume of $Fe_{54}N$ increases 19.5% (with N), and that of $Fe_{54}O$ increases 26.8% (with O). With two atoms dissolved, the octahedral volume increases 21.2% in $Fe_{54}N_2$-i (with 2N), and 27.7% in $Fe_{54}O_2$-i (with 2O); and the octahedral volume in $Fe_{54}N_2$-ii increases 21.9% (with 2N), and that in $Fe_{54}O_2$-ii increases 28.4% (with 2O). From Fig. 3, the differences of the bond length for Fe—N and Fe—O bonds in the supercells can be found. In $Fe_{54}N$ and $Fe_{54}O$, interstitial atoms (N and O) are in the center of the octahedron, while the interstitial atoms (N and O) are off the center position of the octahedrons in $Fe_{54}N_2$ and $Fe_{54}O_2$. The lengths of the Fe—N bonds are 0.1896, 0.1907, and 0.1905 nm in $Fe_{54}N$, $Fe_{54}N_2$-i, and $Fe_{54}N_2$-ii respectively. The lengths of the Fe—O bonds are 0.1934, 0.1967, and 0.1943 nm in $Fe_{54}O$, $Fe_{54}O_2$-i, and $Fe_{54}O_2$-ii respectively.

The formation enthalpy (ΔH) of Fe_mN_n from the elements(bcc Fe, molecular N_2 and molecular O_2) can be shown as:

$$E_f = E(Fe_{54}N_n/O_n) - E(Fe_{54}) - nE(N/O) \quad (1)$$

At T = 0 K and p = 0 Pa, the formation enthalpy equals the calculated formation energy (ΔE), i.e., $\Delta H_f = \Delta E_f$, when the zero-vibration contribution is ignored [21,22].

The formation energy can be used to represent the thermo-stability of the bcc-Fe supercells with N or O, as shown in Table 1. The formation energies of the six solid solutions are negative, which shows they are of higher stability than the Fe_{54} supercell system. Atoms N and O decrease the formation energies of the bcc-Fe supercells, in other words, interstitial atoms N and O increase the stability of them. The formation energy of $Fe_{54}O$ is -4.22 eV/cell, and the formation energy of $Fe_{54}N$ is -0.68 eV/cell. This indicates that the effect of O on the stability of bcc-Fe system is stronger than that of N. The phase stability order is as follows: $Fe_{54}O_2$-i > $Fe_{54}O_2$-ii > $Fe_{54}O$ > $Fe_{54}N_2$-ii ≈ $Fe_{54}N_2$-i > $Fe_{54}N$.

3.2. Electronic and magnetic properties

In this part, the electronic structures and properties of the supercells Fe_{54} with N or O atoms are characterized and compared, and the roles of nitrogen and oxygen atoms on the bcc-Fe supercell system will be