



## $\omega$ structure in steel: A first-principles study



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### ABSTRACT

Recent experimental works reported observation of the  $\omega$  structure in steel. Here, stability of the  $\omega$  structure in steel is investigated based on first-principles with special interests in effects of interstitial C atoms. The interstitial C atoms increase the energy of the  $\omega$  structure compared with the ferromagnetic (FM) BCC. The  $\omega$  structure incorporating C atoms is also dynamically unstable unless the C concentration is 25 at.%. It is concluded that the  $\omega$  structure is mostly unstable in steel, and the  $\omega$  structure in steel may be formed under special atomic constraints at twin boundaries or other interfaces.

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## 1. Introduction

Nanometer-size domains of the  $\omega$  structure have recently been reported in steel, i.e., Fe–C-based alloys, by detailed transmission electron microscopy observations [1,2]. This motivated us to investigate the stability of the  $\omega$  structure in steel. The present authors' group has emphasized the importance of the  $\omega$  structure on transformation between the BCC and the FCC structures in metallic systems. Togo and Tanaka developed a search algorithm for transformation pathways based on a systematic set of first-principles calculations and revealed that the  $\omega$  structure was located on a transformation pathway between the BCC and the FCC structures [3]. Ikeda et al. suggested that the pressure-induced phase transition between the BCC and the FCC Fe at high temperature occurred along this transformation pathway [4]. The present authors recently performed a systematic investigation into the  $\omega$  structure of transition elements [5]. The elemental  $\omega$  Fe with antiparallel magnetic moments (+ – – magnetic state) was found to be the lowest in energy among the investigated magnetic states and to be dynamically stable. The + – –  $\omega$  Fe was, however, 170 meV/atom higher in energy than the ferromagnetic (FM) BCC Fe. This implies that the elemental  $\omega$  Fe should be difficult to be

formed. In experiments, however, the nanometer-size  $\omega$  structure was observed in steel [1,2]. The largest difference between elemental Fe and steel may be the presence of C atoms, but little has been known about effects of the C atoms on the stability of the  $\omega$  structure in steel.

Here we report a first-principles study on the stability of the  $\omega$  structure in steel with special interests in effects of interstitial C atoms. Four different magnetic states of the  $\omega$  structure investigated in our previous study [5] (see Fig. 1(c) in Ref. [5] for notations of the magnetic states) are focused on. Possible interstitial sites for C atoms in the  $\omega$  structure are first systematically searched, and then the energy of the  $\omega$  structure is compared with that of the FM BCC at several C concentrations using supercell models. Finally, dynamical stability of the  $\omega$  structure is analyzed based on phonon frequencies at the  $\Gamma$  point of the supercell models.

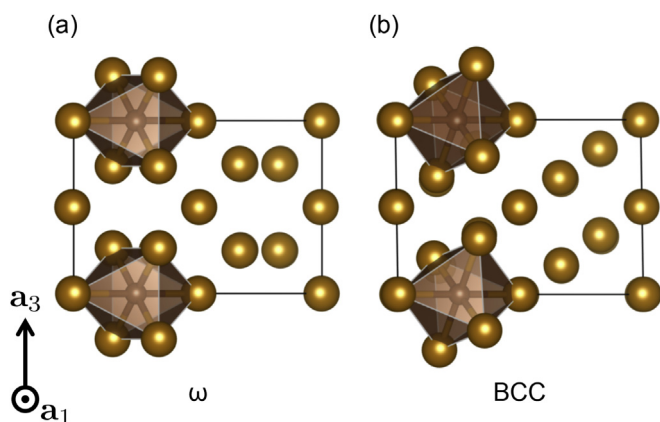
## 2. Computational details

The  $\omega$  structure belongs to the hexagonal crystal system, and hence its primitive unit cell is specified by two lattice constants  $a_\omega$  and  $c_\omega$ . The  $\omega$  structure has three atoms inside the primitive unit cell, and their positions are (0, 0, 0), (2/3, 1/3, 1/2), and (1/3, 2/3, 1/2) in fractional coordinates. The  $\omega$  structure can actually be obtained from the BCC structure by repeating to collapse a pair of neighboring {111} planes and to hold the next plane unaltered.

Four magnetic states, which were focused on in our previous study [5], were investigated for the  $\omega$  structure. The FM BCC

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**Fig. 1.** (a) Structure of the  $\omega$   $\text{Fe}_{24}\text{C}_1$  model where the C atom is located at the octahedral site. (b) Structure of the BCC  $\text{Fe}_{24}\text{C}_1$  model where the C atom is located at the octahedral site. Gold spheres represent Fe atoms, and grey spheres inside the octahedra represent C atoms.  $\mathbf{a}_1$  and  $\mathbf{a}_3$  denote two lattice vectors of the models. Visualization is performed using the VESTA code [15]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

structure and cementite  $\text{Fe}_3\text{C}_1$  were also calculated for comparison. The  $\omega$ -based BCC unit cell (see Fig. 1(b) in Ref. [5] for details) was used for the calculation of the FM BCC structure so that computational conditions for the  $\omega$  and the BCC structures are as similar to each other as possible.

To systematically search possible interstitial sites for C atoms in the  $\omega$  structure in Fe, we used the  $\omega$   $\text{Fe}_{24}\text{C}_1$  model composed of the  $2 \times 2 \times 2$  supercell of the primitive  $\omega$  unit cell for Fe and an interstitial C atom. The possible interstitial sites were searched in the following procedure. First, we divided a primitive  $\omega$  unit cell into the  $6 \times 6 \times 4$  mesh and put a C atom on the mesh points that are symmetrically inequivalent to each other. The numbers of the inequivalent points were 30 for the  $++-$  magnetic state and 21 for the other magnetic states. Then, we optimized lattice parameters and internal atomic positions of the structures of the supercell models. Some of the supercell models showed atomic positions largely deviated from those of the initial  $\omega$  structure after the structural optimization. These models were excluded from further consideration. Similarly, some models were excluded because the initially given magnetic state was broken after the structural optimization.

Energies of the models were calculated based on the plane-wave basis projector augmented wave method [6] in the framework of density-functional theory (DFT) as implemented in the VASP code [7–9]. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof form [10] was employed for the exchange-correlation functional because it is known that the GGA provides the correct ground state of Fe (FM BCC) [11]. A plane-wave energy cutoff of 400 eV was used. The Brillouin zones were sampled by the  $\Gamma$ -centered  $12 \times 12 \times 18$  mesh per primitive  $\omega$  unit cell, and the Methfessel-Paxton scheme [12] with a smearing width of 0.4 eV was employed. Total energies were minimized until the energy convergences to be less than  $10^{-8}$  eV. Lattice parameters and internal atomic positions were optimized under zero external stress.

Phonon frequencies were investigated within the harmonic approximation for a lattice Hamiltonian using the finite-displacement method. Atomic displacements of 0.01 Å were used to obtain the second-order force constants. Phonon modes at the  $\Gamma$  point of the supercell models were calculated to investigate their dynamical stability. When there are phonon modes with imaginary frequencies, the structure is considered to be dynamically unstable. The PHONOPY code [13,14] was used for these phonon calculations.

### 3. Results and discussion

In our previous study [5], we made a systematic first-principles study on thermodynamical and dynamical stability of the  $\omega$  structure in 27 transition elements (Sc to Cu, Y to Ag, and Lu to Au). Only the  $\omega$  structures of the group 4 elements (Ti, Zr, and Hf), the group 7 elements (Mn, Tc, and Re), and Fe were found to be dynamically stable in their lowest-energy magnetic states. For the elemental  $\omega$  Fe, the  $+ - -$  magnetic state was the lowest in energy among the investigated magnetic states. It was, however, 170 meV/atom higher in energy than the FM BCC Fe. This implies that the elemental  $\omega$  Fe is difficult to be formed from the viewpoint of thermodynamical stability. In the following, we investigate whether the presence of interstitial C atoms stabilizes the  $\omega$  structure in Fe.

First, we search possible interstitial sites for C atoms in the  $\omega$  structure based on the systematic procedure described above. Table 1 summarizes calculated energies of the obtained  $\omega$   $\text{Fe}_{24}\text{C}_1$  models. Calculations from the inequivalent initial positions of the C atom converged to seven positions as listed in Table 1. When the initial position of the C atom is (0, 1/2, 0) in fractional coordinates for a primitive  $\omega$  unit cell, the energy is the lowest among those of the interstitial sites for all the magnetic states. The (0, 1/2, 0) interstitial site can be referred to as the octahedral site of the  $\omega$  structure, as shown in Fig. 1(a). The octahedral site of the  $\omega$  structure is actually similar to that of the BCC structure, as shown in Fig. 1(b). It has been well investigated that C atoms favor the octahedral site in the BCC Fe [16]. The present calculations reveal good correspondence of the favorable interstitial sites between the two crystal structures.

To investigate dependence of energies on the concentration of C atoms, we use the  $1 \times 1 \times 1$ ,  $1 \times 1 \times 2$ ,  $1 \times 1 \times 3$ ,  $2 \times 2 \times 1$ ,  $2 \times 2 \times 2$ ,  $2 \times 2 \times 3$ , and  $3 \times 3 \times 2$  supercells of the primitive  $\omega$  unit cell with a C atom at an octahedral site. Hereafter supercell models incorporating a C atom are collectively referred to as  $\text{Fe}_n\text{C}_1$  ( $n = 3, 6, 9, 12, 24, 36, 54$ ), where  $n$  indicates the number of Fe atoms in the supercell models. Energies of the FM BCC  $\text{Fe}_n\text{C}_1$  where the C atom is located at an octahedral site are also investigated using the corresponding supercells for comparison. Fig. 2 shows the calculated energies of the  $\omega$   $\text{Fe}_n\text{C}_1$  relative to those of the FM BCC  $\text{Fe}_n\text{C}_1$ . The  $\omega$  structure is higher in energy than the FM BCC up to 25 at.% C for all the magnetic states. This result indicates that the  $\omega$  structure is thermodynamically less favorable than the FM BCC even when interstitial C atoms are incorporated. Furthermore, the relative energy of the  $\omega$  structure below 14 at.% C is higher than that of the elemental  $\omega$  Fe for the  $++-$ ,  $+ - -$ , and nonmagnetic (NM) states. This indicates that interstitial C atoms thermodynamically

**Table 1**

Calculated energies of the  $\omega$   $\text{Fe}_{24}\text{C}_1$  models in meV/(Fe atom). The energies are relative to that for the FM BCC  $\text{Fe}_{24}\text{C}_1$  models where the C atom is located at an octahedral site. The first column shows the initial position of the interstitial C atom in fractional coordinates for a primitive  $\omega$  unit cell in the supercell models before the structural optimization. "NA" indicates that the corresponding structure could not be obtained because the optimized structure was largely deviated from the initial  $\omega$  structure and/or because the initially given magnetic state was broken during the structural optimization.

Initial position of C	FM	$++-$	$+ - -$	NM
(0, 1/2, 0)	182	212	182	276
(1/6, 1/3, 0)	224	NA	196	299
(1/6, 1/3, 1/2)	207	NA	214	325
(0, 1/6, 1/2)	216	NA	223	330
(0, 1/2, 1/2)	251	NA	274	389
(1/3, 2/3, 0)	NA	365	NA	417
(0, 0, 1/2)	NA	NA	349	428

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