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Structural transformations among austenite, ferrite and cementite in Fe–C alloys: A unified theory based on *ab initio* simulations

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ABSTRACT

Structural transformations in Fe–C alloys are decisive for the mechanical properties of steels, but their modeling remains a challenge due to the simultaneous changes in Fe lattice and redistribution of C. With a combination of the orientation relationships between austenite, ferrite and cementite, we identify a metastable intermediate structure (MIS), which can serve as a link between the three phases. Based on this framework, different mechanisms depending on the local conditions (C concentration, strain, magnetism) are revealed from *ab initio* nudged elastic band simulations, which allow us to construct a unified theory for the structural transformations among austenite, ferrite and cementite.

1. Introduction

The kinetics of structural phase transitions belongs to the most fundamental and fascinating fields of materials science and condensed matter physics [1–4]. One of the materials that owes many of its extraordinary mechanical properties to structural phase transitions is the Fe–C system, the basis of steels. While one would assume that Fe–C belongs to the best studied materials (see e.g., [5–8]), the atomistic processes involved in the structural transformation from the high-temperature face-centered cubic (fcc) austenite to the low-temperature body-centered cubic (bcc) ferrite are still insufficiently understood. This does not only apply to the complicated thermodynamics of the cooling process, but also to structural relationships independent of temperature [9].

The complexity of the transformation is mainly due to the combination of the two subsystems, Fe and C. Considering on the one hand the Fe atoms only, the martensitic rearrangement of the atoms from fcc to bcc is typically described by processes like the Bain path. This assumes a homogeneous transition of the whole grain and cannot account for large lattice mismatches that occur when considering the more realistic scenario of a moving austenite/ferrite interface during cooling. An atomistic investigation of possible adaptation processes [10] at the interface has so far not been performed for steels. The C atoms, on the other hand, occupy interstitial positions in Fe lattices, but show a remarkably lower solubility in bcc Fe as compared to fcc Fe. Therefore, a redistribution of C atoms is required when the austenite/ferrite interface moves during cooling. Thermodynamically, this is captured by the formation of orthorhombic cementite (Fe_3C) precipitates during cooling. However, this requires local C concentrations in the order of 25 at.%, which cannot be the result of random fluctuations, but only a well-defined nucleation process. Again, an atomistic understanding of this nucleation process is currently missing.

We believe that only a sophisticated atomic-scale interplay between the change of the Fe matrix and the redistribution of C can explain the complex transformations of the Fe–C system among austenite, ferrite and cementite. We therefore employ first-principles calculations to obtain atomistic insights into underlying mechanisms as well as details about the crystallographic orientation relationships (ORs) and the energetics of the different phases. Our study reveals the occurrence of a metastable intermediate structure (MIS), which acts as a central connection among austenite, ferrite and cementite. Depending on the local conditions (C concentration, strain, magnetism) different mechanisms are observed for the transformations between the MIS and the three phases. However, the MIS is not a stable bulk phase, but acts as a buffer layer at the austenite/ferrite and austenite/cementite interfaces similar to the concept of complexions [11]. The formation of the MIS is triggered by interface reconstructions and it can further facilitate the decomposition of austenite into ferrite and cementite. With these insights a clear atomistic picture how the phase

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transformations among austenite, ferrite and cementite can happen at the interfaces is thus provided.

In the following, we will firstly describe our computational details in Section 2. Secondly, the lattice correspondence between austenite, ferrite and cementite is established and illustrated in Section 3. Then we evaluate the minimum energy paths (MEPs) of the structural transformations in bulk under different conditions and discuss the corresponding mechanisms of the atomistic processes in Section 4. Moreover, we combine all the phases/structures at the interfaces and try to interpret a realistic picture for the phase transformations among austenite, ferrite and cementite in Section 5. In addition, all the aspects that need to be considered to prove this picture are also discussed in this section. Finally, the achievement of this work is summarized in Section 6.

2. Computational details

All *ab initio* calculations in this work are performed employing spin-polarized density functional theory (DFT). For the description of the electron–ion interactions, we use Blöchl's projector augmented wave (PAW) potentials [12] combined with the Perdew–Burke–Ernzerhof (PBE) parameterization [13] of the exchange–correlation functional, as implemented in the Vienna *Ab Initio* Simulation Package (VASP) [14].

In order to produce reliable calculation results, systematic convergence tests are carried out for fcc and bcc Fe as well as the orthorhombic Fe_3C unit cells. It is found that the use of a plane-wave energy cutoff $E_{cut} = 400$ eV, and ~10,000 **k**-points × atoms resulting from a homogeneous Monkhorst–Pack sampling [15] of the Brillouin zone can ensure accurate descriptions of the three phases (the lattice constants converge to a computational error of less than 0.001 Å and the maximum deviation from experimental results is 0.94%). A first order Methfessel–Paxton scheme [16] with a thermal smearing parameter of 0.2 eV is used for integration over the **k**-points. The optimized lattice constant and local magnetic moment of the ferromagnetic high-spin (FM-HS) fcc Fe are 3.640 Å and 2.5 μ_B/atom, respectively. Those of the FM bcc Fe are 2.834 Å and 2.2 μ_B/atom, respectively. The lattice constants of cementite are also optimized and provided in Table 1. The local magnetic moments of Fe atoms in cementite in the two sublattices are 1.97 μ_B/atom (Fe_{4c}) and 1.88 μ_B/atom (Fe_{8d}), respectively. Both the optimized structural and magnetic properties of the three phases show good agreement with previous experimental data and theoretical results [17–19,8].

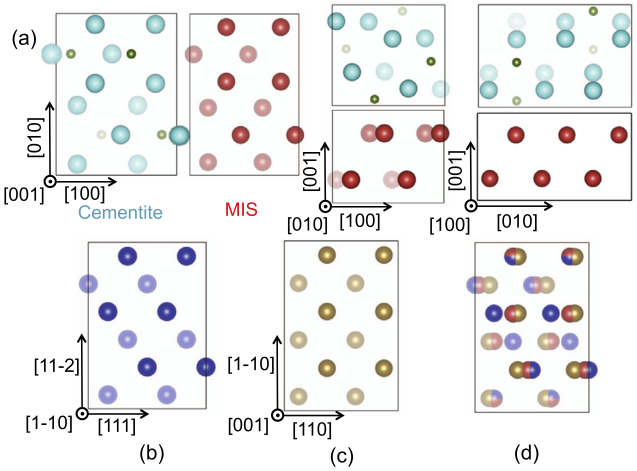

Fig. 1. (a) shows the comparison between cementite and the MIS in three projections. Large spheres represent Fe atoms and small green spheres refer to C. In the second row the orthorhombic unit cells of ferrite (b) and austenite (c) are shown. In (d) a comparison of the atomic positions of the MIS, ferrite and austenite is shown. Lower-lying atoms are shaded with gray color. The structures in this paper are visualized with the VESTA program [36]. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

Table 1
Optimized lattice constants of the orthorhombic cells of austenite, ferrite, the MIS and cementite. All values are given in Å.

Phases/structures	*a*	*b*	*c*
Austenite (before tetragonal distortion)	5.148	7.722	3.640
Austenite (after tetragonal distortion)	4.841	7.264	4.016
Ferrite	4.909	6.942	4.008
MIS (without C)	4.860	7.164	4.033
MIS (25 at.% C)	5.415	7.670	3.919
Cementite	5.038	6.727	4.484

For the paramagnetic (PM) calculations of austenite and the MIS, we employ the special quasi-random structures (SQS) approach as implemented in the ATAT code [20]. The SQS is originated from the cluster expansion method which is based on the generalized Ising model. Spin-up (50%) and spin-down (50%) moments (±2.4 μ_B/atom) are randomly distributed within a 1.5 × 1 × 2 supercell (36 Fe atoms) using a binary SQS. Notably, here we have a multiple of 1.5 because the unit cells for austenite, ferrite and the MIS as will be shown in Fig. 1 are not primitive.

3. Lattice correspondence between austenite, ferrite and cementite

To unify the phase transitions among austenite, ferrite and cementite, a consistent description of the lattice correspondence is required. This motivates us to seek for a combination of the commonly observed ORs between austenite, ferrite and cementite [21–35]. In reality, the transformation behavior of Fe and C redistribution are always coupled, in particular if cementite is involved. However, in our aim to disentangle the two aspects [namely, the change in Fe lattice and the C redistribution] we artificially remove for a moment all C atoms from the crystal structure of cementite (Fig. 1) and fully relax it (volume, cell shape and atomic positions) using DFT calculations. The optimized structure is for reasons that become clearer below labeled as "MIS" (short for metastable intermediate structure) in Fig. 1(a) and the lattice constants are given in Table 1. Comparing this optimized structure to cementite it can be seen that the overall arrangement of Fe atoms is very similar for the projection in the (001) plane, but significant atomic shifts are observed for the other two projections.

To understand how the MIS relates to austenite and ferrite, we investigate different ORs. For ferrite an orthorhombic cell can be constructed (shown in Fig. 1(b)) with which the correspondence of the atomic positions to those in the MIS becomes clearly visible. This orthorhombic cell of ferrite captures the general idea behind the Bagaryatsky OR [27,35]. For austenite the previously reported ORs between austenite and cementite [31–34] do not provide a suitable unit cell. To achieve a lattice correspondence between austenite and the MIS we construct the orthorhombic unit cell shown in Fig. 1(c). This orientation has to our knowledge not been used before to describe the OR between austenite and cementite, but a similar concept has been used by Pitsch [25] to discuss the OR between austenite and martensite. Comparing the atomic positions of the MIS and the chosen representation of ferrite and austenite as shown in Fig. 1(d), one can already now realize that the MIS does crystallographically act as an intermediate step for the austenite → ferrite transition. This role will be further validated by our simulations below.