



The role of silicon, vacancies, and strain in carbon distribution in low temperature bainite[☆]



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ABSTRACT

We investigated the phenomenon of carbon supersaturation and carbon clustering in bainitic ferrite with atom probe tomography (APT) and ab-initio density functional theory (DFT) calculations. The experimental results show a homogeneous distribution of silicon in the microstructure, which contains both ferrite and retained austenite. This distribution is mimicked well by the computational approach. In addition, an accumulation of C in certain regions of the bainitic ferrite with C concentrations up to 13 at % is observed. Based on the DFT results, these clusters are explained as strained, tetragonal regions in the ferritic bainite, in which the solution enthalpy of C can reach large, negative values. It seems that Si itself only has a minor influence on this phenomenon.

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1. Introduction

The mechanisms behind carbon supersaturation in bainitic ferrite formed at low temperature in steel are still not well understood. Recent atom probe tomography (APT) results showed that as the transformation temperature is decreased, higher amounts of carbon remain after the transformation in solid solution in the bainitic ferrite free of linear and surface defects [1,2]. In fact, the recorded composition profiles revealed that the carbon content in bainitic ferrite, which can be over ten times above that expected from para-equilibrium phase boundaries, is rather homogeneously distributed, indicating that carbon had sufficient time to be

distributed to a state close to a certain kind of equilibrium.

In addition, carbon clusters randomly dispersed throughout the bainitic ferrite matrix with a carbon content of 11–16 at % and no evidence of substitutional solute partitioning were observed [3]. The nature of the carbon atom clustering process seems to be associated with a redistribution of solute to lattice defects, where they might signify the onset of, or precursor to, carbide precipitation during the bainite reaction [4,5].

Scientific efforts to understand the complex distribution of carbon in the ferritic lattice are mainly running into two directions; first, a change in symmetry from the conventional cubic unit cell into a tetragonal lattice, and second, the presence of a high density of defects, particularly vacancies.

Regarding the tetragonality of bainitic ferrite, there are numerous experimental indications so far, evidenced by well-developed techniques such as X-ray diffraction [6,7] and synchrotron radiation [8,9]. Computational simulations [10,11], hand-in-hand with experimental results, advocate that a shift in the *c/a* parameters caused by the presence of carbon changes the equilibrium between austenite and ferrite. This is also indicated by ab initio studies of the individual phases [12,13]. The solution enthalpy of carbon in cubic iron is calculated to be +0.74 eV in an octahedral site in ferrite and −0.17 eV in austenite [12,14], demonstrating the

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low solubility of C in ferrite. However, the solution enthalpy in ferrite increases with compressive strain and decreases with tensile strain [13]. For large strains, it can indeed become negative, as in γ -Fe. These findings support the idea that a tetragonal distortion of the lattice can increase the C solubility, but it also suggests the segregation of the C to defects at which it can find an expanded Fe lattice, e.g. at the core of edge dislocations, or the excess free volume at grain boundaries.

On the other hand, vacancies contribute to the transport of substitutional atoms during bainitic transformation and are also utilized by interstitial solute atoms to flatten their pile-up in the parent phase near the advancing boundary [15]. Specific interstitial lattice sites near the defects in bainitic ferrite provide lower-energy sites for carbon than the regular interstitial lattice positions because of the stress field around these defects [16,17]. Ab initio results show a strong binding energy of C or N with vacancies, whereas a repulsion is observed with self-interstitial atoms [17]. Furthermore, a vacancy can trap up to two C atoms, and a covalent bond forms between them. The ease in formation of a vacancy-carbon pair or a vacancy-carbon complex by the motion of the carbon atom and vacancy under irradiation, deformation, or quenching, has been proven theoretically and experimentally in the Fe–C system [18–22].

Although the formation of C-vacancy complexes in pure Fe is favorable, the situation changes when substitutional alloying elements are involved. The design of modern low-temperature bainitic steels implies a non-negligible amount of Si in the composition (2.5 at.% at a minimum) as the key element to avoid massive carbide precipitation. Contradictory results exist as to whether silicon additions enhance [23] or decrease [24] carbon solubility. In any case they cannot explain the carbon supersaturation levels encountered in low-temperature bainitic ferrite.

In general, ab initio results indicate a repulsive interaction of C with substitutional Si in ferrite [24,25], but the excess solution enthalpy for Fe–C and Fe–Si-strongly depends on the interatomic distance. From the binding energies calculated for the octahedral and tetrahedral positions for C, the activation energy or energy barrier to diffuse the C atom from one octahedral to another octahedral position through the tetrahedral interstitial in a pure Fe system, was determined to be $\Delta E = 0.87$ eV [12,24], which agrees well with experimental results [26,27]. The changes of these energy barriers in the presence of Si lead to the effect that at lower C concentrations, Si diminishes the C diffusivity [25].

Investigations have so far shown that vacancies can increase the solubility of C in bcc iron, but in the case of Si it is questionable. In addition, vacancies and Si reduce the C diffusivity in bcc iron. Both facts are prone to the influence of lattice strain, due to a tetragonal distortion or due to the presence of other defects such as dislocations. In the present study, results of APT investigations of carbon distributions in bainitic ferrite at low transformation temperatures are reported, motivating a detailed ab initio study of the interaction between an interstitial C atom in both bcc and fcc Fe, with and without substitutional Si and an iron vacancy. In addition to the individual cubic phases, we also take into account different tetragonal states along the Bain path.

1.1. Experimental details

The chemical composition of the alloy investigated is 3.1C-2.7Si-1.3Mn-0.1Ni-1.0Cr-0.1Mo at.% (0.7C-1.4Si-1.3Mn-0.1Ni-1.0Cr-0.2Mo wt.%). The bainite start temperature (B_s) and the martensite start temperature (M_s) of the steel are 350 and 120 °C respectively. Samples were isothermally transformed at 220 °C during 24 h after austenitization and subsequently quenched to ambient temperature. The resulting microstructure exhibits a nanocrystalline

bainitic structure, which has been illustrated in previous work [7].

APT needle-shaped samples were cut from the bulk material and electropolished with the standard double-layer and micro-polishing methods. Atom probe analyses were performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory (ORNL) using local electrode atom probes (Cameca Instruments LEAP 2017 and LEAP 4000X HR). The LEAPs were operated in voltage-pulse mode with a specimen temperature of 50 K, a pulse repetition rate of 200 kHz, and a 20% pulse fraction. APT silicon and carbon content values are estimated using proximity histograms across the concentration isosurfaces corresponding to austenite/ferrite interfaces.

1.2. Computational details

Ab-initio density-functional theory (DFT) [28,29] calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) [30,31]. The generalized gradient approximation in the formulation of Perdew, Burke, and Ernzerhof [32] for the exchange correlation effects and the planar-augmented wave method were applied to describe valence-core interactions using an energy cut-off of 450 eV for the basis set. Magnetism was considered in a scalar relativistic fashion, i.e. the net magnetic moments are a result of different occupation of majority and minority spin bands in a spin-polarised DFT calculation. For bcc-Fe $3 \times 3 \times 3$ supercells consisting of 54 Fe atoms, were set up and a $6 \times 6 \times 6$, k-point sampling on a Monkhorst-Pack grid [33] was used. fcc-Fe was simulated in two ways: (1) to study the influence of a tetragonal distortion on the solubility of C, the c/a ratio of the abovementioned bcc supercells were changed at fixed volumes following the Bain path. Here $c/a = \sqrt{2}$ corresponds to the distortion needed in the cubic ferrite phase to build the austenite lattice [34]. Thus, carried out at the corresponding equilibrium volume, this path ends in a relaxed fcc structure. In these calculations the magnetic state was always initialized as ferromagnetic, in a way treating all structures as distorted bcc structures. (2) To investigate in greater detail the influence of magnetism on the solubility of C in austenite, a $2 \times 2 \times 2$ cubic supercell consisting of 32 Fe atoms and a $6 \times 6 \times 6$ k-point mesh were used. A ferromagnetic high-spin (FM-HS) as well as antiferromagnetic (110)-single (AFMS) and antiferromagnetic (100)-double layered (AFMD) magnetic states for fcc-Fe were initialized. Energy-volume data for fcc-Fe in different magnetic states is shown in Fig. 1, which is in good agreement with former

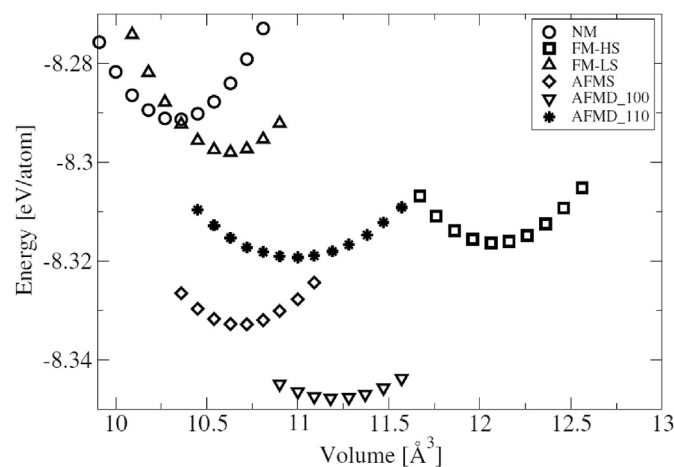


Fig. 1. Ab-initio energies as a function of volume for various magnetic states of austenite-non-magnetic (NM), ferromagnetic high-spin (FM-HS), ferromagnetic low-spin (FM-LS), antiferromagnetic single layer and double layer (AFMS and AFMD).

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