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.

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 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.

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 micropolishing 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.

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 3x3x3 supercells consisting of 54 Fe atoms, were set up and a 6x6x6, 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 2x2x2 cubic supercell consisting of 32 Fe atoms and a 6x6x6 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 Figure 1, which is in good agreement with former atomistic studies [12, 35]. For further calculations of the solubility in the undistorted structures, two configurations were used: The (100) AFMD structure, since it represents the minimum energy structure, as well as the FM-HS structure for discussion of magnetic effects and better comparison to the solubility along the Bain path. As mentioned, for the calculations along the Bain path, all structures were initialized as ferromagnetic. The relaxed parameters for pure Fe are shown in Table 1.

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

Phases	a_0 [Å]	M [μ_B]	B [GPa]
bcc (FM)	2.83	3.00	188
fcc (FM-HS)	3.64	2.57	202
fcc (AFMD)	3.55	1.78	113

Table 1: Relaxed lattice parameter, magnetic moment per atom, and bulk modulus for pure Fe obtained from ab-initio calculations.

Subsequently, one interstitial C atom in an octahedral site and relaxed volume, as well as the atomic positions in the supercell, was added. The same calculation procedure was conducted for the case of one substitutional silicon atom (in fcc and bcc) or two substitutional silicon atoms (in bcc), corresponding to 3.1, 1.8, and 3.6 at.% Si, respectively, or a vacancy. In these cases different C positions were evaluated. In the system containing both a substitutional Si and a vacancy, the most favorable position for the vacancy turned out to be a nearest-neighbor site to the Si. This spatial arrangement was also used for the calculations with interstitial C.

The energy of formation or solution energy of C in these phases was calculated according to equation (1):

$$E_s = E_{Fe_xSi_yC} - E_{Fe_xSi_y} - E_C \quad (1)$$

Where $E_{Fe_xSi_yC}$ is the total energy of the supercell after inserting the C atom, $E_{Fe_xSi_y}$ is the reference Fe-Si phase without carbon in the supercell, and E_C is the energy per C atom in the graphite phase. Other reference states for C could have been chosen for

E_C , leading to a constant shift of all datapoints in Figures 3 and 4. However, such a constant shift does not affect the discussion of the increase or decrease of solution energy due to the presence of vacancies or strain.

Results

APT measurements of C distribution

A carbon atom map of a sample transformed at 220°C for 24 hours in the studied steel is shown in Figure 2. The distribution of carbon atoms in the analyzed volume is not uniform, e.g., carbon-rich and carbon-depleted regions are distinguishable. APT does not provide crystallographic information, but the large carbon-enriched region of the atom map can be assumed to represent an austenitic region since its carbon content is higher than the average value of 3.1 at.%, while the low carbon (<1 at.%) regions correspond to the ferrite phase.

Carbon is heterogeneously distributed in ferrite in the form of small carbon-enriched features, which are identified as carbon clusters. These clusters are revealed by a 3.2 at. % C isoconcentration surface and exhibit a characteristic branchlike structure and a diffuse interface with the bainitic ferrite matrix. The C clusters are ~6-nm thick and have a maximum carbon content of ~13 at.%. The absence of substitutional solute partitioning across interfaces, as shown in the proximity histogram in Fig. 2a, suggests that the clusters are basically a preferential agglomeration of atoms in the bainitic ferrite matrix that form as a result of the redistribution of carbon to lattice defects, rather than a well-defined carbide phase or that form as a consequence of spinodal decomposition [29].

The stated carbon concentration was measured in ferrite regions far away from any defects and interfaces, and is indicated by the box shown in Fig. 2a. The APT results show the presence of a significant amount of carbon in bainitic ferrite, up to 1 at.%, which is consistent with the para-equilibrium phase boundary when ferrite is considered as a body centered tetragonal (bct) structure with ~1.1 at.% C [7].

The proximity histogram across the ferrite/austenite interface in Fig. 2b reveals that the Si concentration is homogeneous, both in the ferrite and austenite, with no partitioning evident at the interface. Redistribution of C atoms between ferrite and austenite is also shown in Fig. 2b. Here, carbon clusters in bainitic ferrite lead to an inhomogeneous carbon distribution in the proximity histogram, as opposed to the plateau obtained in the austenite away from the interface.

Therefore, Si and C distribution trends in nanocrystalline bainitic steels are opposed. Whereas Si distributes homogeneously in both phases, C exhibits a complex, scattered behavior in bainitic ferrite with partitioning at the austenite/ferrite interface. These measurements have been repeated with consistent results.

Fig. 2: APT measurements showing a carbon isoconcentration surface at 3.2 at.% superimposed on the carbon atom map. At this isoconcentration both C clusters and the austenite/ferrite interface are well visible. Proximity histograms across the a) C clusters (determined on isoconcentration surfaces of 5 at.% C) and b) ferrite/austenite interface (determined on isoconcentration surfaces of 3.2 at.% C) indicated by arrows. The carbon concentration reported was measured in austenite and ferrite regions far away from any linear defects and interfaces, indicated by boxes in a) and b).

Calculated energies of solution in ferrite and austenite

To investigate the influence of structure, strain, and composition on the solubility of C in an Fe-Si alloy, two strategies were followed. In a first step, ferrite and austenite were considered separately, with the main goal of investigating the influence of interatomic distance and magnetism on the solution enthalpy. For this, only the 3x3x3 supercell for ferrite, with Si-C distances up to 4.49 Å, was used. For the different antiferromagnetic states of austenite, a 2x2x2 fcc cell is appropriate.

The relaxed lattice parameters of the 3x3x3 different supercells are shown in Table 2. In ferrite, the changes of the lattice parameter are negligible, which shows that our supercells are large enough to consider interstitial C in the dilute limit. However, notice that the cubic symmetry of ferrite is broken whenever C is present. In austenite, with a higher Si and C concentration, the changes in the lattice parameter are also small, but in the AFMD state, the c/a ratio varies significantly with the composition. This can be

understood based on the fact that the interplanar distance is rather sensitive to disturbances in the magnetic state.

Ferrite (bcc)			Austenite (fcc)				
Composition	a [Å]	c/a	Composition	FM-HS		AFMD	
				a [Å]	c/a	a [Å]	c/a
Fe	2.84	1.0	Fe	3.64	1.0	3.55	1.0
Fe ₅₄ C	2.86	1.02	Fe ₃₂ C	3.66	1.0	3.50	1.07
Fe ₅₃ Si	2.84	1.0	Fe ₃₁ Si	-	-	3.47	1.08
Fe ₅₂ Si(vac)	2.83	1.0	Fe ₃₀ Si(vac)	3.59	1.0	3.45	1.08
Fe ₅₃ SiC	2.85	1.02	Fe ₃₁ SiC	3.64	1.0	3.547	1.0
Fe ₅₂ SiC(vac)	2.84	1.02	Fe ₃₀ SiC(vac)	3.60	1.01	3.54/1.06*	1.06/0.97*
Fe ₅₂ Si ₂	2.84	1.0					
Fe ₅₁ Si ₂ C(vac)	2.84	1.01					

Table 2: Relaxed lattice parameters and c/a ratio for various compositions of FM ferrite and high-spin ferromagnetic (HS) as well as AFMD austenite.* In the case of AFMD Fe₃₀SiC with a vacancy, all three lattice parameters are different. The second number indicates the b/a ratio.

The solution energies for an interstitial C atom in the different structures are shown in Fig. 3a for bcc and Fig. 3b for fcc as a function of the Si-C distance. In supercells with an Fe-vacancy, the Si-vacancy distance was kept constant, with the vacancy at a nearest neighbor site of Si. As mentioned above, such a Si-vacancy complex is energetically favorable. Then two interstitial positions for C close to Si (initial distance $d_{\text{Si}} = 1.44$ Å) were taken into account, one neighboring both Si and the vacancy, and one on the opposite side of Si away from the vacancy (marked with an asterisk in legend of Fig. 3a).

Fig. 3 Solution energy of carbon in a) bcc Fe with 0, 1.8, and 3.6 at. % Si, with and without a vacancy. The horizontal dashed line is the carbon solution energy in pure bcc Fe. Compositions marked with an asterisk indicate configurations in which the initial position of C at $d_{Si}=1.44$ Å is on the opposite side of Si as the vacancy and b) fcc Fe with 0 and 3.1 at.% Si, with and without a vacancy, and in different magnetic states (the initial magnetic moment m in units of μ_B is given in the legend). The dashed and dot-dashed horizontal lines represent the solution energies in pure Fe in the FM-HS and the AFMD structures, respectively.

The general trend is the same for both ferrite and austenite structures. The solution enthalpy or energy of formation of C in an octahedral site is significantly enhanced in the vicinity of Si compared to the reference value for C in pure Fe. With increasing distance from the Si atom, the solution enthalpy approaches this reference value. The presence of a vacancy partially compensates the increase in energy due to the silicon, as it can be seen e.g. by comparing the energies of formation at the second nearest neighbor position ($d=1.98$ Å) in ferrite (Fig. 3a). In the austenite phase, the solution enthalpy is generally lower in the high-spin ferromagnetic state.

Coordination and bond lengths

Coordination	System	Bond length [Å]						Energy [eV]
		C-Fe (1)	C-Fe (2)	C-Fe (3)	C-Fe (4)	C-Fe (5)	C-Fe (6)
Fe ₅₄ C	1.77	1.97	1.97	1.77	1.97	1.97	0.72
	Fe ₅₃ SiC	1.76	1.96	1.96	1.84 [#]	1.96	1.96	1.34
	Fe ₅₂ SiCvac	1.43	(vac)	2.07	1.48 [#]	1.51	2.07	1.45
	Fe ₅₁ Si ₂ Cvac	1.60	(vac)	1.51	1.67 [#]	1.51	2.41	1.65
	Fe ₅₂ SiCvac*	1.51 [#]	2.35	2.02	1.48	1.64	2.02	1.03
	Fe ₅₁ Si ₂ Cvac*	1.52 [#]	2.35	2.02	1.48	1.64	2.02	0.97

Table 3: The bond length of the nearest neighbor bonds of C for various compositions of ferrite and C in a nearest neighbor position of Si (corresponding to the first set of data points in Fig. 3a). * C is occupying an octahedral site away from the vacancy and is fully coordinated, [#] indicates a C-Si bond, all others are C-Fe bonds.

For a better understanding of the vacancy effect, the length of the C bonds with nearest neighbor atoms close to Si are summarized in Table 3. Taking Fe₅₄C as the reference, the length of the C-Si bond is higher than the C-Fe1/Fe4 bond. If C is also close to the vacancy, it is lacking one bonding partner, leading to the largest increase in the solution energy. In the cases marked with an asterisk in Table 3, C is occupying the octahedral site away from the vacancy and is fully coordinated, although the lengths of the individual bonds differ quite a bit, the shortest bonds being those to atoms 1 (Si) and 4 (Fe). At this position, the solution enthalpy is reduced compared to those with a missing bonding partner, but also compared to the one in Fe₅₃SiC, i.e., without the vacancy. This analysis shows that the vacancy is increasing the solubility of C in the Fe-Si system by altering the bond lengths in its surrounding rather than by providing a bonding site for C.

Solubility along the Bain path: influence of tetragonality

In a second step, the solution enthalpy of C in a pure Fe (composition Fe_{54}C) and Fe_{53}Si lattice was investigated for different tetragonal distortions along the Bain path. In the supercell containing Si, C was placed far away from the Si atom to obtain maximum solubility. The results are shown in Fig. 4. The c/a ratio was varied while keeping the volume fixed at different reference values, either the equilibrium of the cubic ferrite for the given composition or at the equilibrium volume of the austenite phase for the given compositions. The respective maximum volumetric strain is roughly 4.4% in the Fe-C system and 4% in Fe-Si-C. The solution enthalpy was calculated according to equation (1), where $E_{\text{Fe}_x\text{Si}_y}$ was taken as the reference energy of the structure at the same c/a , i.e., a pre-deformed structure compared to the equilibrium structures listed in Table 1. For calculations at the equilibrium volume of the respective ferrite phase, the structure is relaxed for $c/a=1$ and under strain for all other c/a ratios. In the case of the volume being the respective austenite phase, it is relaxed for $c/a = \sqrt{2}$ and strained for all others. In other words, the solution energies, which have been discussed so far, correspond to those at $c/a = 1$ and the volume of the bcc / ferrite phase (black symbols in Fig. 4), and roughly those at $c/a = 1.4$ and the volume of the fcc / austenite phase (red symbols in Fig. 4). However, the latter differs in composition. The magnetic state was initialized as FM-HS in all calculations, which, as shown above, reduces the energy of formation in the austenite phase.

Figure 4: Solution energy for interstitial C on an octahedral site for different compositions and volumes.

By comparing black and red symbols at $c/a=1$ and $c/a=1.4$ in Fig. 4, it is shown that the presence of volumetric strain lowers the energy of formation dramatically and by looking at the energy difference of open and full symbols of the same color, it becomes obvious that the influence of Si is negligible in comparison. But the most striking result

is that for the calculations carried out at the equilibrium volume of the austenite phase, the minimum solution energy no longer occurs in the cubic austenite phase, but in a tetragonal phase with $c/a = 1.2-1.3$.

Discussion

The APT results show a very homogeneous Si distribution in both the ferrite and austenite phases. Thus, the supercell approximation of the single crystal phases, which represents an ideal, homogeneously distributed Si content of 1.8 to 3.6 at%, is directly comparable to the experimental situation.

In both ferrite and austenite, the minimum energy of formation, which could be found in the calculations by moving C away from Si, was comparable to the one in pure Fe (+0.7 eV in ferrite and slightly negative in austenite, in agreement with literature results [12, 24-27]). Thus, the presence of Si does not seem to increase the solubility of C but rather decreases it. The situation partially changes if a vacancy is included in the supercell of ferrite. Interestingly, it is not the binding of C to a vacancy (which prefers to bind to the Si) that enhances the solubility, but rather a change in bond lengths surrounding the vacancy. In any case, we can find situations where the energy of formation for interstitial C away from both the Si and the vacancy, is lower than in the pure ferrite, but still at a high positive value (+0.6 eV). Nevertheless, from the ab initio calculations, the supersaturation of ferrite with C can only be partially explained by the changes in solubility with Si content in combination with the presence of a vacancy. It might be that the repulsive effect of Si on C leads to complex diffusion paths, which retard the partitioning of C to austenite. This is supported by the results of a combined DFT/Monte Carlo study in the literature [25]. However, from our results of the solution energies with and without Si in austenite, we expect the same retardation in the austenite phase as well, so that in total the effect of Si on the diffusion behavior should not influence the carbon distribution.

The more likely explanation is indeed the tetragonality of the structure, in combination with strain of the overall lattice. As the results of the solubility of 1.8 at.% C along the Bain path show large negative values for the solution energy, a strained, tetragonal lattice can be obtained. The exact c/a at which the solution energy exhibits a minimum will of course depend on the amount of strain as well as the composition. In the example at hand, the absolute value of the solution enthalpy can become an order of magnitude higher than that of C in austenite, removing any driving force for C to re-partition. Furthermore, even if the solution enthalpy should become less negative with increasing C content, C concentrations up to 13 at.% in a distorted ferrite, as observed in the APT measurements, become plausible.

Conclusions

The solubility and distribution of C in a Si-containing bainitic steel have been investigated by APT and DFT calculations. The set-up of the supercells for the calculations mimics the homogeneous Si distribution, which was observed in the APT measurements. The calculations show that Si has a repulsive effect on C, decreasing its solubility in both ferrite and austenite by increasing the enthalpy of solution by a comparable amount. Therefore, a big influence of Si on the partitioning of C via a change in solubility is not expected after bainitic ferrite formation. Vacancies, however, improve the solubility of C in the Fe-Si system by altering the bond lengths in their nearest-neighbor surroundings.

In both the Fe and Fe-Si systems, a tetragonal distortion decreases the solution enthalpy of C, with Si imparting a minor influence on this effect. However, if the distortion is associated with a small superimposed volumetric strain, the effect is quite drastic, making the accumulation of C observed by APT plausible.

Acknowledgements

APT measurements and analyses were conducted at ORNL's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

The authors gratefully acknowledge the support of the Research Fund for Coal and Steel for funding this research under the Contract RFSR-CT- 2012-00017.

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