Atomistic Simulation of Fe-C Austenite

A. Oila*, S.J. Bulla

*School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

* Corresponding author. Tel.: +44 191 222 5357; Fax: +44 191 222 5292
E-mail address: Adrian.Oila@ncl.ac.uk (A. Oila)
Abstract

The free energy minimization method using an embedded atom interatomic potential was employed to predict the atomic configuration of Fe-C austenite. A number of mechanical properties as well as the heat capacity for γ-Fe and Fe-C austenite with various carbon concentrations have been calculated. The results are in good agreement with data available in the literature.

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Keywords: Austenite; EAM; free energy minimisation, mechanical properties
1. Introduction

γ-Fe and the interstitial solid solution of C in γ-Fe known as austenite are normally stable at temperatures above 912°C and 727°C respectively. In steels, Fe-C austenite can be stabilized at room temperature by alloying with austenite-forming elements such as Ni and Mn – the commonly used method for the production of austenitic stainless steels. In hardened steels a fraction of the austenitic phase will remain untransformed after quenching and tempering and this is known as retained austenite. The retained austenite together with the tempered martensite and the iron carbides are the predominant phases in the surface hardened steels which are largely used to manufacture power transmission components such as heavy-duty gears and bearings. On an industrial scale the premature failure of these components due to surface contact fatigue phenomena (micropitting, pitting, spalling) remains an unsolved problem in spite of significant progress made in understanding the mechanisms involved. Despite many years of research an optimum amount of retained austenite for fatigue resistance is unknown as is the configuration of interstitial atoms in austenite. Typically, the retained austenite content in the case of direct carburised steels is between 20 and 30 % which means that a significant part of the applied load will be carried by the austenitic phase. In order to estimate the role played by the retained austenite in surface contact fatigue processes it is necessary to know its mechanical and thermal properties such as elastic modulus, elastic constants, and heat capacity. The calculation of these properties for unalloyed and unstrained austenite would also allow for a better understanding of the influence of alloying elements.
The dimensional distortions due to volume differences between different phases caused by heat treatments in steel components are usually predicted by computational models which require the phase fractions to be known. Based on dilatometry these fractions can be calculated but they require precise lattice parameters for each phase. Because $\gamma$-Fe and Fe-C austenite are not stable at room temperature the reported experimental lattice parameters are usually calculated by extrapolating the lattice parameter measured from austenite in steels either at room temperature or at elevated temperatures. One method (Method 1 in Table 3) to determine the lattice parameter of $\gamma$-Fe consists in extrapolating the lattice parameter at room temperature measured from retained austenite in martensitic steels to zero carbon content [1, 2]. Because these types of measurements are normally performed on quenched steels the retained austenite is heavily strained. Higher lattice parameters are obtained if the measurements are performed on unstrained austenite. These approaches use the measured lattice parameter of austenite in austenitic stainless steels and extrapolate it to zero content of alloying elements [3, 4] (Method 2 in Table 3) or, the measured lattice parameter at elevated temperatures and extrapolated to room temperature [5, 6] (Method 3 in Table 3). Computer simulation provides a route to investigate $\gamma$-Fe and unalloyed and unstrained Fe-C austenite and to determine their lattice parameters and mechanical properties.

In austenite C atoms occupy a limited number of equivalent octahedral interstitial sites in the $\gamma$-Fe lattice situated at the centre and in the middle of the edges of the unit cell. The experimentally observed non-ideal behaviour of the Fe-C austenite solid solution is usually
explained by the site exclusion model [7, 8] which is based on the fact that the repulsion between the carbon atoms reduces the probability that a neighbouring interstitial site is occupied [9]. The proposed models available in the literature are based on the results of Mössbauer spectroscopy measurements coupled with Monte Carlo simulations [10, 11] or ab initio calculations [12-14]. A model in which the carbon atoms can occupy all octahedral interstices without blocking the neighbouring sites has been also proposed [15]. However, to date no agreement on the atomic configuration has been reached. For instance the Fe₈C₁₋ₓ structure proposed as describing the austenite [16] has been found by others [14, 17] to be improbable.

In this work we propose a crystallographic model for Fe-C austenite in steel based on the minimum free energy of the possible configurations within the solubility limit of carbon in γ-Fe. The bulk modulus, B, shear modulus, K, Poisson’s ratio, ν, Young’s modulus, E, elastic constants, Cᵢⱼ, and the heat capacity at constant volume, Cᵥ, have been calculated as a function of carbon content and compared with the values calculated for γ-Fe. Where other data were available, the data calculated in this work were compared with those obtained by other authors.

2. Methods

2.1. Austenite unit cells

The main objective of this work was to calculate the mechanical properties of Fe-C austenite over a range of carbon content. The structure of γ-Fe is face-centred cubic, space group Fm-3m (225) with the lattice parameter a = 3.5730 Å [3] and Wyckoff positions of
the atoms Fe 4a (0, 0, 0). In austenite the carbon atoms occupy the octahedral interstices given by the Wyckoff positions C 4b (0.5, 0.5, 0.5). Because the maximum solubility of carbon in γ-Fe is 8.3 at. % [18] only a limited number of the crystallographically equivalent octahedral interstices can be occupied by carbon. In order to be able to study the mechanical properties of austenite over a range of carbon content we considered a 5 x 5 x 5 γ-Fe supercell in which the minimum carbon concentration of 0.79 at. % is achieved by placing the carbon atoms at the centre and at the midpoints of the edges of the cubic unit cell according to the Wyckoff positions C (0.5, 0.5, 0.5). From all the remaining possible combinations, while keeping the (0.5, 0.5, 0.5) carbon atoms there are only four equivalent atomic positions at which the carbon content do not exceed 8.3 at. %. The atomic positions of carbon atoms and the corresponding carbon concentration are listed in Table 1.

2.2. Embedded atom method and free energy minimisation method

The Embedded Atom Method (EAM) [19] has been successfully applied to metallic systems before [20, 21]. In EAM the electron density is a superposition of the atomic densities and the energy is expressed as a function of the density at the nucleus of an atom, summed over all atoms. The total energy of an atom $i$ is given by

$$E_{\alpha,i} = -A_{\alpha} \left( \sum_{j \neq i} \rho_{j \alpha}(r_{ij}) \right)^{1/2} + \frac{1}{2} \sum_{j \neq i} \phi_{j \alpha}(r_{ij}) \quad (\text{Eq. 1})$$

where $j$ is the nearest neighbour from atom $i$, $\alpha$ is the element type of atom $i$, $\beta$ is the element type of atom $j$, $A_{\alpha}$ is a positive coefficient, $\rho_{j \alpha}(r_{ij})$ is the density contribution of atom $j$ to atom $i$, and $\phi_{j \alpha}(r_{ij})$ is the pair interaction between atom $i$ and its neighbours.
Of a number of empirical potentials available for Fe-C system [22-24] we opted for that developed by Lau et al. [25] because it considers the C-C interactions and it can be applied to Fe-C systems of arbitrary carbon concentrations.

All calculations in this study have been performed using GULP (General Utility Lattice Program) [26]. The geometry of the austenite cells was optimized with respect to the Gibbs free energy by the Newton-Raphson method [27] based on the Hessian matrix calculated from the second derivatives. The Hessian matrix is recursively updated during optimization using the BFGS algorithm (Broyden-Fletcher-Goldfarb-Shanno [28-31]). GULP uses symmetry to restrict geometry optimization to the asymmetric unit variables which significantly improves the speed of calculations. The phonon calculation is performed by integrations across the Brillouin zone using the Monkhorst-Pack scheme [32], in which a grid is specified by the number of points along each axis, with the mesh being offset from the gamma point. The analytical free energy minimization method was recently developed [33] and the analytical derivatives of the free energy have been implemented in GULP [34]. The reader is referred to Ref. [33] and [34] for theoretical details behind the free energy minimization method.

2.3. Calculation of mechanical properties

In general, at the macroscopic scale the correlation between technological properties of materials such as hardness, fatigue and wear resistance and elastic properties such as bulk and shear modulus is empirical in nature. In [38] it has been found that hardness of
annealed alloys is proportional with the shear modulus, $K$. The bulk modulus, $B$ is related to the cohesive energy or the binding energy of the atoms in the crystal [39].

The bulk modulus, $B$ (Eq.2) and shear modulus, $K$ (Eq.3) have been calculated using the Reuss-Voight-Hill convention [35].

$$B = \left( S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23}) \right)^{-1} \quad (Eq. \, 2)$$

$$K = \frac{15}{4(S_{11} + S_{22} + S_{33} - S_{12} - S_{13} - S_{23}) + 3(S_{44} + S_{55} + S_{66})} \quad (Eq. \, 3)$$

where $S_{ij}$ are the components of the elastic compliance matrix.

In engineering the elastic constants are important parameters in design and they are required in the calculations of displacements caused by mechanical or thermal stresses.

The elastic constants represent the second derivatives of the energy density with respect to strain:

$$C_{ij} = \frac{1}{V} \left( \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \right) \quad (Eq. \, 4)$$

The Young’s modulus has been calculated using Eq. 5 [37] and heat capacity at constant volume is calculated using Eq. 6.

$$E = \frac{9BK}{3B + K} \quad (Eq. \, 5)$$

$$C_v = RT \left( 2 \left( \frac{\partial \ln Z_{vib}}{\partial T} \right) + T \left( \frac{\partial^2 \ln Z_{vib}}{\partial T^2} \right) \right) \quad (Eq. \, 6)$$

where $Z_{vib}$ is the vibrational partition function.
3. Results and Discussion

In order to perform the calculations with a sufficient accuracy, we examined the convergence of the Brillouin zone integration scheme to establish the required grid size for all structures presented in Table 1. In Table 2 the Gibbs free energy and the optimized cell parameters at 298 K for a 5 x 5 x 5 $\gamma$-Fe supercell and for five hypothetical austenite structures (see Table 1) are given as a function of the number of $k$ points in the Brillouin zone. Convergence has been achieved for all structures for a grid size 4 x 4 x 4 which gives 20 unique $k$ points in the Brillouin zone.

We used the minimum free energy criterion to choose the most probable configuration. The calculated Gibbs free energies indicate that between structure 3 and 4 the most probable one is number 3 ($G_3 = -5.05$eV/atom, $G_4 = -4.98$eV/atom) and between the structures 5 and 6 the most probable is number 5 ($G_5 = -5.25$eV/atom, $G_6 = -5.22$eV/atom). The austenite cells used for the calculation of the mechanical and thermodynamic properties as a function of carbon content are shown in Fig. 1.

The calculated lattice parameter of $\gamma$-Fe at T=298K is given in Table 3 together with a number of values taken from the literature. Experimental measurements on unstrained austenite and atomistic calculations yield higher values for the lattice parameter. The value calculated in this work is about 3% higher than the average of the values given in Table 3.

The influence of the carbon content, $C_\gamma$ on the lattice parameter of austenite $a_\gamma$ is usually given by an expression of the form

$$a_\gamma = a_0 + k_C C_\gamma \quad \text{(Eq. 7)}$$

where $a_0$ is the lattice parameter of $\gamma$-Fe at 25°C and $k_C$ is the carbon coefficient.
The lattice parameter calculated in our work is plotted versus the carbon content in Fig. 2. A linear fit of these data results in a carbon coefficient $k_C = 0.00567 \text{Å}/(\text{at.}%C)$ which is very close to the experimental value $k_C = 0.00528 \text{Å}/(\text{at.}%C)$ determined in [1].

The values calculated for bulk modulus, $B$, shear modulus, $K$, and Young’s modulus, $E$, are best fitted by 3rd order polynomial functions (Eq.8-10) as shown in Figs. 3-5. The values calculated in our work are in good agreement with those experimentally determined in [39] on a range of austenitic stainless steel: $B = 161$-178 GPa, $K = 75$-81 GPa.

$$B (\text{GPa}) = 0.03 \cdot C_γ^3 - 0.103 \cdot C_γ^2 + 0.505 \cdot C_γ + B_0 \text{ (Eq. 8)}$$

$$K (\text{GPa}) = 0.027 \cdot C_γ^3 - 0.133 \cdot C_γ^2 + 0.442 \cdot C_δ + K_0 \text{ (Eq. 9)}$$

$$E (\text{GPa}) = 0.087 \cdot C_γ^3 - 0.4 \cdot C_γ^2 + 2.139 \cdot C_γ + E_0 \text{ (Eq. 10)}$$

The heat capacity at constant volume $C_v$ varies linearly with the carbon content (Fig. 6) according to the following relation:

$$C_v (\text{J/mol·K}) = 22.738 + 0.139 \cdot C_γ \text{ (Eq. 11)}$$

The values of the heat capacity calculated in this work lie in a range of experimental data obtained on austenitic steels 21.94 J/mol·K [40] and 26.16 J/mol·K [41].

The Poisson’s ratio varies from $\nu = 0.346$ for $\gamma$-Fe, $\nu = 0.344$ for austenite with 0.79 at. % C, $\nu = 0.336$ for austenite with 5.30 at. % C to $\nu = 0.330$ for austenite with 6.71 at. % C, a range of values normally reported for steels.

The elastic constants, $C_{11}$, $C_{12}$ and $C_{44}$ are presented in Table 4. The values calculated in our work are in good agreement with experimental values determined on single crystals stainless steel [41] $C_{11} = 204.6$ GPa, $C_{12} = 137.7$ GPa, $C_{44} = 126.2$ GPa.
4. Conclusions

Free energy minimization method has been employed to determine the atomic configuration in Fe-C austenite with three different carbon concentrations. Based on the minimum free energy the most probable structures of Fe-C austenite have been determined. The influence of carbon content on the lattice parameter of austenite has been estimated by the carbon coefficient \( k_C = 0.00567 \, \text{Å/(at.%C)} \) a value very close to the experimental value \( k_C = 0.00528 \, \text{Å/(at.%C)} \).

The values determined for the bulk modulus, \( B \), shear modulus, \( K \), elastic modulus, \( E \), Poisson’s ratio, \( \nu \), and the heat capacity at constant volume, \( C_v \), show good agreement with experimentally determined values. Equations describing the influence of carbon concentrations on the properties mentioned above have been derived.

The results generated in this work can be used in mesoscale simulations of steels and the authors intend to apply these results to simulate microstructure evolution due to surface contact fatigue [43-44]. As mentioned in the Introduction, surface contact fatigue phenomena in engineering applications, such as gears and rolling element bearings lead to the premature failure of the affected components. The change in the material structure that causes this kind of failure involves a number of phenomena such as plastic deformation, carbide precipitation, decomposition of retained austenite which makes the study of microstructure evolution a complex subject. Atomistic methods such as the one presented here can be employed to calculate fundamental properties such as elastic constants and thermodynamic parameters of different phases. The properties obtained in this way can
then be used as input in simulations performed at the continuum scale to find failure criteria based on microstructure evolution by simulating the propagation of fatigue cracks within the newly formed microstructure.
References


Figure Captions

Fig. 1. Unit cells of Fe-C austenite: (a) Fe$_{125}$C (0.79 %C); (b) Fe$_{125}$C$_7$ (5.30 %C); (c) Fe$_{125}$C$_9$ (6.71 %C).

Fig. 2. Lattice parameter of Fe-C austenite as a function of carbon content. The carbon coefficient determined from the linear fit is $k_c=0.0025 \text{ nm/}(\% \text{ wt. C})$.

Fig. 3. Bulk modulus as a function of the carbon content.

Fig. 4. Shear modulus as a function of the carbon content.

Fig. 5. Young’s modulus as a function of the carbon content.

Fig. 6. Heat capacity as a function of the carbon content.
## Table 1. The atomic positions of carbon atoms in austenite unit cells considered in this study

<table>
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<th>No</th>
<th>Structure</th>
<th>Atomic positions</th>
<th>at. % C</th>
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<tr>
<td>1</td>
<td>γ-Fe</td>
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</tr>
<tr>
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<tr>
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<td></td>
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<td>Fe$<em>{125}$C$</em>{7}$</td>
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</tr>
<tr>
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<td></td>
<td>(0.1, 0.5, 0.5)</td>
<td></td>
</tr>
<tr>
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<td>Fe$<em>{125}$C$</em>{9}$</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>(0.1, 0.1, 0.1)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Fe$<em>{125}$C$</em>{9}$</td>
<td>(0.5, 0.5, 0.5)</td>
<td>6.71</td>
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<tr>
<td></td>
<td></td>
<td>(0.3, 0.3, 0.3)</td>
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Table 2. The Gibbs free energy, $G$, and the lattice parameter, $a$, as a function of the number of $k$ points for the structures considered.

<table>
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<th>$k$ points</th>
<th>$G$ (eV/atom)</th>
<th>$a$ (Å)</th>
<th>$G$ (eV/atom)</th>
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Table 3. Lattice parameter of strained and unstrained γ-Fe.

<table>
<thead>
<tr>
<th>Method 1</th>
<th>Method 2</th>
<th>Method 3</th>
<th>Atomistic simulation</th>
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<td>Ref.</td>
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Table 4. Elastic constants of γ-Fe and Fe-C austenite of various carbon content.

<table>
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<tr>
<th>Structure</th>
<th>% at C</th>
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<th>$C_{12}$ (GPa)</th>
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<td>Fe$_{125}$C$_7$</td>
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<td>Fe$_{125}$C$_9$</td>
<td>6.71</td>
<td>248.31</td>
<td>122.69</td>
<td>103.16</td>
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Figures

Fig. 1. Unit cells of Fe-C austenite: (a) Fe\textsubscript{125}C (\(C_\gamma=0.79\) at. % C); (b) Fe\textsubscript{125}C\textsubscript{7} (\(C_\gamma=5.30\) at. %); (c) Fe\textsubscript{125}C\textsubscript{9} (\(C_\gamma=6.71\) at. %).
Fig. 2. Lattice parameter of Fe-C austenite supercell as a function of the carbon content. The carbon coefficient determined from the linear fit is \( k_c = 0.00567 \text{ Å/(at. % C)} \).
Fig. 3. Bulk modulus as a function of the carbon content.
Fig. 4. Shear modulus as a function of the carbon content.
Fig. 5. Young’s modulus as a function of the carbon content
Fig. 6. Heat capacity as a function of the carbon content.