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Carbon–Carbon Interactions in Iron

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ABSTRACT

Carbon atoms occupy interstitial sites in iron so that the configurations of any solid–solution at constant composition depend solely on the distribution of carbon atoms on the interstitial sub–lattice, this in turn being influenced by interactions between carbon atoms in close proximity. The carbon–carbon interaction energy, which influences the distribution of carbon atoms, is reviewed with a view to understanding the nature of the interaction and to highlight some recent developments in the subject. It appears that the C–C interaction energy for ferrite cannot be deduced from the thermodynamic data currently available, primarily because of the very low solubility of carbon in ferrite. On the other hand, there is ample evidence to support the view that the corresponding energy for austenite is consistent with a strong repulsion between near neighbour pairs of carbon atoms.

INTRODUCTION

There are no solutions of iron which are ideal. The iron–manganese liquid phase is close to ideal, though even that has an enthalpy of mixing which is about $-860\,\mathrm{J\,mol^{-1}}$ for an equiatomic solution at 1000 K, which compares with the contribution from the configurational entropy of about $-5800\,\mathrm{J\,mol^{-1}}$. A finite enthalpy of mixing implies that at 0 K the atoms are not indifferent to their neighbours, but rather that there is a preference to associate with like or with unlike neighbours.

No solutions of iron can therefore be expected to be truly random and this applies also to the iron–carbon interstitial solutions. However, a particular feature of an interstitial solution is that the number of Fe–Fe and Fe–C pairs does not change for a given composition for all configurations. The configurational change (at fixed composition) is related solely to the distribution of carbon atoms on the interstitial sub–lattice. This is why the interactions between carbon atoms themselves become important, since they determine the probability whether a site adjacent to another carbon atom can be occupied.

The purpose of this paper is to review and assess these carbon–carbon interactions in both austenite (γ) and ferrite (α). For the sake of completeness, the interaction of carbon with high–entropy defects (*i.e.* atomic scale defects such as vacancies and interstitials *etc.*) is also reviewed.

SOLUTION THERMODYNAMICS

One method for studying the configuration of atoms in a solution is to compare experimental data against a solution model. An ideal solution is one in which the enthalpy of mixing is zero so that the only contribution to the free energy of mixing comes from the change in configurational entropy when atoms mix at random (Table 1). The regular solution model assumes, as an approximation, a random distribution of atoms even though the enthalpy of mixing is not zero. In reality, a random solution is only expected at very high temperatures when the entropy term overwhelms any tendency for ordering or clustering of atoms. It follows that the configurational entropy of mixing must vary with the temperature.

The *quasi–chemical* solution model has a better treatment of configurational entropy which accounts for a non–random distribution of atoms and the required variation in the degree of randomness with temperature. It is capable of dealing with biased solutions. For this reason we shall focus on just the quasichemical model and introduce it briefly, focusing on aspects relevant to the present purpose.†

Solution model	Entropy of mixing ΔS_M	Enthalpy of mixing ΔH_M
Ideal	Random	0
Regular	Random	$\neq 0$
Quasichemical	Not random	$\neq 0$

Table 1: Elementary thermodynamic properties of solution models

It is useful to rigorously define the carbon–carbon interaction energy ω in the context of the quasichemical theory. The derivation of the partition function as presented below is due to McLellan and Dunn [2,3]. As stated earlier, the number of Fe–Fe pairs and the number of Fe–C pairs does not change for a given composition for all configurations. The partition function can therefore be described solely in terms of the carbon atoms u in the interstitial sites (u_o).

Consider a system with N_u carbon atoms, N_{Fe} iron atoms and therefore, βN_{Fe} octahedral sites where β is the number of octahedral interstices per iron atom; $\beta = 1$ for octahedral holes in austenite and $\beta = 3$ for octahedral interstices in ferrite, Fig. 1. The variety of pairs of species is listed in Table 2, where the number of u–u_o and u_o–u pairs is written $W\lambda$ where W is the number of octahedral sites around a single such interstice ($W = 12$ for austenite and $W = 4$ for ferrite). Naturally, W is identical for an octahedral hole and for the carbon that resides in those holes.

The configurational partition function using the data listed in Table 2 is, therefore,

$$\Omega = \sum_{\lambda} g_{\lambda} \exp\left\{ -W \left[\lambda \epsilon_u + \frac{N_u - \lambda}{2} \epsilon_{uu} \right] / kT \right\} \tag{1}$$

For a given value of λ, the different non–interacting pairs of atoms can be arranged in the

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† The first approximation of the quasichemical model permits a non–random distribution of carbon atoms but relies on the absence of interference between atom–pairs. Better approximations can be obtained by considering larger clusters of atoms. Such calculations belong to the "cluster variation" method proposed originally by Kikuchi [1]. The improvements obtained with these higher approximations are usually rather small except in ordered systems, so we shall deal only with the first approximation.

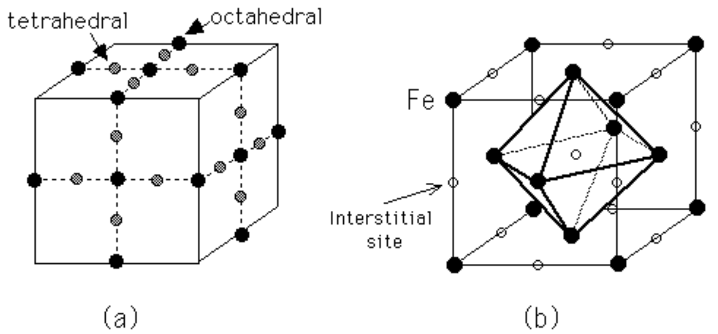

Fig. 1: Interstices in ferrite and in austenite. Carbon mainly occupies the octahedral interstices in both cases. (a) One unit cell of body–centered cubic ferrite. The iron atoms are not illustrated for clarity, just the octahedral and tetrahedral interstices. (b) Octahedral interstices in a unit cell of austenite.

Kind of pair	No. of such pairs	Energy per pair	Total energy
u_o–u_o	$\frac{1}{2}W(N_{Fe}\beta - N_u - \lambda)$	0	0
u_o–u and u–u_o	$W\lambda$	ϵ_u	$W\lambda\epsilon_u$
u–u	$\frac{1}{2}W(N_u - \lambda)$	ϵ_{uu}	$\frac{1}{2}W(N_u - \lambda)\epsilon_{uu}$
Total	$\frac{1}{2}WN_{Fe}\beta$		$W\left[\lambda\epsilon_u + \frac{N_u-\lambda}{2}\epsilon_{uu}\right]$

Table 2: Pair interactions in Fe–C quasichemical model (after McLellan and Dunn [2]). The energy zero is for an atom at rest in a vacuum so that the energies listed are numerically negative. Carbon atoms and octahedral vacancies are referred to as u and u_o respectively. Therefore, $u - u_o$ refers to a carbon atom – octahedral interstitial vacancy pair.

following number of ways:

$$g_\lambda \propto \frac{[\frac{1}{2}WN_{Fe}\beta]!}{\underbrace{[\frac{1}{2}W(N_{Fe}\beta - N_u - \lambda)]!}_{u_o-u_o}\ \underbrace{[\frac{1}{2}W(N_u - \lambda)]!}_{u-u}\ \underbrace{[\frac{1}{2}W\lambda]!\ [\frac{1}{2}W\lambda]!}_{u-u_o \text{ and } u_o-u}} \tag{2}$$

The degeneracy gives the number of states with the same energy.

It is usual to convert this proportionality into an equality by using a normalisation procedure which considers the degeneracy of a completely random solution, for which λ has the value λ^* given by the product of the number of solute atoms (N_u) and the chance of finding an unoccupied octahedral site:

$$\lambda^* = N_u\left(1 - \frac{N_u}{N_{Fe}\beta}\right) \tag{3}$$

Therefore,

$$\begin{aligned} g_\lambda = &\frac{[N_{Fe}\beta]!}{[N_{Fe}\beta - N_u]!\ N_u!} \\ &\times \frac{[\frac{1}{2}W(N_{Fe}\beta - N_u - \lambda^*)]!\ [\frac{1}{2}W(N_u - \lambda^*)]!\ [\frac{1}{2}W\lambda^*]!\ [\frac{1}{2}W\lambda^*]!}{[\frac{1}{2}W(N_{Fe}\beta - N_u - \lambda)]!\ [\frac{1}{2}W(N_u - \lambda)]!\ [\frac{1}{2}W\lambda]!\ [\frac{1}{2}W\lambda]!} \end{aligned} \tag{4}$$

The partition function Ω is now solved, but to proceed and obtain some useful thermodynamic quantities, we follow the normal approximation which is to replace the summation in equation 1 by the largest term corresponding to $\lambda = \overline{\lambda}$, which can be obtained by differentiation with respect to λ:

$$\overline{\lambda} = \frac{N_{Fe}\beta}{2\phi}\left\{1 - \left[1 - 4\phi\frac{\theta}{\beta}\left(1 - \frac{\theta}{\beta}\right)\right]^{\frac{1}{2}}\right\} \tag{5}$$

where $\theta = N_u/N_{Fe}$,

$$\phi = 1 - \exp\left\{\frac{-\omega}{kT}\right\} \tag{6}$$

and $\omega = \epsilon_{uu} - 2\epsilon_u$ is the **carbon–carbon interaction energy**.

The partition function now becomes

$$\begin{aligned} \Omega = &\frac{[N_{Fe}\beta]!}{[N_{Fe}\beta - N_u]!\ N_u!} \\ &\times \frac{[\frac{1}{2}W(N_{Fe}\beta - N_u - \lambda^*)]!\ [\frac{1}{2}W(N_u - \lambda^*)]!\ [\frac{1}{2}W\lambda^*]!\ [\frac{1}{2}W\lambda^*]!}{[\frac{1}{2}W(N_{Fe}\beta - N_u - \overline{\lambda})]!\ [\frac{1}{2}W(N_u - \overline{\lambda})]!\ [\frac{1}{2}W\overline{\lambda}]!\ [\frac{1}{2}W\overline{\lambda}]!} \\ &\times \exp\left\{-W\left[\overline{\lambda}\epsilon_u + \frac{N_u - \overline{\lambda}}{2}\epsilon_{uu}\right]/kT\right\} \end{aligned} \tag{7}$$

which clearly reduces to a partition function for a random solution when $\overline{\lambda} = \lambda^*$. This can happen when the temperature is very high so that thermal agitation mixes up the atoms irrespective of their binding tendencies. The configurational free energy F and chemical potential (μ) follow:

$$F = -kT\ln\{\Omega\} \tag{8}$$

$$\mu = -kT\ln\left\{\frac{\partial\ln\{\Omega\}}{\partial N_u}\right\}_{N_{Fe},T} \tag{9}$$

After some very lengthy algebra [4], it is possible to show that the activity of carbon relative to pure graphite as the standard state is given by

$$\begin{aligned} a_u = &\frac{\theta/\beta}{1 - (\theta/\beta)}\exp\left\{\frac{\Delta\mu_C^o}{kT}\right\} \\ &\times\left\{\frac{\theta}{\beta}^{\frac{2\theta}{\beta}}\left[\frac{\theta}{\beta} - \left(\frac{\theta}{\beta}\right)^2\right]^{1-\frac{2\theta}{\beta}}\left[1 - \frac{\theta}{\beta} - \left(\frac{\overline{\lambda}}{N_{Fe}\beta}\right)\right]^{\frac{1}{2}(1+\dot{\overline{\lambda}})}\right\}^{-W} \\ &\times\left\{\left[\frac{\overline{\lambda}}{N_{Fe}\beta}\right]^{\dot{\overline{\lambda}}}\left[\frac{\theta}{\beta} - \frac{\overline{\lambda}}{N_{Fe}\beta}\right]^{\frac{1}{2}(1-\dot{\overline{\lambda}})}\left[1 - 2\frac{\theta}{\beta} + \left(\frac{\theta}{\beta}\right)^2\right]^{1-\frac{\theta}{\beta}}\right\}^{W} \\ &\times\exp\left\{\frac{(1-\dot{\overline{\lambda}})W\omega}{2kT}\right\} \end{aligned} \tag{10}$$

where

$$\dot{\overline{\lambda}} = \frac{\partial \overline{\lambda}}{\partial N_u} = \frac{1 - 2(\theta/\beta)}{[1 - 4\phi(\theta/\beta) + 4\phi(\theta/\beta)^2]^{\frac{1}{2}}}$$

and $\Delta\mu^o_C$ is the change in free energy accompanying the transfer of carbon from its standard state of graphite to a standard state based on an infinitely dilute solution as the reference state (it is also called the *relative* partial free energy of a solute atom in solution with respect to the pure solute at infinite dilution). The value of $\Delta\mu^o_C$ is determined experimentally from thermodynamic data measured at sufficiently low concentrations.

Notice that the carbon–carbon interaction energy pervades this equation both directly as ω and also via $\overline{\lambda}$ and $\dot{\overline{\lambda}}$. Relationships like equation 10 have been used with experimentally measured activities of carbon in austenite and ferrite, together with measured values of $\Delta\mu^o_C$ to determine ω. There is general agreement that the carbon–carbon interaction energy in austenite is $\omega_\gamma \simeq 8250\,\mathrm{J\,mol^{-1}}$, giving a repulsion between near neighbour carbon atoms [3].

The problem for ferrite is more complicated. Equation 10 is a recent development [4], which corrects earlier work [2,3] in which the activity function was different:

$$\begin{aligned} a_u =& \frac{\theta/\beta}{1 - (\theta/\beta)} \exp\left\{\frac{\Delta\mu^o}{kT}\right\} \\ & \times \left(\frac{\theta/\beta}{1 - (\theta/\beta)}\right)^{-W} \left(\frac{1 - (\theta/\beta) - (\overline{\lambda}/N_{Fe}\beta)}{(\theta/\beta) - (\overline{\lambda}/N_{Fe}\beta)}\right)^{\frac{-W}{2}} \exp\left\{\frac{W\omega}{2kT}\right\} \end{aligned} \tag{11}$$

On the basis of this equation 11, ω_α is found to be very large, probably greater than $150000\,\mathrm{J\,mol^{-1}}$ [5,6]. However, both studies [5,6] reported large and unsystematic variations in the value of ω_α as a function of different experimental data†

The corrected quasichemical theory (equation 10) in fact compounds the problem of deducing ω_α. Whereas in equation 11 the activity (even at small concentrations) is a significant function of ω_α, this is not the case for equation 10. This can be seen from the behaviour of $\overline{\lambda}$ and $\dot{\overline{\lambda}}$ at small concentrations. As $\theta \rightarrow 0$, $\overline{\lambda} \rightarrow N_{Fe}\beta$ and $\dot{\overline{\lambda}} \rightarrow 1$. Equation 10 therefore ceases to be a function of ω_α, but equation 11 does not because the extreme right–hand exponential terms are different:

$$\text{Eq. 10:} \qquad \exp\left\{\frac{(1 - \dot{\overline{\lambda}})W\omega}{2kT}\right\} \qquad\qquad \text{Eq. 11:} \qquad \exp\left\{\frac{W\omega}{2kT}\right\}$$

For equation 10 this exponential term tends to zero via $(1 - \dot{\overline{\lambda}})$ as $\theta \rightarrow 0$ whereas this is not the case for equation 11.

The sad conclusion is that it is not possible, using the very low carbon concentration data available for ferrite, to deduce the value of ω_α if the correct quasichemical model is used. On the other hand, this must be a reasonable common sense conclusion since the probability of finding a pair of carbon atoms in close proximity also vanishes as the concentration tends to zero. Thus, for carbon in ferrite, it does not seem relevant to worry about the magnitude of the interaction. This may not, of course, be the case for supersaturated solutions of carbon

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† It has been believed that ω_α may be negative *i.e.* that carbon atoms in ferrite attract each other [7]. However, the analysis used an incorrect coordination number [5].

in ferrite, such as in martensitic transformations, but no acitivity measurements have been conducted for those solutions (supersaturated solutions of carbon are not stable).

REPULSION BETWEEN CARBON ATOMS IN SOLUTION

There are good reasons why there should be a large difference between the measured C–C interaction energy in austenite and in ferrite. It is well established that $\omega_\gamma = 8250\,\mathrm{J\,mol^{-1}}$ or 0.086 eV per C–C pair [3] and we *assume* for the moment that $\omega_\alpha > 150,000\,\mathrm{J\,mol^{-1}}$ or 1.54 eV per C–C pair.

It has been deduced from the properties of graphite that the short–range *repulsive component* of the C–C interaction can be written [8,9]

$$U_{rep} = 1856\exp(-35.75r) \qquad \mathrm{eV} \tag{12}$$

per C–C interaction at distance r in nm. The closest approach distance of carbon atoms in austenite is 0.252 nm, giving $U_{rep} = 0.23$ eV per pair. The closest approach distance of carbon atoms in ferrite is 0.143 nm, giving $U_{rep} = 11.0$ eV per pair. Notice that these values are not intended as a direct comparison with w, which is a net interaction energy. But it is clear that the reason why ω_α is so much greater than ω_γ is the much shorter near neighbour C–C distance in ferrite.

Equation 12 is derived for graphite, where the C–C spacing between planes is large (0.335 nm) and it refers to the residual repulsion when the bonding molecular orbitals of the carbon atoms are filled. The equation should not be structure dependent provided that the carbon orbitals are saturated, as they probably are for carbon in transition metals. However, the expression strictly applies at large C–C distances. While in principle, there could be a very close distance of approach in ferrite (0.143 nm), in practice the C atoms are never likely to get as close as that. They are a good deal apart even in cementite.

The carbon atoms can, however, get very close (*e.g.* 0.127 nm) in certain transition metal carbides [9]. This happens when there is direct carbon–carbon covalent bonding, similar to that in diamond and within the basal planes of graphite, where the bond length is just 0.13 nm. In the unlikely event that the carbon atoms get as close as this in ferrite, then the expression for U_{rep} would have to be used alongside a very strong molecular bonding term. There is, of course, much evidence to the contrary, that carbon atoms are not bonded together, for example from the very high mobility of carbon in ferrite.

There is no evidence for molecular bonding between carbon atoms in ferrite. It appears therefore that the much larger C–C interaction energy of ferrite is probably due to the smaller spacing of adjacent interstitial sites in ferrite than in austenite. For all intents and purposes, carbon atoms should not ever be expected to occupy adjacent interstitial sites in ferrite.

MÖSSBAUER SPECTROSCOPY

We have seen that the pairwise C–C interaction energy in austenite, $\omega_\gamma = \epsilon_{uu} - 2\epsilon_u$, features prominently in the quasichemical models for Fe–C solutions. It determines the distribution of carbon atoms in solution. Its specific value to some extent depends on the nature of the quasichemical model that is used to interpret measured activity data, but it is generally accepted that carbon atoms in austenite repel with $\omega_\gamma \simeq 8250\,\mathrm{J\,mol^{-1}}$ [3].

Mössbauer spectroscopy can be used to study more directly, the distribution of carbon atoms relative to an iron atom. The measured probabilities of different kinds of clusters of atoms can then be compared against Monte Carlo simulations to deduce interaction energies [10,11].

The Mössbauer data show that it is necessary to consider four kinds of Fe–C configurations (Fig. 2): iron atoms which do not have neighbouring carbon atoms; an iron atom with a single near neighbour carbon atom; an iron atom with two neighbouring carbon atoms in a 180° configuration; an iron atom with two neighbouring carbon atoms in a 90° configuration. The pair of carbon atoms in the 90° configuration are near neighbours whereas those in the 180° configuration are next–near neighbours. A surprising result is that the repulsion between near neighbour carbon pairs is smaller than that between next–near neighbours. The mechanism for this apparently strange behaviour, which is not found for nitrogen–nitrogen pairs, does not seem to have been considered.

Oda *et al.* [10] compared the local interaction energies derived from Mössbauer results, with the global value obtained by applying quasichemical theory to thermodynamic data, by taking a weighted average:

$$W\omega_\gamma \simeq W\omega_\gamma^{(1)} + W_2\omega_\gamma^{(2)}$$

where, as usual, $W = 12$ is the number of C–C near neighbour pairs that can form about one C atom whereas $W_2 = 6$ is the number of C–C next near neighbour pairs that can form about one C atom. $\omega_\gamma^{(1)}$ and $\omega_\gamma^{(2)}$ are the C–C interaction energies for the 90° and 180° configurations respectively. As shown in Table 3, the Mössbauer and quasichemical data compare well except for nitrogen where there is some uncertainty in the thermodynamic data.

	Mössbauer Results			Quasichemical
	$\omega_\gamma^{(1)}$	$\omega_\gamma^{(2)}$	$\omega_\gamma \simeq (W\omega_\gamma^{(1)} + W_2\omega_\gamma^{(2)})/W$	ω_γ
C–C	3500	7333	7167	$\simeq$ 8000
N–N	8167	1000	8667	$\simeq$ 4000

Table 3: Comparison of the overall interaction energy between interstitial atoms determined from the Mössbauer method (column 4) against values derived using quasichemical models (column 5). The energies are in J mol^{-1} (after Oda *et al.*, [10]).

IMPLICATIONS ON DIFFUSION

The diffusion coefficient of carbon in austenite increases by a factor of five as the concentration changes from 0 to 0.05 mole fraction [12,13]. It is well established that this effect cannot be explained in terms of the usual Darken type thermodynamic factors common in diffusion theory [14–16]. In fact, the repulsive forces between the carbon atoms affect the migration of the carbon in a differential manner with respect to motion up or down a gradient of concentration. The carbon–carbon repulsion thereby enhances diffusion down a gradient, to an extent greater than would be expected from normal diffusion theory [14–16]. This effect has been thoroughly modelled and verified quantitatively for austenite, where large gradients can arise, but not in ferrite where the small solubility of carbon greatly limits the development of concentration gradients.

CLUSTERING OF INTERSTITIAL ATOMS

Any suggestion of the clustering of carbon atoms seems to contradict all the previous discussion which indicates that neighbouring carbon atoms repel. We shall see, however, that longer range

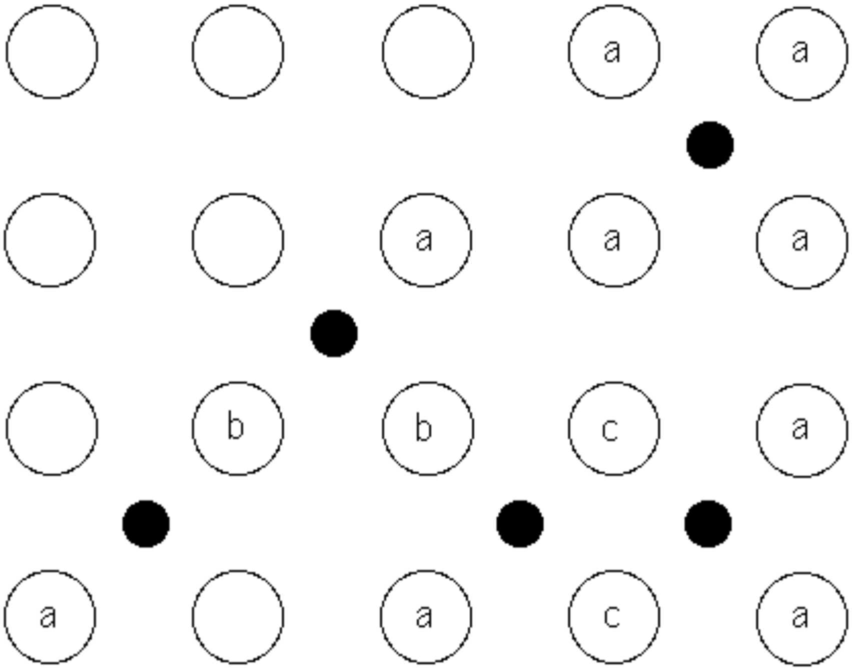

Fig. 2: An illustration of the distribution of carbon atoms (dark) on a single $\{0\ 0\ 1\}_\gamma$ plane of austenite. a represents an iron atom with a single carbon neighbour, b the case where Fe has two C atoms forming a 180° configuration, and c where Fe has two C atoms in a 90° configuration.

interactions make it possible to have a variety of conglomerates of interstitial atoms but with large spacings between the atoms.

The random chance of interstitial atoms occupying adjacent sites is proportional to x^2 where x is the mole fraction of interstitial atoms. In ferrite the adjacent sites are so close $(a_\alpha/2)$† that electrostatic, thermodynamic and elastic strain considerations completely exclude them from occupation. In austenite the nearest approach distance for a pair of interstitials is bigger (a_γ) so that adjacent sites can indeed be occupied, but the probability is much less than expected in a random solution because of repulsion between the carbon atoms. Associations between interstitial atoms have been studied intensively for ferrite. This is because the interstices located at $<0\ 0\ \frac{1}{2}>$ and $<0\ \frac{1}{2}\ \frac{1}{2}>$ all have tetragonal symmetry with their tetragonal axes lying along the edges of the body–centred cubic unit cell of ferrite. Carbon atoms which might initially be distributed at random amongst the three kinds of site tend to order under the influence of external stress as one of the three sets of sites becomes distorted by the stress in a manner which makes it easier to accommodate the carbon. This stress–induced ordering causes the Snoek effect in which the damping of vibrations by the migration of atoms between sites can be used to estimate the mobility and concentration of dissolved carbon. A similar effect does not exist in austenite where all the octahedral interstices (which have cubic symmetry) are equivalent even under the influence of an external load. Consequently, the only information available about the distribution of carbon in austenite comes from thermodynamic analysis or Mössbauer spectroscopy.

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† a_α and a_γ are the lattice parameters of ferrite and austenite respectively.

The clustering of nitrogen and carbon in ferrite has been studied in great detail using methods which model the strain energy caused by the interstitial. These methods range from macroscopic elasticity [17] to those in which the strain energies are calculated using interatomic potentials. We shall focus on the latter which ought to be more reliable since the distortions involved far exceed the assumptions of linear elasticity theory. Before discussing the results, it is worth emphasizing that clusters involving near–neighbour pairs are impossible in ferrite; the calculations therefore refer to more distant pairs of atoms of the type illustrated in Fig. 3. And the results rely on strain interactions alone, without taking into account possible electrostatic effects given that the interstitials are positively charged when in iron.

Strain interactions undoubtedly support a tendency for the interstitials to cluster [18–21]; carbon and nitrogen are, in this respect, similar. The calculated cluster binding energies are found to be insensitive to the carbon concentration in martensite. In ferrite, the dicarbon, tricarbon and tetracarbon binding energies have been estimated to be about 0.13, 0.36 and 0.66 eV respectively, with the binding energies for even larger clusters increasing by 0.31 eV per additional atom. The clusters are predicted to form very thin plates on $\{0\ 0\ 1\}$ planes with the carbon atoms in octahedral sites. These large clusters can even be imagined to migrate but obviously with a large activation energy, via a mechanism involving the movement of atoms about the periphery of the plates.

There is some experimental evidence for the existence of carbon atom clusters in ferrite, and even for their diffusion as groups of atoms. Keefer and Wert [22,23] studied the stress–induced ordering of interstitials in ferrite and were able to detect the clustering of interstitial atoms. They found that at low temperatures ($\simeq 250\,\mathrm{K}$) the vast majority of nitrogen or carbon atoms in ferrite are isolated from each other. However, about 5% were found to be associated as pairs or even triplets. The binding energies for carbon and nitrogen pairs were estimated to be about 0.08 eV and 0.065 eV respectively, which are in very good agreement with the calculations by Johnson *et al.* [19]. For triplets, the corresponding binding energies were found to be 0.26 eV and 0.22 eV for carbon and nitrogen respectively. The mobility of clusters must naturally be smaller than that of individual atoms since their diffusion requires either the coordinated movement of the constituent atoms, or the breaking and reforming of the groups.

Keefer and Wert's experiments measured the damping of vibrations so it was not possible to obtain a precise definition of the clusters. They presumably do not involve nearest neighbour pairs but clusters with the interstitials spaced at a_α.

Referring again to Fig. 3, for the carbon pairs illustrated in (a) and (b), the strain fields of the atoms in each pair are parallel. The pair of carbon atoms in (a) or (b) could both translate to the right by $a_\alpha/2$ [19]. Such motion would reorient the strain fields in both cases and so could be detected in an internal friction experiment. For case (c), the two carbon atoms are in sites whose tetragonal axes are perpendicular to start with and this would remain the case after diffusion; such motion could not significantly contribute to internal friction and hence may not be detected in Keffer and Wert's experiments.

ASSOCIATION OF CARBON WITH DEFECTS

Much of the information on the migration of carbon atoms associated with defects such as iron vacancies and interstitials comes from experiments on irradiated iron. There are in addition, some revealing calculations using interatomic potentials to simulate the defect–clusters and their mechanisms of migration. The formation of complexes has implications in technology, because the trapping of solutes at defects can sometimes retard the precipitation of deleterious phases in irradiated materials.

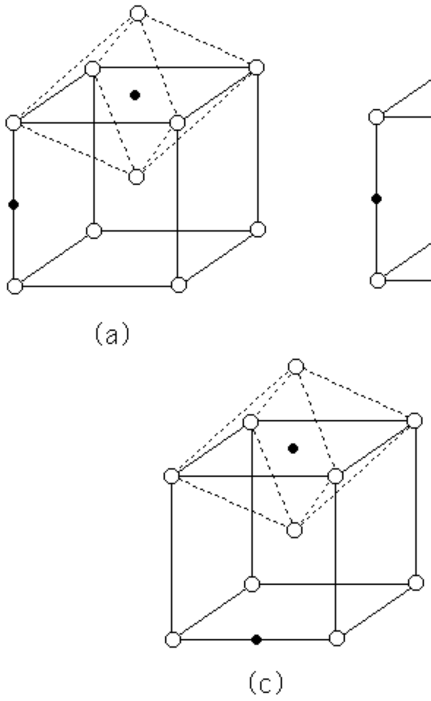

Fig. 3: Three possible di–carbon clusters, which on the basis of strain energy alone are stable with binding energies of 0.13 eV, 0.11 eV and 0.08 eV for (a), (b) and (c) respectively. Note that in all cases the carbon atoms do not occupy near–neighbour interstitial sites which have a spacing of only $a_\alpha/2$. After Johnson, Dienes and Damask, [19].

Interstitial type complexes

The stable Fe–interstitial in α–iron has a "split" configuration in which two atoms are symmetrically split in a $< 110 >$ direction about a normal site which is vacant. In Fig. 4a, the carbon atom is lower than its normal position by $0.025a_\alpha$; the centre of the split interstitial is similarly displaced downwards by $0.06a_\alpha$, the distance between the atoms of the split interstitial being $0.75a_\alpha$ [18]. An interstitial such as this has a binding energy with the carbon atom of about 0.5 eV. The migration energy for the isolated iron interstitial is 0.3 eV. A complex may be formed when a migrating iron interstitial is trapped by association with carbon. In order for the interstitial to escape from the carbon it will therefore require an energy greater than 0.8 eV. The alternative proposal that the carbon can escape from the cluster is not relevant because the migration energy of carbon is larger (0.86 eV), meaning that it would need 1.36 eV to escape. It goes against intuition to think that the carbon is less mobile than the Fe–interstitial, but the latter is in fact able to migrate freely above approximately 80 K, whereas carbon becomes mobile at much higher temperatures ($\simeq$ 200 K).

An iron di–interstitial consisting of two parallel split interstitials is also possible and has a binding energy with the Fe–interstitial/carbon complex of about 1 eV. This grande complex therefore dissociates at higher temperatures.

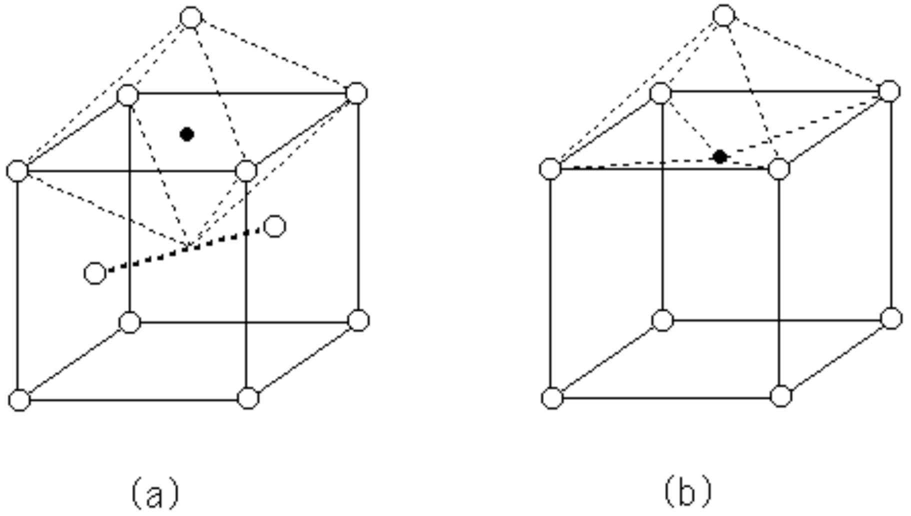

Fig. 4: The most stable position of a carbon atom (black) in a defective unit cell of ferrite [18,24]. (a) There is a split interstitial of a pair of iron atoms (heavy dashed line along $< 110 >$ causing the carbon atom to relax downwards by 2.5% of the lattice parameter. (b) The effect of an iron vacancy on the position of carbon.

Vacancy type complexes

An iron vacancy in ferrite has a binding energy of about 0.41–0.48 eV with an atom of carbon [25]. It turns out that a carbon atom encountering a vacancy does not fall into it, but moves towards it along $< 100 >$ as illustrated in Fig. 4b, remaining attached to five of the adjacent iron atoms. Positron annihilation studies indicate that the carbon atom is about $0.365a_\alpha$ from the vacancy center, forming a dumbell configuration with the vacancy [26]. In irradiated samples precipitation causes the carbon–vacancy complexes to dissociate at approximately 250 °C [27]. Notice that this dissociation does not mean, as is sometimes argued, that under equilibrium conditions the complex decomposes above 250 °C, since at that temperature the binding energy is almost an order of magnitude larger than the thermal energy kT.

An iron vacancy in ferrite could in principle accommodate a pair of carbon atoms. However, kinetic data suggest that such di–carbon/vacancy clusters do not form in practice, presumably because of electrostatic repulsion between the atoms [18].

There appears to be a strong repulsion (-7 eV) between a carbon atom and an iron vacancy in austenite [25]. The carbon should therefore remain in the octahedral holes even in the presence of adjacent vacancies. This is because a carbon atom in an iron vacancy would hardly interact with its now more distant iron atom neighbours.

SUMMARY

There is little doubt that there is a net repulsion between near neighbour carbon atoms in both austenite and in ferrite. The indications are that the repulsion is much larger for ferrite because the near neighbour distance is much smaller, although this cannot be deduced from the available thermodynamic data. The repulsion does not rule out the formation of stable clusters of carbon atoms in ferrite, as long as the distance between pairs of carbon atoms is greater than the near neighbour distance $a_\alpha/2$. Similar clusters do not seem to have been investigated for austenite, presumably because the strain interactions between carbon atoms are much smaller in austenite. This is because the carbon atom causes an isotropic strain in austenite whereas it leads to a tetragonal distortion in ferrite. Isotropic strains can only interact with the hydrostatic components of stress, which tend to be rather feeble in most experiments.

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