Quasichemical Model of a Ternary Solution

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Abstract

A quasichemical model is one type of statistical models of solutions. It is more realistic than the ideal and regular models. The solutions in a quasichemical model have a finite enthalpy change and non-random atomic configuration of mixing. Two improvements to the previous ternary interstitial quasichemical model[3] have been made in this work. The new model is more general and rigorous, which means it could deal with more solutions and the predictions from the model should be more accurate. Besides, the consistency between the current quasichemical model and the previous binary and ternary models has been approved.

Introduction

In a solution, atoms prefer like or unlike atoms as their neighbours, if the binding energy can be lowered. A completely random solution can only be found at very high temperature where heat overwhelms any tendency for ordering or clustering. Therefore, the ideal and regular solution models are not realistic because both of them assume a random distribution of atoms. The quasichemical model has a better approach to deal with the non-zero Enthalpy and Entropy change. The name of the model comes from two mass action equations derived from the model, which describes the number of various pairs in the equilibrium state.

The binary quasichemical model was firstly introduced by Guggenheim in his book 'Mixtures'[1]. McLellan and his colleagues applied this method on the *Fe-C* binary[2] and then the *Fe-X-C* (where *X* represents any substitutional solute atom) ternary[3] system. Those models can be used to interpret the Thermodynamic data from the experiment and to predict the carbon-carbon interaction energy in ferrite.

To make a quasichemical model, the major work is to construct the partition function Ω of the system, because most other thermodynamic functions can be easily deduced from the partition function. For example, Helmholtz free energy F can be obtained by the equation

$$F = -kT \ln \Omega$$

where k is the Boltzmann constant and T is the absolute temperature.

Previous ternary quasichemical model

The solution Alex and McLellan concerned consists of N_v solvent atoms (*v*), N_u substitutional solute atoms (*u*) and N_i octahedral interstitial solute atoms (*i*) (Fig.1). The empty squares represent the empty interstitial gaps (*e*).

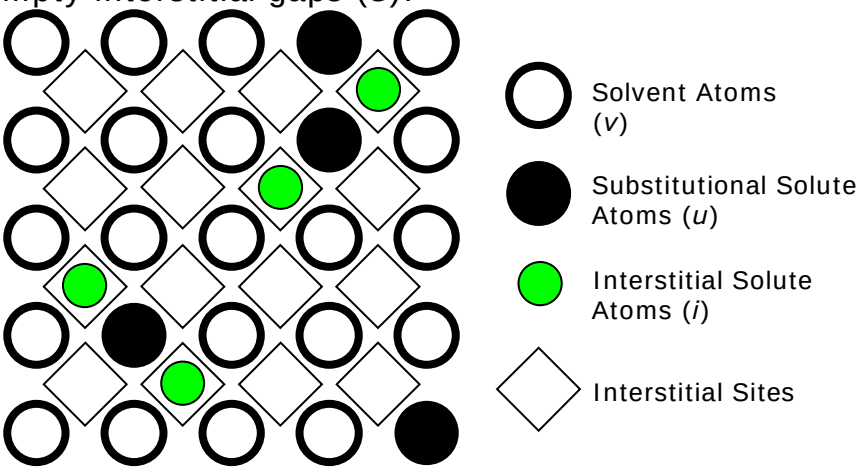

Figure 1 Schematic diagram of the *Fe-X-C* solution

Parameter definitions

N_v	Number of solvent atoms
N_u	Number of substitutional solute atoms
N_i	Number of interstitial solute atoms
ε	Pair energy. Use subscripts *v, i, u,* and *e* to indicate the solvent, interstitial, substitutional solute atoms and the empty interstitial gaps respectively
W_1	Coordination number, the number of nearest-neighbouring interstitial sites around any given interstitial site
W_2	Coordination number, the number of nearest-neighbouring main lattice atoms around any given interstitial site
β	Number of interstitial sites per one main lattice atom
$W_1\lambda_1$	Number of $i-e$ pairs
$W_2\lambda_2$	Number of $i-u$ pairs
θ_i	$N_i/(N_v+N_u)$
θ_u	$N_u/(N_v+N_u)$

Table 1 the definitions of the parameter used in the ternary solution

Therefore, the total number of these interstitial sites is $(N_v+N_u)\beta=M$. Suppose the number of *i-e* and *e-i* pairs is $W_1\lambda_1$ and the number of *i-u* pairs is $W_2\lambda_2$. Consequently, the remaining various pair-number equations are listed together in the Tab.2

Kinds of pairs	Number of pairs	Pair energy
$i-i$	$\frac{W_1}{2}(N_i-\lambda_1)$	ε_{ii}
$i-e$ & $e-i$	$W_1\lambda_1$	$\varepsilon_{ie}=0$
$e-e$	$\frac{W_1}{2}(M-N_i-\lambda_1)$	$\varepsilon_{ee}=0$
$i-u$	$W_2\lambda_2$	ε_{iu}
$i-v$	$W_2(N_i-\lambda_2)$	ε_{iv}
$e-u$	$W_2(N_u-\lambda_2)$	$\varepsilon_{eu}=0$
$e-v$	$W_2(N_v-N_i+\lambda_2)$	$\varepsilon_{ev}=0$

Table 2 Equations of numbers of various pairs in the ternary solution and the corresponding interaction energies. The pairs having *e* are assumed to be at the ground-level energy.

Subtle problem

There is a subtle problem with these definition equations of pair numbers. To illustrate it, let's simply calculate the total number of *main_lattice_atom* − *e* pairs. Because *e* can only pair with *u* and *v*, according to the last two equations in Tab.1, the total number of such pairs equals

$$N_{eu}+N_{ev}=W_2(N_v+N_u-N_i)$$

Another way to get the number of *main_lattice_atom* − *e* pairs is to count how many main lattice atoms surrounding *e*. This simply equals the number of sites *e* times W_2 (give the number of nearest-neighbouring main lattice sites to any given interstitial site).

$$N_{eu}+N_{ev}=W_2\left[(N_v+N_u)\beta-N_i\right]$$

These two equations can only be equal when $\beta=1$, corresponding to austenite. But in ferrite, $\beta=3$. To summarize, the problem in the 1971's model comes from presuming the number of main lattice atoms around a given interstice is the same as the number of interstices around a given main lattice atom, but actually, they can be different. A correct set of the definition equations of pair numbers has been given in the work, which can be applied on both austenite and ferrite.

Results

The chemical potential μ of an interstitial solute atom *i* of this 1971's ternary *Fe-X-C* quasichemical model takes the form

$$\mu = kT\ln\left\{\frac{\theta_i/\beta}{1-\theta_i/\beta}\right\}$$
$$-\frac{W_1 kT}{2}\ln\left\{\left(\frac{\theta_i/\beta}{1-\theta_i/\beta}\right)^2\left(\frac{1-\theta_i/\beta-\overline{\lambda}_1/(N_v+N_u)\beta}{\theta_i/\beta-\overline{\lambda}_1/(N_v+N_u)\beta}\right)\exp\left\{\frac{-\varepsilon_{ii}}{kT}\right\}\right\}$$
$$-W_2 kT\ln\left\{\left(\frac{\theta_i}{1-\theta_i}\right)\left(\frac{1-\theta_u-\theta_i+\overline{\lambda}_2/(N_v+N_u)}{\theta_i-\overline{\lambda}_2/(N_v+N_u)}\right)\right\}+W_2\varepsilon_{iv}$$

$$\theta_i = N_i/(N_v+N_u)$$
$$\theta_u = N_u/(N_v+N_u)$$

where $W_1\overline{\lambda}_1$, $W_2\overline{\lambda}_2$ represent the numbers of *i-e* and *i-u* pairs in an equilibrium solution respectively.

Simplified assumption

A simplified assumption was made in the previous model. In the deduction of the above chemical potential equation from the partition function, variables $\overline{\lambda}_1$ and $\overline{\lambda}_2$ are assumed to be constant

$$\frac{\partial\overline{\lambda}_1}{\partial N_i}=0\,,\qquad \frac{\partial\overline{\lambda}_2}{\partial N_i}=0$$

although they are not. Bhadeshia found this assumption is avoidable. An improved the binary *Fe-C* quasichemical model is proposed in 1998[4].

Compared with the chemical potential equation obtained in the previous binary quasichemical model

$$\mu = kT\ln\left\{\frac{\theta_i/\beta}{1-\theta_i/\beta}\right\}$$
$$-\frac{W_1 kT}{2}\ln\left\{\left\{\frac{\theta_i/\beta}{1-\theta_i/\beta}\right\}^2\left\{\frac{1-\theta_i/\beta-\overline{\lambda}_1/\beta N_v}{\theta_i/\beta-\overline{\lambda}_1/\beta N_v}\right\}\exp\left\{\frac{-\varepsilon_{ii}}{kT}\right\}\right\}$$

the new equation in the modified binary model in 1998 has one more term.

$$\mu = kT\ \ln\left\{\frac{\theta_i/\beta}{1-\theta_i/\beta}\right\}$$

$$-\frac{W_1 kT}{2}\ln\left\{\begin{array}{l}\left\{\frac{\theta_i/\beta}{1-\theta_i/\beta}\right\}^2\left\{\frac{1-\theta_i/\beta-\overline{\lambda}_1/\beta N_v}{\theta_i/\beta-\overline{\lambda}_1/\beta N_v}\right\}\exp\left\{\frac{-\varepsilon_{ii}}{kT}(1-\frac{\partial\overline{\lambda}_1}{\partial N_i})\right\}\\ \left\{\frac{(\theta_i/\beta-\overline{\lambda}_1/\beta N_v)(1-\theta_i/\beta-\overline{\lambda}_1/\beta N_v)}{(\overline{\lambda}_1/\beta N_v)(\overline{\lambda}_1/\beta N_v)}\right\}^{\frac{\partial\overline{\lambda}_1}{\partial N_i}}\end{array}\right\}$$

Improved ternary quasichemical models

New model will deal with the same solution, but a correct set of pair number equations and more sophisticated mathematical treatment has been used.

Solution for the problem

To remove that problem mentioned before, we could define W_2 (the number of nearest-neighbouring main lattice atoms around an interstitial site) and the number of nearest-neighbouring interstitial sites around a main lattice atom separately, say nW_2. Because of that, the number of *e-u* pairs equals

$$(nW_2)N_u - W_2\lambda_2 = W_2(nN_u - \lambda_2) \qquad (1)$$

In a similar manner, the number of *e-v* pairs has the form

$$(nW_2)N_v - W_2(N_i - \lambda_2) = W_2(nN_v - N_i + \lambda_2) \qquad (2)$$

The new variable n can be proved to equal β. As we know, the total number of interstices is

$$(N_v + N_u)\beta$$

Using the new coordination number nW_2, this number can be obtained by another route

$$\frac{nW_2 \times (N_v + N_u)}{W_2}$$

The reason of dividing $nW_2 \times (N_v + N_u)$ by the factor W_2 is because the interstitial sites' number has been over-counted W_2 times. These two equations should be equal

$$\frac{nW_2 \times (N_v + N_u)}{W_2} = \beta(N_v + N_u)$$

Hence, we got the prove

$$n = \beta$$

New pair equations

Replay n in equations (1) and (2) by β, we establish the correct set of equations of pair numbers Tab.3

Kind of pair	Number of pairs	Pair energy

$i-i$	$\frac{W_1}{2}(N_i-\lambda_1)$	ε_{ii}
$i-e$ & $e-i$	$W_1\lambda_1$	$\varepsilon_{ie}=0$
$e-e$	$\frac{W_1}{2}(M-N_i-\lambda_1)$	$\varepsilon_{ee}=0$
$i-u$	$W_2\lambda_2$	ε_{iu}
$i-v$	$W_2(N_i-\lambda_2)$	ε_{iv}
$e-u$	$W_2(N_u\beta-\lambda_2)$	$\varepsilon_{eu}=0$
$e-v$	$W_2(N_v\beta-N_i+\lambda_2)$	$\varepsilon_{ev}=0$

Table 3: The new set of pair-number equations, for austenite $\beta=1$ and for ferrite $\beta=3$

The partition function

To make a quasichemical model, the major work is to construct the partition function Ω of the system

$$\Omega=\sum_i g_i \exp\left\{\frac{-E_i}{kT}\right\} \tag{3}$$

where g_i is the degeneracy number (number of states within the same energy), E_i is the energy of the system at the state i.

The energy of each configuration of the solution is given by summing up the interaction energies between pairs, where the assumption that atoms at rest in vacuum is at the ground-level energy is taken

$$E_{\lambda_1\lambda_2}=\frac{W_1}{2}(N_i-\lambda_1)\varepsilon_{ii}+W_2\lambda_2\Delta\varepsilon+W_2N_i\varepsilon_{iv} \tag{4}$$

where $\Delta\varepsilon=\varepsilon_{iu}-\varepsilon_{iv}$.

If pairs are treated as independent entities (although they are not. If three out of four pair types have been determined on the sides of a square, the last one is also determined), the degeneracy number at λ_1 and λ_2 is

$$g_{\lambda_1\lambda_2}\propto\frac{(N_{ii}+N_{ie}+N_{ei}+N_{ee}+N_{iu}+N_{iv}+N_{eu}+N_{ev})!}{N_{ii}!N_{ie}!N_{ei}!N_{ee}!N_{iu}!N_{iv}!N_{eu}!N_{ev}!}$$

which is proportional to the real degeneracy number.

The correct estimation of the degeneracy could be obtained using normalization method firstly introduced by Guggenheim[1]. Since the

summation of $g_{\lambda_1\lambda_2}$ over all possible values of λ_1 and λ_2 should equal the number of all possible arrangements of the atoms *i* and *e*

$$\sum_{\lambda_1\lambda_2} g_{\lambda_1\lambda_2} = \frac{M!}{(N_i)!(M-N_i)!}$$

Because of this, the real degeneracy number at specific λ_1 and λ_2 equals

$$g_{\lambda_1\lambda_2} = \frac{M!}{(N_i)!(M-N_i)!} \times \frac{\dfrac{(N_{ii}+N_{ie}+N_{ei}+N_{ee}+N_{iu}+N_{iv}+N_{eu}+N_{ev})!}{N_{ii}!N_{ie}!N_{ei}!N_{ee}!N_{iu}!N_{iv}!N_{eu}!N_{ev}!}}{\displaystyle\sum_{\lambda_1\lambda_2}\frac{(N_{ii}+N_{ie}+N_{ei}+N_{ee}+N_{iu}+N_{iv}+N_{eu}+N_{ev})!}{N_{ii}!N_{ie}!N_{ei}!N_{ee}!N_{iu}!N_{iv}!N_{eu}!N_{ev}!}} \tag{5}$$

where N_{ii} are the number of *i-i* pairs, similar with the other *Ns*

Because the summation in the denominator is a vast number, it can be replaced by its largest term, in which λ_1 and λ_2 are denoted by λ_1^* and λ_2^*. And their values are gained by

$$\left(\frac{\partial \ln g_{\lambda_1\lambda_2}}{\partial \lambda_1}\right)_{\lambda_2} = 0, \qquad \left(\frac{\partial \ln g_{\lambda_1\lambda_2}}{\partial \lambda_2}\right)_{\lambda_1} = 0$$

which gives

$$\lambda_1^* = \frac{N_i(M-N_i)}{M}, \qquad \lambda_2^* = \frac{N_i N_u}{N_v + N_u}$$

The λ^*s can be obtained by substituting equations in the Tab.3 into equation 5. Note that these are the same values in an ideal solution, where atoms are randomly mixed.

So far, the degeneracy has the expression

$$g_{\lambda_1\lambda_2} = \frac{M!}{(N_i)!(M-N_i)!} \times \frac{N_{ii}^*!N_{ie}^*!N_{ei}^*!N_{ee}^*!N_{iu}^*!N_{iv}^*!N_{eu}^*!N_{ev}^*!}{N_{ii}!N_{ie}!N_{ei}!N_{ee}!N_{iu}!N_{iv}!N_{eu}!N_{ev}!} \tag{6}$$

Inserting equation (4) and (6) in the partition function (3). To make the equation even more compactable, we play the same trick to replace the summation in the partition function by its largest term. To find it

$$\left(\frac{\partial \ln\left\{g_{\lambda_1\lambda_2}\exp\left\{\dfrac{-E_{\lambda_1\lambda_2}}{kT}\right\}\right\}}{\partial \lambda_1}\right)_{\lambda_2} = 0, \qquad \left(\frac{\partial \ln\left\{g_{\lambda_1\lambda_2}\exp\left\{\dfrac{-E_{\lambda_1\lambda_2}}{kT}\right\}\right\}}{\partial \lambda_2}\right)_{\lambda_1} = 0$$

These result the following two equations, which has the form of mass action law in Chemistry

$$\frac{\overline{\lambda}_1\overline{\lambda}_1}{(N_i-\overline{\lambda}_1)\times(M-N_i-\overline{\lambda}_1)} = \exp\left\{\frac{\varepsilon_{ii}}{kT}\right\}$$

$$\frac{(N_v\beta - N_i + \bar{\lambda}_2)\bar{\lambda}_2}{(N_u\beta - \bar{\lambda}_2)(N_i - \bar{\lambda}_2)} = \exp\left\{-\frac{\Delta\varepsilon}{kT}\right\}$$

$\bar{\lambda}_1$ and $\bar{\lambda}_2$ give the numbers of *i-e* and *i-u* pairs in an equilibrium quasichemical solution

$$\bar{\lambda}_1 = \frac{(N_v + N_u)\beta}{2\phi_1}\left\{1 - \sqrt{1 - 4\frac{\theta_i}{\beta}(1 - \frac{\theta_i}{\beta})\phi_1}\right\} \tag{7}$$

$$\bar{\lambda}_2 = (N_v + N_u)\left\{\frac{(\beta + (\theta_i + \theta_u\beta)\phi_2) - \sqrt{\{\beta + (\theta_i + \theta_u\beta)\phi_2\}^2 - 4\theta_i\theta_u\beta(\phi_2 + 1)\phi_2}}{2\phi_2}\right\} \tag{8}$$

where

$$\theta_i = N_i/(N_v + N_u) \quad \text{and} \quad \theta_u = N_u/(N_v + N_u)$$

$$\phi_1 = 1 - \exp\{-\varepsilon_{ii}/kT\} \quad \text{and} \quad \phi_2 = \exp\{-(\varepsilon_{iu} - \varepsilon_{iv})/kT\} - 1$$

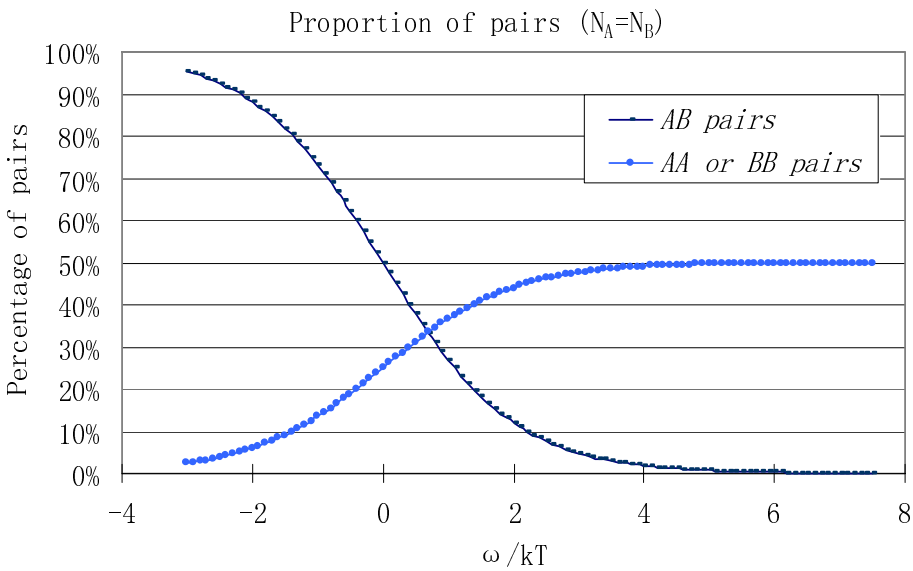

Figure 2 Proportion of various pairs in the solution

Finally, by plugging the equation (), () and (), () into the partition equation, it becomes

$$\Omega = \frac{(N_v + N_u)\beta!}{N_i![(N_v + N_u)\beta - N_i]!}$$
$$\times \frac{\left\{\begin{array}{l}(1/2W_1(N_i - \lambda_1^*))!(1/2W_1\lambda_1^*)!(1/2W_1\lambda_1^*)!(1/2W_1[(N_v + N_u)\beta - N_i - \lambda_1^*])! \\ (W_2\lambda_2^*)!(W_2(N_i - \lambda_2^*))!(W_2(N_u - \lambda_2^*))!(W_2(N_v - N_i + \lambda_2^*))!\end{array}\right\}}{\left\{\begin{array}{l}(1/2W_1(N_i - \bar{\lambda}_1))!(1/2W_1\bar{\lambda}_1)!(1/2W_1\bar{\lambda}_1)!(1/2W_1[(N_v + N_u)\beta - N_i - \bar{\lambda}_1])! \\ (W_2\bar{\lambda}_2)!(W_2(N_i - \bar{\lambda}_2))!(W_2(N_u - \bar{\lambda}_2))!(W_2(N_v - N_i + \bar{\lambda}_2))!\end{array}\right\}} \tag{9}$$
$$\times \exp\left\{-\left[\frac{W_1}{2}(N_i - \bar{\lambda}_1)\varepsilon_{ii} + W_2\bar{\lambda}_2\Delta\varepsilon + W_2N_i\varepsilon_{iv}\right]/kT\right\}$$

Chemical potential μ

Because of the difference between Gibbs free energy G and Helmholtz free energy (i.e. *pressure times volume*) is very small in the solid or liquid, the Gibbs free energy almost equals $G \approx -kT\ln\Omega$. In the ternary solution, the chemical potential of an interstitial solute atom μ has the form

$$\mu = \left(\frac{\partial G}{\partial N_i}\right)_{N_v,N_u} = -kT\left(\frac{\partial \ln\Omega}{\partial N_i}\right)_{N_v,N_u}$$

Substitute equation (9)

$$\begin{aligned}
\mu = {} & kT\ln\left\{\frac{\theta_i/\beta}{1-\theta_i/\beta}\right\} \\
& -\frac{W_1 kT}{2}\ln\left\{\begin{array}{l}\left(\frac{(\theta_i/\beta)}{1-(\theta_i/\beta)}\right)^2\left(\frac{1-\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)}{\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)}\right)\exp\left\{\frac{-\varepsilon_{ii}}{kT}(1-\frac{\partial\bar{\lambda}_1}{\partial N_i})\right\} \\ \left(\frac{\left(\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)\right)\left(1-\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)\right)}{\left(\bar{\lambda}_1/\beta(N_v+N_u)\right)\left(\bar{\lambda}_1/\beta(N_v+N_u)\right)}\right)^{\frac{\partial\bar{\lambda}_1}{\partial N_i}}\end{array}\right\} \\
& -W_2 kT\ln\left\{\begin{array}{l}\left(\frac{\theta_i}{\beta-\theta_i}\right)\left(\frac{\beta-\theta_u\beta-\theta_i+\bar{\lambda}_2/(N_v+N_u)}{\theta_i-\bar{\lambda}_2/(N_v+N_u)}\right) \\ \left(\frac{\left(\theta_i-\bar{\lambda}_2/(N_v+N_u)\right)\left(\theta_u\beta-\bar{\lambda}_2/(N_v+N_u)\right)}{\left(\bar{\lambda}_2/(N_v+N_u)\right)\left(\beta-\theta_u\beta-\theta_i+\bar{\lambda}_2/(N_v+N_u)\right)}\right)^{\frac{\partial\bar{\lambda}_2}{\partial N_i}}\end{array}\right\} \\
& +W_2(\varepsilon_{iu}-\varepsilon_{iv})\frac{\partial\bar{\lambda}_2}{\partial N_i}+W_2\varepsilon_{iv}
\end{aligned} \tag{10}$$

where

$$\frac{\partial\bar{\lambda}_1}{\partial N_i} = \frac{1-2\frac{\theta_i}{\beta}}{\sqrt{1-4\frac{\theta_i}{\beta}(1-\frac{\theta_i}{\beta})\phi_1}}$$

$$\frac{\partial\bar{\lambda}_2}{\partial N_i} = \frac{1}{2}\left\{1-\frac{\beta+\theta_i\phi_2-\theta_u\beta\phi_2-2\theta_u\beta}{\sqrt{\{\beta+(\theta_i+\theta_u\beta)\phi_2\}^2-4\theta_i\theta_u\beta(\phi_2+1)\phi_2}}\right\}$$

Verification

To verify the new model, we compared the chemical potential equation derived from the improved model in several scenarios with those from the previous models.

Consistency with the previous ternary quasichemical model

Both the current and previous models are constructed for the same ternary solution, but they use different sets of the pair number equations. Hence we can exam whether the improved model were equivalent to the old one, when the βs in all the terms describing *e-*

u, *e-v* pair numbers (simply terms having W_2) are set to be $\beta=1$ and the variables $\bar{\lambda}_1$ and $\bar{\lambda}_2$ are assumed to be constant. First of all, set $\beta=1$

$$
\begin{aligned}
\mu &= kT\ln\left\{\frac{\theta_i/\beta}{1-\theta_i/\beta}\right\} \\
&-\frac{W_1 kT}{2}\ln\left\{\begin{array}{l}\left(\frac{\theta_i/\beta}{1-\theta_i/\beta}\right)^2\left(\frac{1-\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)}{\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)}\right)\left(\exp\left\{\frac{-\varepsilon_{ii}}{kT}(1-\frac{\partial\bar{\lambda}_1}{\partial N_i})\right\}\right) \\ \left(\frac{\left(\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)\right)\left(1-\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)\right)}{\left(\bar{\lambda}_1/\beta(N_v+N_u)\right)\left(\bar{\lambda}_1/\beta(N_v+N_u)\right)}\right)^{\frac{\partial\bar{\lambda}_1}{\partial N_i}}\end{array}\right\} \\
&-W_2 kT\ln\left\{\begin{array}{l}\left(\frac{\theta_i}{1-\theta_i}\right)\left(\frac{1-\theta_u-\theta_i+\bar{\lambda}_2/(N_v+N_u)}{\theta_i-\bar{\lambda}_2/(N_v+N_u)}\right) \\ \left(\frac{\left(\theta_i-\bar{\lambda}_2/(N_v+N_u)\right)\left(\theta_u-\bar{\lambda}_2/(N_v+N_u)\right)}{\left(\bar{\lambda}_2/(N_v+N_u)\right)\left(1-\theta_u-\theta_i+\bar{\lambda}_2/(N_v+N_u)\right)}\right)^{\frac{\partial\bar{\lambda}_2}{\partial N_i}}\end{array}\right\} \\
&+W_2\left(\varepsilon_{iu}-\varepsilon_{iv}\right)\frac{\partial\bar{\lambda}_2}{\partial N_i}+W_2\varepsilon_{iv}
\end{aligned}
\tag{11}
$$

where

$$\bar{\lambda}_1 = \frac{(N_v+N_u)\beta}{2\phi_1}\left\{1-\sqrt{1-4\frac{\theta_i}{\beta}(1-\frac{\theta_i}{\beta})\phi_1}\right\}$$

$$\bar{\lambda}_2 = (N_v+N_u)\left\{\frac{\left(1+(\theta_i+\theta_u)\phi_2\right)-\sqrt{\{1+(\theta_i+\theta_u)\phi_2\}^2-4\theta_i\theta_u(\phi_2+1)\phi_2}}{2\phi_2}\right\}$$

$$\frac{\partial\bar{\lambda}_1}{\partial N_i} = \frac{1-2\frac{\theta_i}{\beta}}{\sqrt{1-4\frac{\theta_i}{\beta}(1-\frac{\theta_i}{\beta})\phi_1}}$$

$$\frac{\partial\bar{\lambda}_2}{\partial N_i} = \frac{1}{2}\left\{1-\frac{1+\theta_i\phi_2-\theta_u\phi_2-2\theta_u}{\sqrt{\{1+(\theta_i+\theta_u)\phi_2\}^2-4\theta_i\theta_u(\phi_2+1)\phi_2}}\right\}$$

Secondly, if we add two unrealistic assumptions, which were assumed in Alex and McLellan's model

$$\frac{\partial\bar{\lambda}_1}{\partial N_i}=0 \text{ and } \frac{\partial\bar{\lambda}_2}{\partial N_i}=0$$

the following four terms become

$$\left(\frac{\left(\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)\right)\left(1-\theta_i/\beta-\bar{\lambda}_1/\beta(N_v+N_u)\right)}{\left(\bar{\lambda}_1/\beta(N_v+N_u)\right)\left(\bar{\lambda}_1/\beta(N_v+N_u)\right)}\right)^{\frac{\partial\bar{\lambda}_1}{\partial N_i}}=1$$

$$\left(\frac{\left(\theta_i-\bar{\lambda}_2/(N_v+N_u)\right)\left(\theta_u-\bar{\lambda}_2/(N_v+N_u)\right)}{\left(\bar{\lambda}_2/(N_v+N_u)\right)\left(1-\theta_u-\theta_i+\bar{\lambda}_2/(N_v+N_u)\right)}\right)^{\frac{\partial\bar{\lambda}_2}{\partial N_i}}=1$$

$$\exp\left\{\frac{-\varepsilon_{ii}}{kT}(1-\frac{\partial\bar{\lambda}_1}{\partial N_i})\right\}=\exp\left\{\frac{-\varepsilon_{ii}}{kT}\right\}$$

$$W_2\left(\varepsilon_{iu}-\varepsilon_{iv}\right)\frac{\partial\bar{\lambda}_2}{\partial N_i}=0$$

Applying these terms, equation (11) thus becomes identical to the chemical potential equation in the previous ternary model.

Consistency with the improved binary quasichemical model

The first scenario one could imagine is that the solvent atoms *v* have no energy difference from the substitution atom *u* to the interstitial atoms *i*, $\varepsilon_{iu}\to\varepsilon_{iv}$.

$$\bar{\lambda}_2=\frac{(N_v+N_u)}{2\phi_2}\left\{\left(\beta+(\theta_u\beta+\theta_i)\phi_2\right)-\sqrt{\left\{\beta+(\theta_u\beta+\theta_i)\phi_2\right\}^2-4\theta_u\beta\theta_i(\phi_2+1)\phi_2}\right\}$$

$$=\frac{(N_v+N_u)}{2\phi_2}\left\{\left(\beta+(\theta_u\beta+\theta_i)\phi_2\right)-\beta\sqrt{1+\left[2\left(\theta_u\beta+\theta_i\right)\frac{\phi_2}{\beta}+(\theta_u\beta-\theta_i)^2\left(\frac{\phi_2}{\beta}\right)^2-4\theta_u\theta_i\frac{\phi_2}{\beta}\right]}\right\}$$

Apply the Taylor expansion $\sqrt{1+x}=1+x/2-x^2/8+\cdots$

$$\bar{\lambda}_2\approx(N_v+N_u)\left\{\frac{-(\theta_u\beta-\theta_i)^2\left(\phi_2/\beta\right)+4\theta_u\theta_i}{4}\right\}$$

The condition $\varepsilon_{iu}\to\varepsilon_{iv}$ brings

$$\lim_{\varepsilon_{iu}\to\varepsilon_{iv}}\phi_2=\left(\exp\left\{-\left(\varepsilon_{iu}-\varepsilon_{iv}\right)/kT\right\}-1\right)=0$$

Therefore

$$\lim_{\phi_2\to 0}\bar{\lambda}_2=(N_v+N_u)\left(\theta_u\theta_i\right)$$

The third and forth terms of the new equation become

$$\lim_{\varepsilon_{iu}\to\varepsilon_{iv}}-W_2kT\ln\left\{\begin{array}{l}\left(\frac{\theta_i}{\beta-\theta_i}\right)\left(\frac{\beta-\theta_u\beta-\theta_i+\bar{\lambda}_2/(N_v+N_u)}{\theta_i-\bar{\lambda}_2/(N_v+N_u)}\right)\\ \left(\frac{\left(\theta_i-\bar{\lambda}_2/(N_v+N_u)\right)\left(\theta_u\beta-\bar{\lambda}_2/(N_v+N_u)\right)}{\left(\bar{\lambda}_2/(N_v+N_u)\right)\left(\beta-\theta_u\beta-\theta_i+\bar{\lambda}_2/(N_v+N_u)\right)}\right)^{\frac{\partial\bar{\lambda}_2}{\partial N_i}}\end{array}\right\}=0$$

and

$$\lim_{\varepsilon_{iu}\to\varepsilon_{iv}}W_2\left(\varepsilon_{iu}-\varepsilon_{iv}\right)\frac{\partial\bar{\lambda}_2}{\partial N_i}=0$$

Substituting these two terms back to the new equation, it becomes identical to that in Bhadeshia's paper.

The second scenario one could imagine is that the concentration of the substitutional solute atoms becomes infinitely sparse, $\theta_u \to 0$. It results in

$$\lim_{\theta_u \to 0} \frac{\bar{\lambda}_2}{(N_v + N_u)} = \left\{ \frac{(\beta + \theta_i \phi_2) - \sqrt{(\beta + \theta_i \phi_2)^2}}{2\phi_2} \right\} = 0$$

$$\lim_{\theta_u \to 0} \frac{\partial \bar{\lambda}_2}{\partial N_i} = \frac{1}{2} \left\{ 1 - \frac{\beta + \theta_i \phi_2}{\sqrt{\{\beta + \theta_i \phi_2\}^2}} \right\} = 0$$

if $\beta + \theta_i \phi_2$ is positive, which can be always satisfied by carefully defining the solvent and substitutional solute atoms. As scenario one, the third and forth terms also become

$$\lim_{\theta_u \to 0} -W_2 kT \ln \left\{ \begin{array}{l} \left(\dfrac{\theta_i}{\beta - \theta_i} \right) \left(\dfrac{\beta - \theta_u \beta - \theta_i + \bar{\lambda}_2 / (N_v + N_u)}{\theta_i - \bar{\lambda}_2 / (N_v + N_u)} \right) \\ \left(\dfrac{(\theta_i - \bar{\lambda}_2 / (N_v + N_u))(\theta_u \beta - \bar{\lambda}_2 / (N_v + N_u))}{(\bar{\lambda}_2 / (N_v + N_u))(\beta - \theta_u \beta - \theta_i + \bar{\lambda}_2 / (N_v + N_u))} \right)^{\frac{\partial \bar{\lambda}_2}{\partial N_i}} \end{array} \right\} = 0$$

$$\lim_{\theta_u \to 0} W_2 (\varepsilon_{iu} - \varepsilon_{iv}) \frac{\partial \bar{\lambda}_2}{\partial N_i} = 0$$

So far, it has been verified that the new model are completely consistent with the old version ternary and the binary models. Logically, because these two previous models had been proved to be consistent with zero order quasichemical models, the new ternary model should also be consistent with them.

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First Principles Calculation of Carbon-Carbon Interactions in Ferritic Iron

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Abstract

The carbon-carbon interaction energy in ferritic steel has been calculated from first principles, for two different pairs, the first when the carbon atoms are separated by the lattice parameter of ferrite and the second when the separation is reduced to half this value. In each case the carbon atoms were located in octahedral interstices within the body-centred cubic arrangement of iron atoms. There is a strong repulsion between the carbon atoms located in close proximity, whereas the pair separated by a lattice parameter has an attractive interaction. These results are discussed in the context of quasichemical thermodynamic models for the solution of carbon in iron and the tetragonality of martensite in steels.

Introduction

Carbon dissolves in octahedral interstices in ferritic iron. A particular feature of such a solution is that the number of Fe-Fe and Fe-C pairs does not, for a given composition, change as a function of the disposition of the carbon atoms. Whether the carbon atoms arrange randomly on the sub-lattice of interstitial sites or whether they order or cluster depends on the carbon-carbon interaction energy.

Experimental data on the activity of carbon in ferrite have in the past been used in conjunction with quasichemical thermodynamic solution models in order to deduce the interaction energy [1-6]. Some of these deductions were based on incorrect equations, which unfortunately, continue to appear in the published literature. The problem has been reviewed recently [7]. It seems that because of the very small equilibrium solubility of carbon in ferrite, it is not possible to reliably deduce the magnitude of the interaction energy although evidence suggests that the interaction should be strongly repulsive for carbon atoms in nearest neighbouring sites. The probability of finding carbon atoms in near—neighbour sites is in any case small when the concentration is small, as is usual for ferrite. However, this is not the case when carbon is trapped in large concentrations in bainitic ferrite or martensite. The problem is also important when extrapolating phase boundaries to domains where equilibrium data do not exist, as is often the case when steels are transformed to highly metastable phases [8].

The purpose of the work presented here was to calculate the carbon-carbon interaction energy using a first-principles method (density functional theory) implemented in the CASTEP software [9] on the Cambridge-Cranfield High Performance Computing Facility (CCHPCF). The theory itself is widely used and has been described fully in the published literature [e.g., 10].

First-Principles Methodology

The calculations presented here were carried out using the CASTEP program. CASTEP is based on density functional theory, which in principle expresses the total groundstate energy of a material as a unique functional of the electron density [11], plus ionic contributions. In practice a set of single-particle wavefunctions [12] are used to construct the electronic density, and in CASTEP these are expressed in a plane-wave basis, where the plane-wave states are chosen to have the same periodicity as the simulation cell. This basis set is semi-infinite, but the coefficients associated with the high-energy basis states are negligible so a cut-off energy is defined and only plane-wave states with lower energies are accepted into the basis. Since the core electrons are relatively inert, CASTEP treats these as frozen and concentrates the computational effort on the valence electrons only.

In principle, the total energy of the ground state is a functional of the density, but this functional is not known. Although most of the energy contributions can be calculated exactly the exchange-correlation energy cannot, and so we must use an approximation. In the calculations presented here both the local density approximation (LDA) and the generalised gradient approximation of Perdew, Burke and Ernzerhof (PBE) have been used, and both sets of results are presented.

The Brillouin zone of the simulation cell is sampled at a finite number of points in reciprocal space, and integrals over the Brillouin zone are approximated by a weighted summation over these points. This sampling must be accurate in order to determine the Fermi surface, and hence the occupation of the single-particle states. In the calculations presented here the states are assumed to be spin-polarised, and so the maximum occupation of any state is 1. The Fermi surface of a metal such as iron is discontinuous at the ground state (*i.e.* 0 K) so a high density of sampling points is required; it is common to introduce a small thermal-like smearing to reduce the number of sampling points, at the cost of introducing an electronic entropy contribution to the total energy.

The calculation of the ground state proceeds as follows: first the ionic positions and cell vectors are kept fixed, whilst the wave function for the valence electrons is relaxed. This relaxation is performed by improving the wave function iteratively until the energy converges to the ground state. Once the grounds state electronic wave function has been found the electronic contributions to the forces and stresses are

computed. The ionic positions and lattice vectors are then adjusted according to a quasi-Newton (BFGS) geometry optimisation scheme [13], and the electrons are relaxed for this new configuration to obtain the new forces and stresses. The entire procedure is repeated until the forces and stresses are negligible and the system has reached the ground state.

Calculations

The system of atoms selected is in calculations like these a compromise between accuracy and computing time. A "supercell" of $3\times3\times3$ body-centred cubic cells was selected, consisting of 56 atoms in total, with two of these atoms being carbon and the rest iron. Calculations were carried out with the carbon atoms located in three different arrangements. In the first (Fig. 1), the pair was spaced the $3a_\alpha$ apart, where a_α is the lattice parameter of the ferrite, taken to be 0.2866 nm. This state serves as a reference state in which the carbon atoms are assumed to be sufficiently far apart in order to have a negligible interaction. In the second configuration the carbon atoms were located in nearest neighbour interstitial sites, spaced $0.5a_\alpha$.

There are three octahedral interstices per iron atom in the ferrite crystal structure; there are therefore three interstital sub-lattices. Martensite in high-carbon steels is tetragonal when the carbon atoms order into one of the three sub-lattices. This ordering occurs because a carbon atom place on a cell-edge causes the parallel edge at distance a_α to expand and orthogonal edges to contract; the parallel edge therefore becomes more accommodating for carbon. Notice that the ordering is opposed by entropy, so the evidence on martensite proves that there is a reduction in enthalpy when a pair of carbon atoms is spaced a_α apart; this effect must be reproduced in the first-principles calculations and hence was the third configuration tested.

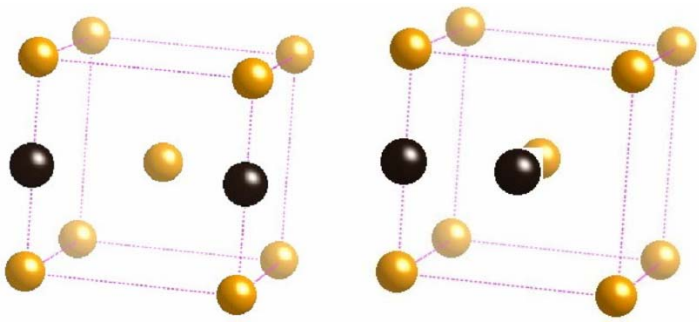

Fig. 1: The configurations of super cells. The carbon atoms are the black circles.

The interaction energy of a pair of carbon atoms is in this work defined relative to carbon atoms spaced $3a_\alpha$. It follows that for the pair located in nearest neighbour interstices (spacing $0.5a_\alpha$), the interaction energy is

$$\Delta E_{a/2} = E_{a/2} - E_{3a}$$

where E is the system energy for a particular configuration. Similarly, the binding energy of carbon atoms spaced one lattice parameter apart is

$$\Delta E_a = E_a - E_{3a}$$

Results

The calculations were carried out in two ways, the first where the iron atoms were not allowed to relax when carbon was introduced into the lattice, and a second calculation in which the iron lattice was allowed to relax. It was anticipated that this would help understand the reason for the tetragonality of martensite.

In the first case, in the absence of relaxation, the interaction between carbon atoms spaced a_α would also be repulsive because of the coulombic forces between carbon atoms.

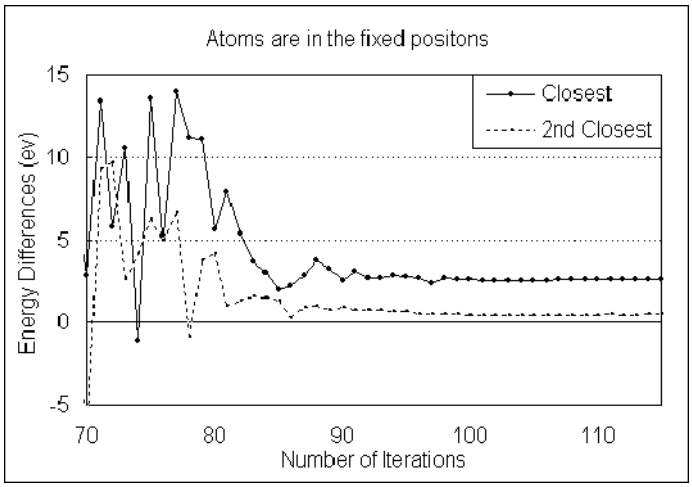

Fig 1 The convergence of the energy differences of when two carbons are put in the closest ($0.5a_\alpha$) and second closest distance (a_α) from when they are $3a_\alpha$ apart with successive iterations. The iron atoms in the calculations are not allowed to relax when carbon is inserted into the lattice. Temperature is 0 K.

The results give $\Delta E_{a/2} = 2.4566815$ eV and $\Delta E_a = 0.43630675$ eV per pair of carbon atoms.

The second set of calculations treated a more realistic scenario in which the iron atoms are allowed to relax whilst keeping the supercell fixed. The initial configuration of atoms is not stable because carbon distorts the octahedral interstice. At the end of every total energy calculation, the atoms adjust their positions to reduce the forces on

them. The system therefore iteratively rearranges its configuration, which results in a global decrease of total energy. Figure 2 illustrates that the total energy difference converges quite well along with the successive iterations of the optimisation algorithm, which indicates that the systems have reached the equilibrium configuration with the minimum global energy.

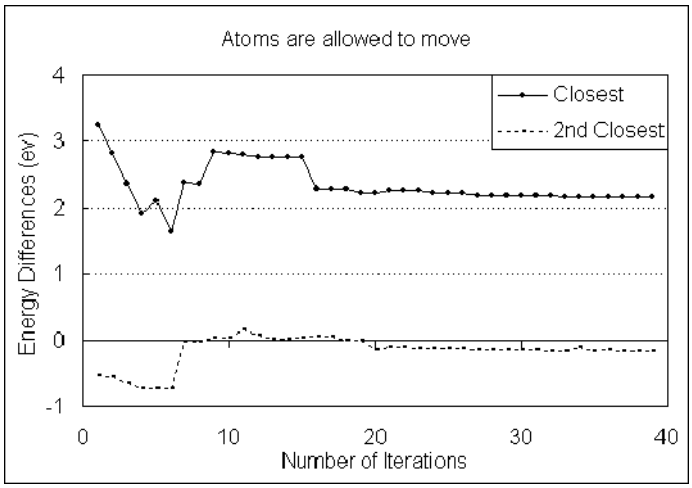

Fig. 2 The convergence of the energy differences of when two carbons are put in the closest and second closest distance from when they are about $3a_\alpha$ apart with successive iterations of the geometry optimization procedure of the total energy (each iteration here in fact consisting of a complete set of iterations in the atom-fixed case). Temperature is 0 K.

The carbon-carbon interaction energy at $0.5a_\alpha$ is found to be strongly repulsive, at $\Delta E_{a/2} = 2.16579$ eV per carbon pair, a value only slightly smaller than that calculated without allowing the iron atoms to relax. This is expected since the coulombic repulsion is expected to dominate the interaction at such a close approach distance. By contrast, the value of $\Delta E_a = -0.16921$ eV not only has changed substantially in magnitude, but also in sign. There is a mild attraction between the carbon pair spaced a_α. This result gives confidence in the calculations since the tetragonality of martensite due to carbon-atom ordering is not possible without this attractive interaction since entropy always opposes ordering.

Summary

First principles calculations of the carbon-carbon interaction energy in ferritic iron suggest that there is a strong repulsion between carbon pairs located in nearest neighbouring octahedral sites which are separated by a distance $0.5a_\alpha$.

On the other hand, there is a mild attraction between a pair of carbon atoms are placed a distance a_α apart. This is expected since the frequently observed tetragonality of martensite in steel relies on the ordering of carbon atoms on one set of octahedral interstices.

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