Short communication

Application of first-order quasichemical theory to transformations in steels

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There are several theoretical and empirical thermodynamic models which adequately describe the equilibrium properties of carbon in ferrite and in austenite (e.g. Refs. 1, 2). These models usually contain unknown parameters which have to be deduced by 'curve-fitting' to experimental thermodynamic data, and this has made it difficult to judge the validity of particular theories, since the curve-fitting procedure always seems to ensure good agreement with the known Fe–C phase diagram. However, the analysis of reactions occurring under metastable equilibrium conditions (such as the bainite and martensite transformations) requires the *extrapolation* of the free energy surfaces of austenite and ferrite; it is clearly desirable to base such extrapolations on physically meaningful laws.

In this respect, one of the most attractive models of interstitial solid solutions is due to Mclellan and Dunn.[3] Their method relies on the first-order formalism of Guggenheim,[4] in which the total energy of a solution is expressed in terms of pairwise interaction energies ω between nearest-neighbouring atoms. By treating the carbon atoms as an atomic gas occupying a lattice of octahedral interstitial sites, Mclellan and Dunn were able to derive the partition function necessary for the evaluation of the configurational free energy. The principle advantages of this approach may be listed as follows:

(i) the method yields the correct solutions in the limiting cases of infinite or zero interaction energies between nearest-neighbouring carbon atoms
(ii) the model is physically realistic in the sense that the number of excluded interstitial sites (nearest to an already occupied site) is treated as an ensemble average non-integral quantity, arising through the existence of a finite repulsive interaction
(iii) the model has been shown to be consistent with both the kinetic and equilibrium thermodynamic behaviour of carbon in austenitic iron.[5–7]

Mclellan and Dunn's final equation relating the activity of carbon a to the atom fraction θ of carbon in solid solution may be stated as[3]

$$a = \left[\frac{\theta/\beta}{1-(\theta/\beta)}\right]\exp\left(\frac{\overline{\Delta G}_u}{kT}\right) \times \left\{\left[\frac{\theta/\beta}{1-(\theta/\beta)}\right]^2\left[\frac{1-(\theta/\beta)-\phi}{(\theta/\beta)-\phi}\right]\right\}^{-z/2}\exp\left(\frac{-z\omega}{2kT}\right) \quad (1a)$$

where

$$\phi = \frac{1-\left\{1-4\left[1-\exp\left(-\frac{\omega}{kT}\right)\right](\theta/\beta)[1-(\theta/\beta)]\right\}^{1/2}}{2\left[1-\exp\left(-\frac{\omega}{kT}\right)\right]} \quad (1b)$$

and

β = number of relevant interstitial sites per iron atom: for octahedral sites, $\beta = 1$ for fcc iron and $\beta = 3$ for bcc iron
T = absolute temperature
k = Boltzmann's constant
z = nearest-neighbour coordination number for the interstitial site concerned
$\overline{\Delta G}_u = \overline{\Delta H}_u - T\overline{\Delta S}_u$, where $\overline{\Delta H}_u$ and $\overline{\Delta S}_u$ are the relative partial enthalpy and non-configurational entropy of the solute atoms u with respect to the pure solvent at infinite dilution respectively.

Equation (1) has been successfully applied to evaluate the behaviour of carbon in austenite, but its corresponding application to ferrite has been less fruitful. Shiflet *et al.*[8] rearranged equation (1) into a form convenient for application to ferrite as follows

$$\ln a_\alpha = f(x, \omega_\alpha) + \overline{\Delta G}_u/RT \quad (2a)$$

where

$$f(x, \omega_\alpha) = 7\ln\left|\frac{3-4x}{x}\right| + \frac{4\omega_\alpha}{RT} + 4\ln\left|\frac{\delta_\alpha - 3 + x(3+2J)}{\delta_\alpha - 3 + 6J + x(3-8J)}\right| \quad (2b)$$

and

a_α = activity of carbon in ferrite
x = mole fraction of carbon in ferrite
R = gas constant
$\delta_\alpha = [9 - 6x(3+2J) + x^2(9+16J)]^{1/2}$
$J = 1 - \exp(-\omega_\alpha/RT)$

However, on comparing equation (2) with published experimental data, Shiflet *et al.* failed to obtain any consistent values for ω_α and even suggested that ω_α may be negative, corresponding to attractive interactions between nearest-neighbouring carbon atoms. While Bhadeshia[9] also failed to deduce any unambiguous value for ω_α using equation (2), he did find that some of the other models of interstitial solution indicated a large positive ω_α.

These difficulties are serious as far as the use of Mclellan

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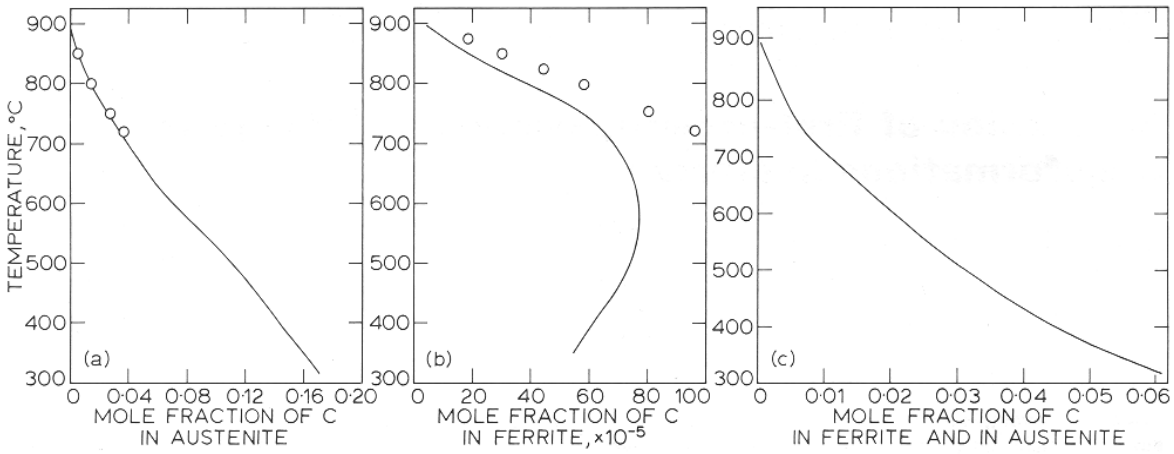

1 *a* calculated Ae_3 curve representing $\gamma/\gamma+\alpha$ phase boundary; points represent experimental data from Hansen's[15] published Fe–C equilibrium phase diagram; *b* calculated curve representing $\alpha/\alpha+\gamma$ phase boundary (experimental points from Hansen); note that retrograde shape of this curve is predicted by all thermodynamic models describing solution of carbon in ferrite; *c* calculated T_0 curve representing points where austenite and ferrite of identical composition have equal free energies

and Dunn's theory for the purposes of studying transformations in steels is concerned, and further investigation has revealed that equation (2) is incorrectly deduced by substituting a value of $z = 8$ into equation (1). However, z really refers to the number of interstitial sites around a given site,[3] and for octahedral intersticies in bcc metals, $z = 4$ (Ref. 10). The corrected version of equation (2) should read

$$\ln a_\alpha = f(x, \omega_\alpha) + \overline{\Delta G_u}/RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

$$f(x, \omega_\alpha) = 3\ln\left|\frac{3-4x}{x}\right| + \frac{2\omega_\alpha}{RT} + 2\ln\left|\frac{\delta_\alpha - 3 + x(3+2J)}{\delta_\alpha - 3 + 6J + x(3-8J)}\right| \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

Using equation (3) and the experimental data of Lobo and Geiger,[11] ω_α was systematically varied until the slope m corresponding to the plot of $\ln a_\alpha$ versus $f(x, \omega_\alpha)$ approached the theoretically expected value of unity.

The results are presented in Table 1, and it appears that ω_α corresponds to a repulsive interaction energy and, in addition, shows no systematic dependence on temperature, consistent with the first-order quasichemical approach of Mclellan and Dunn. The small amount of scatter in the ω_α values is most likely attributable to experimental error in the activity measurements, and it seems justified to assume a constant, temperature-independent ω_α value of 132 400 J mol^{-1} (i.e. the average of the ω_α values quoted in Table 1). Table 1 also includes the $\overline{\Delta G_u}$ values obtained from the intercepts in the plots of $\ln a_\alpha$ versus $f(x, \omega_\alpha)$. By conducting a regression analysis of $\overline{\Delta G_u}$ against temperature, it was possible to estimate $\overline{\Delta H_u}$ and $\overline{\Delta S_u}$ as 105 150 J mol^{-1} and 35·5 J mol^{-1} K^{-1} respectively, in good agreement with the data of Lobo and Geiger (i.e. $\overline{\Delta H_u} = 105\,437 - 112\,130$ J mol^{-1} and $\overline{\Delta S_u} = 45{\cdot}3 - 51{\cdot}4$ J mol^{-1} K^{-1}).

Table 1 Analysis of activity data of Ref. 11 using equation (3)

Temperature, °C	ω_α, J mol^{-1}	Slope m	$\overline{\Delta H_u} - \overline{\Delta S_u}T$, J mol^{-1}
682	110 000	1·001794	71 946
702	132 000	0·992551	70 460
727	137 000	1·001312	69 981
753	133 000	0·999904	67 962
783	131 000	1·000137	67 080
797	144 000	0·997851	66 800
813	123 000	0·999520	66 518
848	149 000	1·010320	66 349

Using the above results and other published data* it was possible to compute the $\alpha/\alpha+\gamma$ and $\gamma/\gamma+\alpha$ phase boundaries by equating the chemical potentials of corresponding elements in austenite and in ferrite. The T_0 line, where stress-free austenite and ferrite free energy surfaces intersect, was calculated by determining the average composition (as a function of temperature) where the two phases have identical free energies. The results are presented in Fig. 1, and agreement between experiment and theory is seen to be reasonable.

Since the ω_α value deduced in the present work is very large, it should be valid to approximate the activity of carbon in ferrite by an equation[3] describing interstitial solution when all nearest neighbours of a given solute atom are excluded from occupancy by other solute atoms. Thus

$$\ln a_\alpha = \frac{\overline{\Delta G_u}}{RT} + \ln\left(\frac{\theta}{\beta - \theta z - \theta}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It has been checked that the use of equation (4) makes virtually no difference to the results presented in Fig. 1.

In summary, the present work is consistent with an earlier analysis which suggested a large positive ω_α and with internal friction experiments (such as those concerned with the Snoek peak) which suggest that carbon atoms in close proximity occupy *second* nearest neighbouring rather than adjacent octahedral interstitial sites in ferrite.

* $\overline{\Delta H_u}$ (austenite) = 38 547 J mol^{-1} (Ref. 8).
$\overline{\Delta S_u}$ (austenite) = 13·5 J mol^{-1} K^{-1} (Ref. 8).
$\Delta F_{Fe}^{\gamma\to\alpha}$ (i.e. the free energy change for transformation in pure iron) from Ref. 12.
Zener ordering energy from Refs. 13 and 14.

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