

Short communication

Computer program:

<https://www.phase-trans.msm.cam.ac.uk/map/steel/programs/Diffuse.html>

Diffusion of carbon in austenite

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The concentration dependence of the diffusivity D of carbon in austenite causes complications in the kinetic analysis of various diffusion-controlled reactions that arise in steels (see, for example, Ref. 1). The existence of substantial carbon concentration gradients at the transformation interfaces involved in such reactions makes it imperative to account for the variation of D with x (where x is the mole fraction of carbon), and it has been demonstrated^{1,2} that, for most purposes, a weighted average diffusivity \bar{D} can adequately represent the effective diffusivity of carbon that is needed for the application of the theory of diffusion-controlled growth. Trivedi and Pound² first considered this problem in detail, and obtained

$$\bar{D} = \int_{x_i^*} \bar{D} dx / (\bar{x} - x_i^*) \quad (1)$$

where \bar{x} is the average carbon content of the alloy and x_i^* is the maximum permissible carbon content in the austenite at the transformation interface.

It is therefore necessary to know $D\{x\}$ at least over the range $\bar{x} - x_i^*$, although experimental determinations of $D\{x\}$ do not extend beyond $x = 0.06$. Kaufman *et al.*³ attempted to overcome this difficulty by assuming a relationship between the activation energy for the growth of a ferrite plate in austenite and that for the diffusion of carbon in austenite. It was additionally assumed that the pre-exponential factor of the diffusion coefficient can be satisfactorily extrapolated beyond the range of experimental observations.

In the present work, a method due to Siller and Mclellan^{4,5} is used to obtain a general expression for $D\{x, T\}$ (where T is the absolute temperature) which is independent of any of the above-mentioned assumptions. Siller and Mclellan have already demonstrated that their elegant theoretical model for D is compatible with both the kinetic and equilibrium thermodynamic behaviour of carbon in austenite. The model takes account of two important factors: the concentration dependence of the activity of carbon in austenite⁶ and the existence of a finite repulsive interaction between nearest neighbouring carbon atoms situated in octahedral sites.⁷ The former effect influences the diffusion of carbon because the virtual force acting on a diffusing species depends on the negative gradient of the chemical potential,^{8,9} and it is on this basis

that Darken's equations¹⁰ relating activity and diffusion are derived. However, as demonstrated by Smith,¹¹ the composition dependence of activity cannot alone account for $D\{x, T\}$, and Siller and Mclellan further refined these concepts by realizing that the repulsive forces between neighbouring carbon atoms should effect diffusivity by acting to reduce the probability of interstitial site occupation in the vicinity of a site already containing a carbon atom. In a concentration gradient, a carbon atom attempting random motion therefore 'sees' an exaggerated difference in the number of available sites in the forward and reverse direction, so that diffusion down the gradient is enhanced. Siller and Mclellan's final equation describing $D\{x, T\}$ may be stated, using their terminology, as

$$D\{x, T\} = D'\xi\{\theta\} \quad (2)$$

where θ is the atom fraction of carbon and D' is a temperature dependent but carbon concentration independent term, which, using absolute reaction rate theory,¹² may be shown,¹³ to be

$$D' = \frac{kT}{h} \exp(-\Delta F^*/kT) (\lambda^2/3\gamma_m) \quad (3)$$

where

k = Boltzmann's constant

h = Planck's constant

ΔF^* = an activation free energy which is independent of composition and temperature, and represents the difference in free energy between the 'activated complex' and the 'reactants' when each is in its standard state at the temperature of 'reaction'

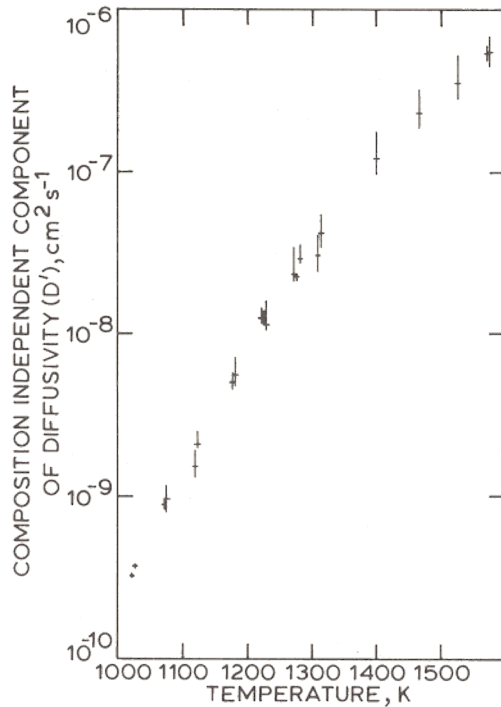
γ_m = activity coefficient of the activated complex, assumed constant

λ = distance between the {002} austenite planes.

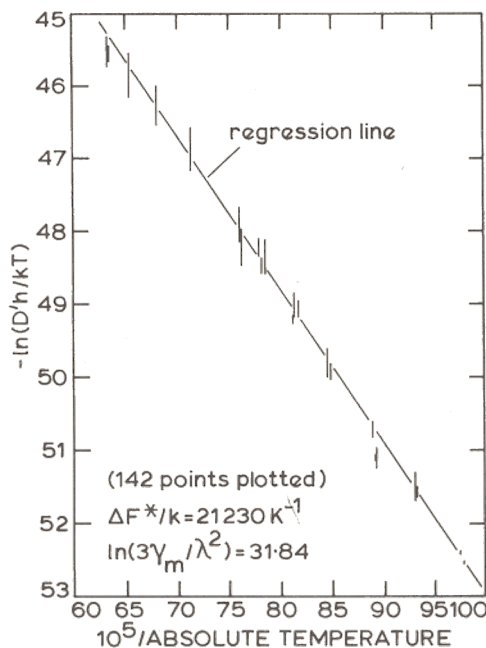
Using a first order quasichemical thermodynamic model⁷ for carbon in austenite together with reaction rate theory, Siller and Mclellan showed that the concentration dependent part of equation (2), i.e. $\xi\{\theta\}$, is given by

$$\xi\{\theta\} = \alpha \left| 1 + \frac{z(1+\theta)}{1 - \left(\frac{z}{2} + 1\right)\theta + \frac{z}{2}\left(\frac{z}{2} + 1\right)(1-\sigma)\theta^2} \right| + (1+\theta) \frac{d\alpha}{d\theta} \quad (4)$$

where z is the coordination number of the octahedral interstitial site in the austenite lattice, α is the activity of



1 Calculations of D' values using equation (2) and experimental data of Refs. 11 and 15; horizontal bars indicate mean value of D' while vertical bars represent range of D' values corresponding to various carbon contents, but constant temperature

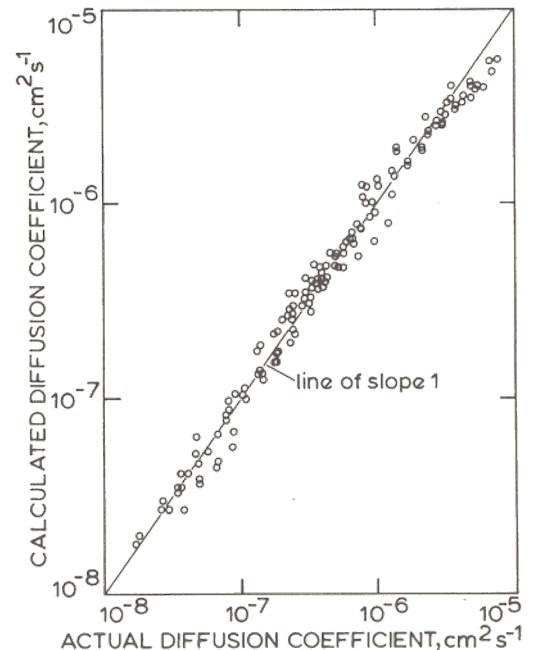


2 Regression analysis with slope $\Delta F^*/k$ and vertical intercept corresponding to $\ln(3\gamma_m/\lambda^2)$; analysis is based on rearrangement of equation (3)

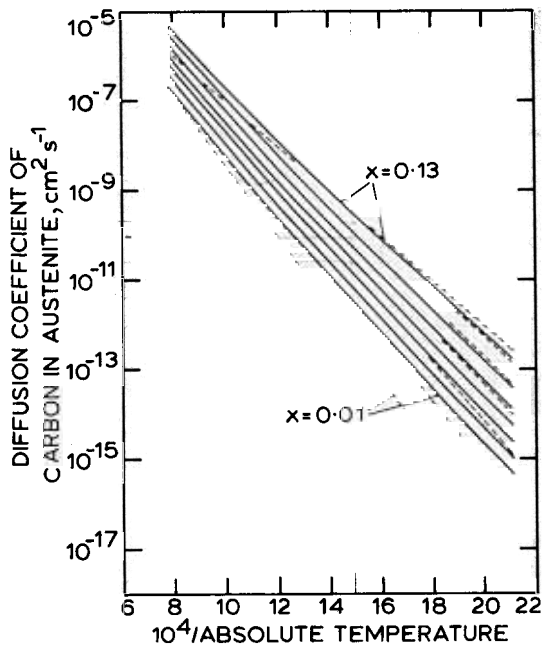
carbon, and $\sigma = 1 - \exp(-\Delta\varepsilon/kT)$, where $\Delta\varepsilon$ is the energy due to the repulsive interaction between neighbouring carbon atoms, taken to be 8250 J mol^{-1} (Ref. 14). With the appropriate data, equation (2) can be solved for D' ; experimental data on $D\{x, T\}$ for x up to 0.06 was obtained from Refs. 11, 15 and equations giving the activity of carbon in austenite were obtained from Ref. 16. The results are presented in Fig. 1, in which the vertical bars represent the range of D' values obtained for a given temperature, and despite variations in x , the range of D' values obtained, for any particular temperature is very small. This is consistent with the fact that the Siller and Mclellan model requires D' to be composition independent. The mean values of D' are indicated by the horizontal bars in Fig. 1.

Using the calculated values of D' (Fig. 1) it was possible to deduce ΔF^* and γ_m/λ^2 through a regression analysis (Fig. 2). The excellent linearity of the plot of Fig. 2 is strong evidence to show that ΔF^* is temperature and composition independent, as expected from equation (3).

Having derived the best values of the various quantities necessary for the use of equation (2), i.e. $\Delta F^*/k = 21230 \text{ K}^{-1}$ and $\ln(3\gamma_m/\lambda^2) = 31.84$, it was possible to compare the predicted and experimental^{11,15} diffusivities, as shown in Fig. 3, and it is clear that equation (2) is able to represent the experimental data. We may therefore confidently compute $D\{x, T\}$ for arbitrary $\{x, T\}$ well beyond the range of experimentally available data, and a set of such calculations is presented in Fig. 4, which also includes calculations using the method of Kaufman *et al.*³ In general, the agreement between the two methods is not bad, but it is believed that the Siller and Mclellan method is more desirable because it does not need any critical assumptions of the type necessary for the other method.



3 Comparison of experimental (Refs. 11, 15) and calculated (equation (2)) diffusion coefficients of carbon in austenite



- 4 Theoretical diffusivity calculations using equation (2) (bold curves) and Kaufman *et al.*³ analysis (dashed straight lines); difference in carbon concentrations between successive lines (corresponding to given method) is $\Delta x = 0.02$

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