Theoretical analysis of changes in cementite composition during tempering of bainite

H. K. D. H. Bhadeshia

An attempt has been made to model the kinetics of changes of composition in cementite during the aging of creep resistant low alloy steels of the type used in power plant. In the model a finite difference method is used for calculating the rate at which alloying elements redistribute between ferrite and cementite, subject to the thermodynamic constraints which determine the equilibrium compositions of these phases. It has also been possible to derive approximate analytical solutions which give good physical insight into the factors controlling the approach to equilibrium. Particle size has been found to have a strong influence on the rate at which the cementite composition is changed. A theoretical basis for the time dependence of cementite composition is also provided. The method is easily adapted to multiple or anisothermal heat treatments. Further work is suggested to account for simultaneous coarsening and changes in composition and also to allow for the formation of alloy carbides at long aging times. MST/874

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List of symbols

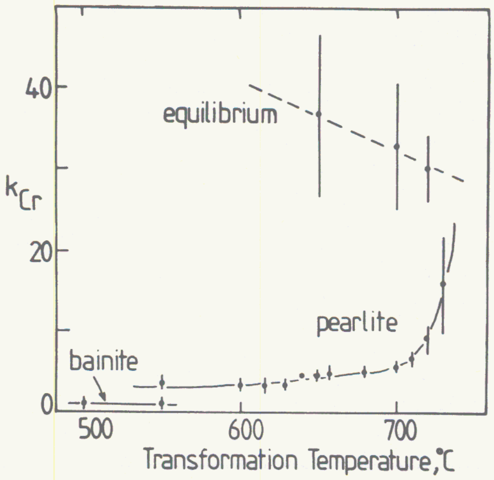
a	radius of spherical particle
$c^{\alpha\theta}$	composition of α in equilibrium with θ, moles/unit volume
$c^{\theta\alpha}$	composition of θ in equilibrium with α, moles/unit volume
$\bar{c}$	average composition of alloy
c'	dimensionless concentration in finite difference method
D_α	diffusivity in ferrite
D_θ	diffusivity in cementite
D_o	pre-exponential factor for diffusion coefficient
k_{Cr}	wt-%Cr in θ/wt-%Cr in α
k_Z	ratio of equilibrium concentration of element Z in M_3C to that in α
M_3C	$(Fe,M)_3C$, where M is a metal atom other than Fe
n_α	number of slices of ferrite
n_θ	number of slices of cementite
Q	activation free energy per mole for diffusion
r	grid parameter in finite difference method
R	universal gas constant
s	distance ahead of particle
t	time
t_c	time required to reach specified concentration
t'	dimensionless time in finite difference method
T	absolute temperature
V_θ	volume fraction of cementite
x_α	half thickness of ferrite in diffusion couple
x_θ	thickness of cementite in diffusion couple
x_s	thickness of slice in finite difference method
x'	dimensionless distance in finite difference method
α	ferrite
α_{lb}	lower bainite
$\alpha_{lb,ss}$	supersaturated lower bainite
$\alpha_{lb,us}$	unsaturated lower bainite
α_{ub}	upper bainite
$\alpha_{ub,ss}$	supersaturated upper bainite
$\alpha_{ub,us}$	unsaturated upper bainite
γ	austenite
γ_{en}	enriched austenite
γ'	austenite (composition of which is changed by partial transformation)
ε	ε-carbide
ε_f	ε-carbide in ferrite
θ	cementite
θ_f	cementite in ferrite
$\theta_{f/f}$	cementite between ferrite plates

Introduction

Many steel assemblies in power generation plant are operated at mean temperatures as high as 565°C, where creep deformation limits the life of their components. The creep life can be rather sensitive to temperature, an increase of 10 K occasionally leading to a reduction in creep life by a factor of ~2.[1] This makes the accurate assessment of creep life difficult, so that relatively large and consequently uneconomical safety factors must be implemented. In principle, improved estimates can be obtained if component temperatures can be recorded continuously during service, but this is not practical over a period of many years and for the vast number of components used.

This problem has inspired some elegant methods in which the steel microstructure is used to reveal the thermal history of the sample.[2–4] The initial microstructure usually consists of a mixture of allotriomorphic ferrite and bainite produced by continuous cooling transformation of thick sectioned material. The components are then tempered at 700°C, perhaps for several hours (in order to stress relieve), before entering service at ~565°C for periods as long as 25 years. During the tempering treatment and during service, the carbides present in the microstructure undergo changes towards equilibrium. These changes should at any instant reflect the integrated time–temperature history of the component concerned and, in principle, could be used to obtain an accurate estimate of the remaining creep life (i.e. remanent life) of the component at any stage during service. A large amount of experimental data on the chemical composition of carbides as a function of tempering treatments have already been accumulated and the present work is a first attempt towards a theoretical assessment of these data.

Some creep resistant steels also contain pearlite, but the chemical composition of pearlitic cementite, immediately after transformation, is for alloy steels always found to be somewhere between equilibrium and paraequilibrium (e.g. *see* Refs. 5, 6). There is as yet no theory which enables the calculation of cementite composition in these circumstances. In addition, there are many instances in which the composition of pearlitic cementite changes as a function of distance from the interface with austenite. For carbides associated with allotriomorphic ferrite, there are no reliable data for their chemical composition immediately after transformation. The same problems exist for bainitic cementite, but as is shown below, the much lower transformation temperatures involved in its formation results in a negligible redistribution of substitutional alloying elements. For these reasons, it is proposed to focus attention on the carbides associated with the regions of the microstructure that were



1 Composition of cementite immediately after isothermal transformation (After Ref. 5)

originally bainitic, in spite of the fact that many of the steels used in the power generation industry often contain phases other than bainite. In the following section, the nature of carbide precipitation in these regions[7] is briefly reviewed.

Carbide precipitation during the bainite transformation

Bainitic carbides can precipitate from austenite or from ferrite and, as discussed below, there are other complications which can influence any subsequent changes in carbide chemical composition and morphology during tempering or during service at elevated temperatures.

Unlike the transformation of austenite to pearlite, the formation of bainite does not involve the *cooperative* growth of bainitic ferrite and carbides. The ferritic component of bainite forms first; the excess carbon in this thermodynamically unstable, supersaturated bainitic ferrite is then removed by either of two competing processes. These processes are the partitioning of carbon into the residual austenite or its precipitation (in the form of carbides) within the bainitic ferrite. At relatively high temperatures, the rejection of carbon into the residual austenite is rapid, so that any carbide precipitation occurs from the carbon enriched residual austenite and the final microstructure obtained is upper bainite. At lower temperatures, carbide precipitation within the bainitic ferrite is predominant, resulting in lower bainite. The sequence of transformation can be summarised as follows.

1. Upper bainite

$$\gamma \rightarrow \gamma + \alpha_{\mathrm{ub,ss}} \rightarrow \alpha_{\mathrm{ub,us}} + \gamma_{\mathrm{en}} \rightarrow \alpha_{\mathrm{ub,us}} + \alpha + \theta$$

This contrasts with the cooperative growth of cementite and ferrite during the formation of pearlite in plain carbon steels

$$\gamma \rightarrow \alpha + \theta$$

and with the formation of pearlite in substitutionally alloyed steels

$$\gamma \rightarrow \alpha + \theta + \gamma'$$

where γ' differs in composition from γ.

2. Lower bainite: the dislocation density of α_{lb} has an effect on the free energy of carbon in the bainitic ferrite and hence can influence the carbide precipitation sequence, determining in particular whether ε forms before the growth of θ.

(i) high dislocation density

$$\gamma \rightarrow \gamma + \alpha_{\mathrm{lb,ss}} \rightarrow \theta_{\mathrm{f}} + \alpha_{\mathrm{lb,us}} + \gamma_{\mathrm{en}} \rightarrow \alpha_{\mathrm{lb,us}} + \alpha + \theta_{\mathrm{f/f}} + \theta_{\mathrm{f}}$$

(ii) low dislocation density

$$\gamma \rightarrow \gamma + \alpha_{\mathrm{lb,ss}} \rightarrow \varepsilon_{\mathrm{f}} + \alpha_{\mathrm{lb,us}} + \gamma_{\mathrm{en}} \rightarrow \alpha_{\mathrm{lb,us}} + \varepsilon_{\mathrm{f}} + \alpha + \theta_{\mathrm{f/f}}$$
$$\rightarrow \alpha_{\mathrm{lb,us}} + \theta_{\mathrm{f}} + \theta_{\mathrm{f/f}} + \alpha$$

Obviously, there are several types of cementite associated with the bainite reaction, but there are no studies of the changes in their individual chemical compositions as a function of heat treatment. In future, it would be useful if in experiments the types of possible carbide could be differentiated, although it is appreciated that any differences may disappear after long times at the tempering temperature.

Approach to equilibrium

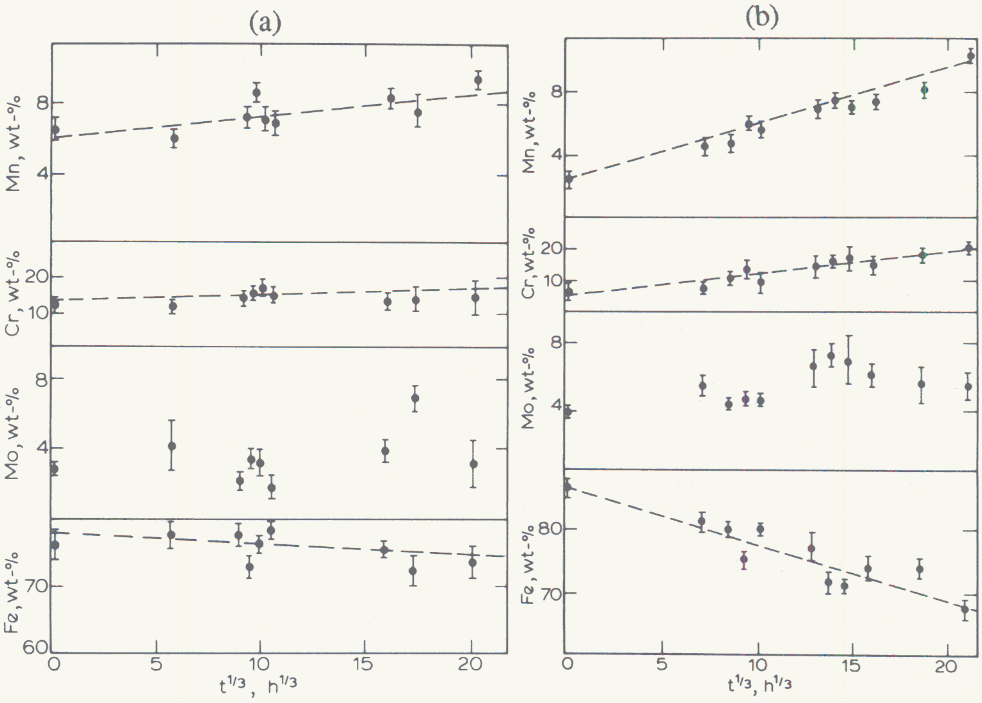
Even after the formation of carbides, bainitic microstructures are far from equilibrium. It has long been established that the cementite associated with upper bainite has a substitutional alloy content close to (or slightly higher than) that of the steel as a whole, even though this may be well below the corresponding equilibrium concentration.[8,9]

Chance and Ridley[5] found that for upper bainite in an Fe–0·81C–1·41Cr alloy, the partition coefficient k_{Cr} could not be distinguished from unity (Fig. 1). Consequently, they concluded that there is no redistribution of substitutional alloying elements during the formation of bainitic cementite. However, because the carbon concentration of cementite is substantially different from that of ferrite or austenite, a transformation to cementite which has the same Fe/Cr ratio as the parent phase should give a partitioning coefficient k_{Cr} which is less than unity. Hence, all the research to date supports the conclusion that the formation of cementite during the upper bainite transformation involves a small degree of redistribution of elements such as chromium into the cementite.

On the other hand, it has been established[5,6,8,9] that the degree of partitioning during transformation is much greater for pearlitic cementite, even when it forms at the same transformation temperature (Fig. 1). The explanation for this may lie in the fact that, unlike pearlitic cementite, upper bainitic cementite forms from carbon enriched austenite, so that the driving force for cementite formation is higher. Thus the tolerable departure from the equilibrium composition can be greater for upper bainitic cementite.[7]

During the tempering of bainite, before any alloy carbides are precipitated, and with the help of diffusion, the cementite tends towards its equilibrium composition. The exact manner in which its composition changes must depend on steel composition, starting microstructure, and tempering conditions. There is as yet no theory to relate these variables. The work discussed below should be interpreted with caution: many of the experiments deal with mixed microstructures (e.g. bainite and allotriomorphic ferrite) produced by continuous cooling transformation and do not distinguish between the bainitic cementite which precipitates from austenite and that which forms from any lower bainitic ferrite.

The remanent life assessment method based on carbide composition was first applied to pearlitic carbides for which it was found that the chromium and manganese concentrations in θ increased approximately with $t^{1/3}$, where t is the time at tempering temperature.[2,4] This relationship has not been justified theoretically, but seems to have been applied simply because it occurs in diffusion controlled coarsening theory. During coarsening, cementite particle size has occasionally been found to vary with $t^{1/3}$, if the coarsening reaction is controlled by the diffusion of solute through the



a service exposed material; *b* reaustenitised fully bainitic material

2 Changes in cementite chemical composition as function of aging time (After Ref. 12)

matrix. However, coarsening reactions in alloys are driven by the fact that the equilibrium composition of the matrix in contact with a particle is dependent on the principal radii of curvature of the particle/matrix interface.[10,11] For example, the matrix adjacent to smaller spherical particles is expected to have a higher equilibrium concentration of solute than that adjacent to larger spherical particles. Consequently, a diffusion flux is stimulated from the smaller to the larger particles, so that the larger particles grow at the expense of smaller particles. The driving force for the process is the reduction in total interfacial energy.

However, the approach of cementite composition towards equilibrium is not a process which can be compared with a coarsening reaction. In fact, the matrix is supersaturated in solute with respect to almost all particles. Thus, the concentration of solute increases in all the particles irrespective of size. The flux of interest is that of solute into a particle from the surrounding matrix, for both small and large particles. In these circumstances, it is not appropriate to draw any conclusions from coarsening theory.

Afrouz *et al.*[12] have reported remanent life experiments on the cementite associated with bainite in an Fe–0·1C–0·24Si–0·48Mn–0·84Cr–0·48Mo (wt-%) steel. Some service exposed material (70 000 h at 565°C) with a mixed microstructure of allotriomorphic ferrite and ~20% bainite was tempered further at 550°C (Fig. 2*a*). As expected, the chromium and manganese concentrations of M_3C were found to increase with time. For manganese, signs of saturation at long times can possibly be inferred and considerable scatter can be seen for the molybdenum data. Afrouz *et al.* also reaustenitised (reheat treated) the service exposed material so that after oil quenching, a fresh fully bainitic microstructure (probably a mixture of upper and lower bainite) was obtained. After stress relieving at 703°C for 1 h, the change in M_3C composition was monitored during tempering at 550°C. The starting composition of the cementite was of course lower than that of the service exposed material and the rate of enrichment was found to be higher for the reheat treated samples. In each case, the composition varied approximately with $t^{1/3}$, the slope being greater for the reheat treated material. The results are of interest and provide a unique method of monitoring the thermal history of creep resistant steels. The details are revealing: it can be inferred from the fact that the service exposed material changes composition at a slower rate that the enrichment process does not really follow a $t^{1/3}$ relationship. In addition, the enrichment of the service exposed M_3C, before the 550°C temper, seems very low considering that it has been held at 565°C for 70 000 h. The discrepancy could occur because the 20% bainite present in the service exposed material originally formed from carbon enriched austenite; then, the cementite particles would be relatively coarse and closely spaced and consequently average composition would change at a lower rate. Much theoretical work is required to model the diffusion process and provide a framework for the interpretation of the results.

Theory

FINITE DIFFERENCE METHOD

The model proposed here is not complete in the sense that it does not account for simultaneous coarsening and composition changes. In the analysis, a mean cementite particle size (0·3 μm) is used which represents the actual size rather well for long times at service temperatures.

The problem is treated using a finite difference method which is summarised below, but which is fully discussed in Ref. 13. The cementite–ferrite aggregate is treated as a composite diffusion couple in which a flat slab of cementite (thickness x_θ) is welded on either side to a slab of ferrite (thickness x_α), such that

$$x_\theta/(2x_\alpha+x_\theta)=V_\theta \qquad (1)$$

where V_θ is the volume fraction of M_3C in the alloy. Using this equation, x_α is determined, since V_θ is given approximately by the lever rule as applied to the $\theta+\alpha/\alpha$ phase field of the binary Fe–C system

$$V_\theta=(\bar{c}-c^{\alpha\theta})/(c^{\theta\alpha}-c^{\alpha\theta}) \qquad (2)$$

Table 1 Parameters[14] used for calculation of partition coefficients

Element Z	*A*, J mol^{-1}	*B*, J mol^{-1} K^{-1}
Cr	47028	−17·45
Mn	42844	−20·21
Mo	27363	−5·86
Ni	−2619	−2·80
Si	0	−25·10

Table 2 Calculated equilibrium concentrations for Fe–0·1C–0·24Si–0·48Mn–0·84Cr–0·48Mo (wt-%) alloy used by Afrouz *et al.*[12] (note that calculations are specific to this alloy and should not be used for any other steels)

	Equilibrium concentration at 976 K, wt-%		Equilibrium concentration at 823 K, wt-%	
Element	α	θ	α	θ
Cr	0·52	21·3	0·30	36·0
Mo	0·40	5·8	0·34	9.3
Mn	0·38	6·7	0·29	13·2

where, in this equation, $c^{\theta\alpha}$ and $c^{\alpha\theta}$ are the equilibrium carbon concentrations of the cementite and ferrite respectively (at ambient temperature) and $\bar{c}$ is the average carbon concentration in the alloy as a whole. Thus, the problem is treated in terms of one dimensional diffusion; this may be a good approximation if the spatial distribution of the plate-like carbides is appropriate.*

The analysis is carried out using non-dimensional variables, the concentrations c being normalised with respect to the average concentration in the alloy and the distance x being normalised with respect to the thickness of the cementite. The normalised variables are

$$x' = x/x_\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$c' = c/\bar{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$t' = Dt/(x_\theta)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where D is the diffusion coefficient.

As is shown below, the partition coefficient k_Z is very high for Z ≡ Mn, Mo, and Cr, at the temperatures of interest in the present study, Hence, the redistribution of elements is controlled by the rate at which the alloying element concerned diffuses through the ferrite to reach the α/θ interface, except at long times when the cementite approaches its equilibrium composition (i.e. saturation).

For the finite difference analysis, the cementite and ferrite are divided notionally into a number n of slices of equal thickness x_s such that

$$n_\theta = x_\theta/2x_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$n_\alpha = x_\alpha/x_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Thus, the ferrite occupies the space $0 \leqslant x' \leqslant (2x_\alpha/x_\theta)$. The x'–t' region is covered by a grid of rectangles of sides $\delta x'$ and $\delta t'$ respectively, so that the coordinates of a grid point (x', t') can be written $(i\delta x', j\delta t')$, where i and j are integers. The normalised concentration at that point (for phase α) is written $c'^{\alpha}_{i,j}$. The explicit finite difference formula is then given by

$$c'^{\alpha}_{1,j+1} = c'^{\alpha}_{i,j} + r(\mathrm{c}'^{\alpha}_{i-1,j} - 2c'^{\alpha}_{i,j} + c'^{\alpha}_{i+1,j}) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $r = \delta t'/(\delta x')^2$ and is taken to be 0·4. The value of r determines the accuracy of the method and also the computation time. A compromise value has been chosen by trial and error.

The normalised concentration c'^{α}_s in the α at the α/θ interface was initially set at $c^{\alpha\theta}/\bar{c}$, although the computer algorithm was designed to allow this to vary as soon as the flux matching condition at the interface necessitated changes. Then, equation (8) was used to calculate the value of c at all points along successive time rows of the grid, for the initial conditions that $c'^{\alpha}_{0,0} = c^{\alpha\theta}/\bar{c}$, and $c'^{\alpha}_{i,0} = 1$ for all $i > 0$.

A similar analysis was applied to the cementite and the diffusion processes in the ferrite and cementite were coupled by the requirement that there should be no build up of solute at the interface between the two phases: in effect this means that $c'^{\theta}_{0,j}$ is determined by the equation

$$D_\theta(c'^{\theta}_{0,j} - c'^{\theta}_{1,j}) = D_\alpha(c'^{\alpha}_{1,j} - c'^{\alpha}_{0,j}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

with $c'^{\theta}_{i,0} = 1$ for all $i > 0$. Since, in the present work, D_θ is assumed to be equal to D_α and since, in general, $c^{\theta\alpha} \gg c^{\alpha\theta}$, this condition ensures that the surface concentration of cementite at the θ/α interface $c'^{\theta}_{0,j}$ is, for a considerable period of time, less than $c^{\theta\alpha}/\bar{c}$.

For both phases, soft impingement eventually occurs in the sense that the concentrations at the maximum values of i for both θ and α are eventually affected by the fluxes originating at the α/θ interfaces. Hence, the concentrations in the slices with $i = i_{\mathrm{max}}$ are given by reflecting the concentration profile across an imaginary boundary located at i_{max}

$$c'^{\theta}_{i_{\mathrm{max}},j+1} = c'^{\theta}_{i_{\mathrm{max}},j} + 2r(c'^{\theta}_{i_{\mathrm{max}}-1,j} - c'^{\theta}_{i_{\mathrm{max}},j}) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

As the diffusion proceeds, $c'^{\theta}_{0,j}$ eventually reaches $c^{\theta\alpha}/\bar{c}$ (for the present work, this occurs at very long times). When this occurs, it is diffusion in the cementite which begins to control the equilibration process and the program switches to adjusting $c'^{\alpha}_{0,j}$ to a value consistent with the condition for conservation of mass at the interface. The value of $c'^{\alpha}_{0,j}$ then begins to increase to a value greater than $c^{\alpha\theta}/\bar{c}$.

EQUILIBRIUM COMPOSITIONS OF CEMENTITE AND FERRITE

The partition coefficients k_Z of alloying elements between cementite and ferrite, for dilute alloys, as a rough approximation can be written as follows[14]

$$k_Z \approx \exp[(A + BT)/RT] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The values of A and B for various elements Z are given in Table 1.

Since $k_Z = c^{\theta\alpha}/c^{\alpha\theta}$, the condition for mass balance at equilibrium requires that

$$\bar{c} = c^{\theta\alpha}V_\theta + (c^{\theta\alpha}/k_Z) - (c^{\theta\alpha}V_\theta/k_Z) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

so that the equilibrium compositions of the two phases can easily be calculated as a function of heat treatment temperature (Table 2). It is emphasised that the procedure used here is approximate. Much improved calculations can be carried out using facilities such as the National Physical Laboratory thermodynamic data bank.

DIFFUSION COEFFICIENTS

The diffusion coefficients (Table 3) for ferrite are all taken from Ref. 15. They are radioactive tracer diffusion coeffi-

Table 3 Diffusion coefficients[15]

Element	D_o, m^2 s^{-1}	*Q*, J mol^{-1}
Cr	$2{\cdot}53 \times 10^{-4}$	240580
Mo	$7{\cdot}8 \times 10^{-1}$	305432
Mn	$3{\cdot}5 \times 10^{-5}$	219660

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* This implies that if all the carbides are notionally swept towards the middle of the sample, then there would result a continuous and uniform slab of cementite of thickness x_θ in a bar of total length $x_\theta + 2x_\alpha$. Also, note that the problem of diffusion is symmetrical about the centre of a cementite slab and only one half of it need be studied.

cients, but for the low alloy concentrations in the ferrite of the steels studied in the present work, they should be a good approximation to the corresponding chemical interdiffusion coefficients.

Results and discussion

As noted above, low alloy steels used in the power generation industry, after being continuously cooled from the austenitising temperature, are given a high temperature (~700°C) stress relief heat treatment before service at a relatively low temperature (~565°C). Consequently, two computer programs have been developed: the first one (FINITE) for modelling the changes that take place during the stress relief heat treatment and the second (FINN), in which the data generated by FINITE are used as an input, for simulating the further compositional changes that occur during service. The results from these programs are of two types: general principles governing the solute redistribution process (e.g. the dependence of enrichment kinetics on particle size) and actual comparisons with published experimental data.

CONCENTRATION GRADIENTS

It is revealed by the computations that both ferrite and cementite contain substantial concentration gradients during their approach towards equilibrium. However, reported experimental measurements are not of a resolution high enough to detect these gradients; when making comparisons between theory and experiment, it is therefore assumed that the experimental data refer to the average solute concentrations in cementite. Consequently, the calculated compositional data reported here are the mean compositions in each phase. At long aging times when the gradients are shallow, this is a good approximation, but whether this is true at relatively short times remains to be demonstrated experimentally.

SOFT IMPINGEMENT

The overlap of the diffusion or temperature fields of adjacent particles, or from active regions of the same particle, is called soft impingement.[11] It generally leads to a slowing down of the process concerned. On the other hand, hard impingement implies physical contact between growing particles.

For cementite, significant soft impingement for the conditions appropriate for the present work is found to occur in less than 1 h during tempering. For ferrite, it typically follows after about 8000 h; thus, until then, the ferrite can be assumed to have a semi-infinite extent. Of course, such an assumption is not necessary for the finite difference method (and indeed is not made), but can be of use in analytical approaches to the diffusion problem.

SURFACE COMPOSITIONS

The surface composition here implies the solute concentration in either phase at the α/θ boundary; it may or may not correspond to the equilibrium concentration. Because the equilibrium concentration of solute (Cr, Mn, Mo) in cementite is, for the present circumstances, much higher than its average concentration in the alloy, the surface concentration in cementite only approaches $c^{\theta\alpha}$ after long periods of aging, when it is almost saturated.

As expected, exactly the opposite situation prevails for ferrite: its surface concentration corresponds to $c^{\alpha\theta}$ for most of the aging process, but begins to exceed $c^{\alpha\theta}$ when the cementite approaches saturation. The gradients within the ferrite are always found to be low because the difference between $\bar{c}$ and $c^{\alpha\theta}$ is not very large for commercial steels (e.g. *see* Table 2).

PARTICLE SIZE

An important result to emerge from the model is the strong effect of particle thickness on its average composition during aging. Obviously, for a given flux across the θ/α interface, small particles are small sinks for solute and must enrich at a higher rate. It can be seen from examination of the data generated by the finite difference method that the time t_c required to achieve a given composition varies as $(x_\theta)^2$. For example, in an Fe–0·28C–0·99Cr (wt-%) alloy tempered at 700°C, a particle of θ of thickness $x_\theta = 100$ nm by calculation is expected to reach its equilibrium concentration (15·2 wt-%) within 8 h, whereas the same process is expected to take 18 h for a particle having $x_\theta = 150$ nm (this particular alloy is one that is currently being investigated at the CERL). Note that this is found to be precisely the correct relationship only when soft impingement has not occurred within the ferrite.

The relationship above can be demonstrated analytically.* Consider a slab of cementite of thickness x_θ embedded in an infinite matrix of ferrite (i.e. no soft impingement in ferrite). If the time required for the cementite to reach a concentration c^θ is t_c, then a standard mass balance procedure[7,13,17,18,19] requires that

$$0{\cdot}5x_\theta(c^\theta-\bar{c}) = \int_0^\infty c^\alpha(x, t_c)\,\mathrm{d}x \qquad (13)$$

where

$$c^\alpha(x, t_c) = (\bar{c}-c^{\alpha\theta})\,\mathrm{erfc}\,[x/2(D_\alpha t_c)^{0{\cdot}5}] \qquad (14)$$

It follows that

$$t_c = \pi[x_\theta(\bar{c}-c^\theta)]^2/16D_\alpha(c^{\alpha\theta}-\bar{c})^2 \qquad (15)$$

This equation is valid until the onset of soft impingement in the ferrite; this means that it should typically not apply after 8000 h of service life. The following statements can be made from the equation.

1. The time required to reach a given concentration in the cementite varies with the square of the particle thickness.
2. For the domain in which the equation is valid, it can be inferred that the composition of cementite (less $\bar{c}$) should vary with $(\text{time})^{1/2}$ rather than with $(\text{time})^{1/3}$. It has been verified that the data of Afrouz *et al.*[12] fit this equation well; if anything, a slightly better fit is obtained when compared with the $(\text{time})^{1/3}$ law.
3. The role of $\bar{c}$, $c^{\alpha\theta}$, and D_α in the aging process are well defined by the equation. Because $c^{\alpha\theta}$ is a relatively weak function of temperature, most of the temperature dependence of the aging process occurs via D_α. Consequently, for experiments carried out at various temperatures, and given that the cementite is not saturated and that the ferrite behaves as if it is semi-infinite in extent, a plot of $\ln(t_c)$ versus $(1/T)$ should give a positive slope the value of which corresponds to the activation energy for diffusion divided by the universal gas constant. A result in agreement with this prediction has been reported by Carruthers and Collins.[2]
4. It is well established that in general the cementite particle size increases and particle spacing decreases as the average carbon concentration of the alloy concerned increases. This has an important consequence on the aging kinetics of steels used in power stations, in which steels the amount of bainite can vary between 20–80 vol.-% within a given batch of material. The remainder of the microstructure is allotriomorphic ferrite, which is the first phase to grow from the austenite, so that the carbon concentration of the residual austenite from which the bainite forms may vary by an order of magnitude. Consequently, for a given batch of

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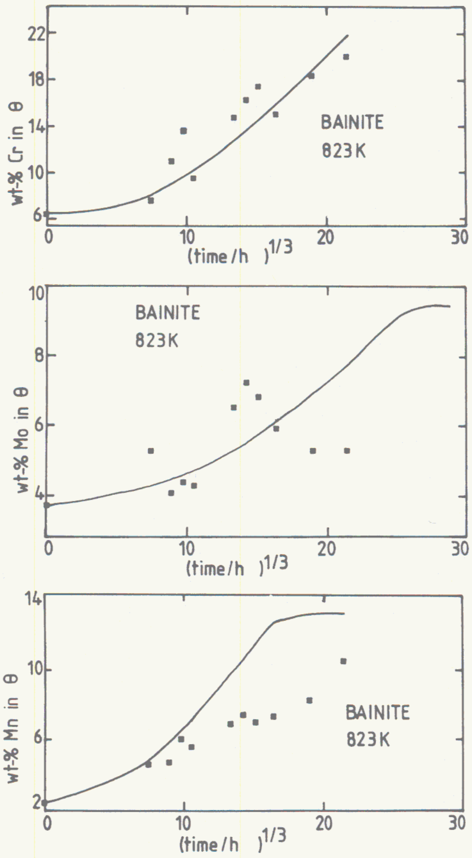
* This analysis that follows does not allow for the coupling of fluxes between the ferrite and cementite and will consequently tend to overestimate the time required to reach a given concentration.[16] However, the form of the relationships that emerge has been verified using the full finite difference method and the degree of overestimation is rather small.



3 Comparison between calculated curves (present work) and experimental data (Ref. 12)

material, the solute enrichment kinetics can be expected to vary considerably. As noted in the introduction to the present paper, the classic experiments of Afrouz *et al.*, in which a fully bainitic sample was compared with a sample containing only 20 vol.-% bainite, are in agreement with the present work, since the latter samples were found to exhibit slower enrichment kinetics. The problems became enhanced in those steels which also contain pearlite.

The analysis presented above was for plate shaped particles of the type usually observed in steels used in power plant. A similar analysis can be carried out for spherical particles. If the particle radius is a and the distance ahead of the particle is designated s, then the solute distribution ahead of the particle is given by[13]

$$c^{\alpha}(s, t_c) = [a(\bar{c}-c^{\alpha\theta})/(a+s)]\,\mathrm{erfc}\,\{s/2(D_\alpha t_c)^{0\cdot 5}\} \quad . \; . \; (16)$$

Using the same procedure as above, it can be demonstrated that

$$a^2(c^{\theta\alpha}-\bar{c})/[3(\bar{c}-c^{\alpha\theta})] = D_\alpha t_c + 2a(D_\alpha t_c/\pi)^{0\cdot 5} \quad . \; . \; . \; . \; (17)$$

As above, an initial enrichment related to $t^{1/2}$ is indicated, with a subsequent reduction in the time exponent; in agreement with the analysis above, the enrichment also varies with the square of the particle radius. However, the interpretation of an activation energy for the process is more complex, even for short time periods, since the equation is no longer linear in D_α.

COMPARISON BETWEEN EXPERIMENT AND THEORY

It has not been possible to find published data which include all the variables that the theory requires, but the experiments of Afrouz *et al.*, in which a reaustenitised sample of steel was by continuous cooling heat treatment transformed to bainite only, provide the most suitable source of information. These data are presented in Fig. 2*b*.

It is assumed here that the initial concentration of substitutional alloying elements of the bainitic cementite is the same as that of the alloy as a whole. As already noted, this may not be justified[7] in detail, but it is the best that can be done at present. With this assumption, the calculated cementite composition after tempering the bainite for 1 h at 967 K ($x_\theta = 300$ nm) is found to be 2·75Mn–2·18Mo–3·7Cr (wt-%) as compared with the experimental value of 2·4Mn–3·65Mo–6·3Cr (wt-%) reported by Afrouz *et al.* The difference between the calculated and experimental cementite compositions is of little consequence after tempering for about 100 h at the service temperature of 823 K. For this reason, and since the primary interest is in aging at the service temperature, the starting composition of the cementite before aging at 823 K was adjusted to comply with the data of Afrouz *et al.* This adjustment must be carried out carefully, since the initial temper at 967 K should cause concentration gradients in both the cementite and ferrite at the interface. The correction was made by adjusting the tempering time at 967 K (as presented to FINITE) until the carbide reached the appropriate composition. The maximum adjustment to time was by a factor of ~2.

The results are presented in Fig. 3. There is good agreement for chromium and reasonable agreement for manganese and molybdenum. For the last two elements, saturation is predicted and indeed appears to be indicated experimentally and it has been checked that the discrepancy between calculation and experiment results largely from the chosen value of the saturation concentration. As noted above, an approximate method has been used to estimate the saturation concentration. The error in prediction is expected to be exaggerated for elements with lower saturation concentrations in cementite.

MISCELLANEOUS

Finally, as far as the construction of future power plant is concerned, it should be possible with the present model to design an alloy which is ideal for the purposes of recording the thermal history of components. This could be applied to critical regions of components for future non-destructive microstructural and microanalytical examination. The alloy would have a uniform starting microstructure of known carbide chemistry and distribution, it would have a very large difference between the starting and saturation states of the carbide, and interference between competing reactions could be designed out.

Conclusions and suggestions for further work

An attempt has been made to model the process of compositional changes in cementite during the aging of creep resistant low alloy steels. The model is in good agreement with published experimental data. A basis for the design of future experiments is also provided, since certain key factors have been identified as being important in controlling the kinetics of the aging process. It is believed that future experiments should include simultaneous determinations of particle thickness, composition, local spacing, and, if possible, ferrite composition. It is also vital that the initial microstructure before service should be fully established.

Further theoretical work is required on simultaneous coarsening and enrichment kinetics and on carbides other than cementite. It is also necessary to model theoretically the formation of cementite from austenite, when the former has a composition which is neither close to equilibrium nor paraequilibrium; the starting composition of pearlitic carbides could then be predicted.

The influence of alloy carbide formation on changes in cementite must be significant at long service times; it is planned to investigate this for both stoichiometric and non-stoichiometric alloys.

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