Development of a computer model of dendritic microsegregation for use with multicomponent steels

A.A. HOWE

British Steel Corporation, Swinden Laboratories, Rotherham, UK

Abstract. Progress is reported in the development of a computer program for modelling the process of microsegregation in multicomponent steels. The program is based on the single phase binary and ternary models described in the previous paper by Ogilvy and Kirkwood but has been extended to consider general, multicomponent alloys. The cooling rate required in the program formulation is currently determined according to a constant, set rate of heat extraction, but any, independently derivable rule could be employed. The peritectic reaction from ferritic to austenitic solidification encountered in a great many steels has been included in the formulation with the relevant, three-phase compositions decreed in pseudo-binary fashion by appropriate carbon equivalents. The onset of the austenite-cementite eutectic is similarly described. Manganese sulphide precipitation is described by removal of the elements from the residual liquid in appropriate ratio so as not to exceed a prescribed solubility product. Such devices can be fashioned similarly for other phase and precipitate developments as required.

Nomenclature

A	Back diffusion term, m wt% s^{-1}	W	Cooling rate, ks^{-1}
B	Correction factor for fast – diffusing species	x	Distance coordinate normal to dendrite plate
C	Concentration in the solid, wt%	X	Distance solidified, m
Cl	Concentration in the liquid, wt%	Z	Correction increment, wt%
C_0	Bulk concentration, wt%	β	Liquidus gradient, k wt%$^{-1}$
Cp	Concentration in the liquid during the peritectic, wt%	θ	Heat capacity, Jm^{-3}k^{-1}
D	Diffusivity in the solid, m^{2}s^{-1}	*Subscripts:*	
f	Fraction solid ($= X/L$)	c	carbon
H	Volumetric latent heat, Jm^{-3}	i	"i"th element
K	Partition coefficient	Mn	manganese
L	Half dendrite arm spacing, m	S	sulphur
M	Atomic weight, (a.m.u.)		
$\dot{Q}$	Heat extraction rate, Jm^{-3}s^{-1}	*Superscripts:*	
R	Atomic weight ratio	bcc	body centred cubic delta ferrite
t	time, s	fcc	face centred cubic austenite
T	Temperature, k		

1. Introduction

The various forms of segregation resulting from solidification are of great importance and dictate the degree to which the material has to be worked subsequent to casting before the required physical property specification can be met. The microsegregation between the dendrite arms is, of itself, important in this respect but is usually an accepted feature and it is the presence of macrosegregation, i.e. larger scale compositional inhomogeneity, which is more frequently described as a problem. It must be remembered, however, that the source of virtually all the macrosegregation in dendritic solidification is this inherent microsegregation, a quantitative understanding of which is therefore central.

A finite difference formulation for microsegregation with temperature dependent diffusivity had been developed at BSC but was deemed inferior to the model due to Kirkwood and Ogilvy [1] because the former required a prescribed, interdendritic growth law and did not include the process of secondary arm coarsening. The latter model was made available to BSC but required modification and extension for proper use with steels.

2. Modification of basic solute balance formulation

The ternary description available at the onset of this work [2] was insufficient even for so-called 'plain carbon' steels and it was therefore necessary to develop a general, multicomponent formulation. Analysis of the source equations revealed that this extension could be readily achieved, assuming that the cooling rate expression can be extended linearly for any number of components, i.e.:

$$W = \sum \frac{\delta Cl_i}{\delta t} \cdot \beta_i.$$

A further aspect was the inherent assumption that this cooling rate was constant through solidification, which was inappropriate for practical casting processes. Again, however, analysis of the source equations indicated that this was not a problem. The cooling rate must be supplied for each program iteration but does not have to be constant. At present, this is derived from an assumption of a constant rate of volumetric heat extraction:

$$\dot{Q} = H \cdot \frac{\mathrm{d}f}{\mathrm{d}t} + \theta \cdot \frac{\mathrm{d}T}{\mathrm{d}t}$$

($f = X/L$ where both X and L are functions of t)

$$W = \frac{1}{\theta} \cdot \left\{ \dot{Q} - \frac{H}{L} \cdot \left(\frac{\mathrm{d}X}{\mathrm{d}t} - f \cdot \frac{\mathrm{d}L}{\mathrm{d}t} \right) \right\}.$$

The basic, simultaneous solution of the solute balance equations for the growth rate is as follows:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{L(1-f) \cdot \frac{\dot{Q}}{\theta} + \frac{\mathrm{d}L}{\mathrm{d}t} \cdot \left(f(1-f) \cdot \frac{H}{\theta} + \sum \beta_i \cdot (Cl_i - Co_i) \right) + \sum \beta_i \cdot A_i}{(1-f) \cdot \frac{H}{\theta} + \sum \beta_i \cdot Cl_i (1 - K_i)}$$

where $A_i = D_i \cdot \dfrac{\delta C_i}{\delta x}$ for substitutional elements or $L \cdot f \cdot K_i \cdot \dfrac{\mathrm{d}Cl_i}{\mathrm{d}t}$ for interstitial elements.

The value of $\mathrm{d}Cl_i/\mathrm{d}t$ for the interstitial elements in the term, A_i, has to be that derived from the previous iteration. The following, improved formulation can be made which fully eliminates this term from the expression. This corresponds to equation 3 in the previous paper suitably modified for the constant heat extraction assumption:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \left[L(1-f) \cdot \frac{\dot{Q}}{\theta} + \frac{\mathrm{d}L}{\mathrm{d}t} \cdot \left\{ f(1-f) \cdot \frac{H}{\theta} + \sum \beta_i \cdot (Cl_i - Co_i) \cdot B_i \right\} \right.$$
$$\left. + \sum^{\text{sub}} \beta_i \cdot A_i \right] \left[(1-f) \cdot \frac{H}{\theta} + \sum \beta_i \cdot Cl_i (1 - K_i) \cdot B_i \right]^{-1}$$

where B_i is the 'correction factor' for interstitial elements:

$$B_i = (1-f)/(1 - (1 - K_i)f)$$

and the superscript, sub, refers to summation for the substitutional elements, only. It is hoped that this revised formulation will solve some of the instability problems at high fractions solid.

3. Compound and eutectic precipitation

The region of the Fe–C–Cr ternary considered in Ogilvy's research work [2] included terminal solidification upon attainment of the austenite-cementite eutectic, with the relevant carbon content in the residual liquid dependent on the chromium content. Similarly, other elements would be expected to influence the carbon content at the eutectic. Provided carbon remains the 'dominant' element in the residual liquid, this can be assessed in pseudo-binary fashion by use of carbon equivalents. Relevant coefficients are employed for cast irons in determining whether a particular composition is hypo- or hyper-eutectic, and these can be applied to the residual, interdendritic liquid composition. The values employed are taken from reference [3] except that the chromium coefficient is replaced by the quadratic equation employed by Ogilvy. A similar approach could be followed for stainless steels if a treatment using both chromium and nickel equivalents, instead of those for carbon, is employed.

The eutectic will terminate solidification at a constant temperature only if it involves each component element but this simple termination would be a reasonable approximation because, even with the highest carbon steels of interest, the eutectic would only be encountered in a very low volume fraction of residual liquid.

The most important compound in terms of this work to be precipitated from the liquid is manganese sulphide, MnS. A great many steels precipitate this compound, albeit in small quantities, towards the end of solidification, but it is not considered to be an adequate approximation to assume that solidification terminates with its development. Consequently, a routine has been introduced to remove manganese and sulphur from the residual liquid in appropriate ratio as it precipitates but which allows this liquid to continue its solidification with decreasing temperature. A maximum solubility product of 0.506 (wt%) [2] in the liquid is employed, as determined by Schwerdtfeger [4]. The resultant formulation is as follows:

$$Cl_{Mn} \rightarrow Cl_{Mn} - R \cdot Z, \quad Cl_S \rightarrow Cl_S - Z$$

where $R = M_{Mn}/M_S$ and

$$Z = \left((Cl_{Mn} + R \cdot Cl_S) - \sqrt{(Cl_{Mn} + Cl_S)^2 - 4R \cdot (Cl_{Mn} \cdot Cl_S - 0.506)} \right)/2R.$$

4. The peritectic reaction

A great many steels undergo the delta-ferrite/austenite peritectic reaction during solidification (Fig. 1) whereas the supplied model [1] only considered single phase solidification. Two additional routines were therefore required: one to determine the relevant phase compositions bounding the reaction, and another to handle the physical progress of the reaction.

In a similar fashion to the case of the eutectic reaction (section 3), the liquid composition at which the peritectic is encountered is treated in a pseudo-binary manner with the use of carbon equivalents. Unfortunately, no such coefficients specific to this reaction appeared to be available from other sources and the values employed (Table 1) were generated for this study from very limited data (20 casts of carbon and low alloy steels). The respective compositions in the ferrite and austenite were determined simply from that in the liquid multiplied by the relevant partition coefficients. The following equation can therefore be generated relating the fraction solid of bcc, delta-ferrite to the overall fraction solid, bulk carbon content and peritectic liquid carbon content:

$$f^{bcc} = \frac{\left(1 - Co_c/Cp_c - f\left(1 - K_c^{fcc} \right) \right)}{\left(K_c^{fcc} - K_c^{bcc} \right)}.$$

The peritectic reaction was assumed to follow equilibrium which, unlike the case in many alloy systems, is a reasonable assumption in steels where its
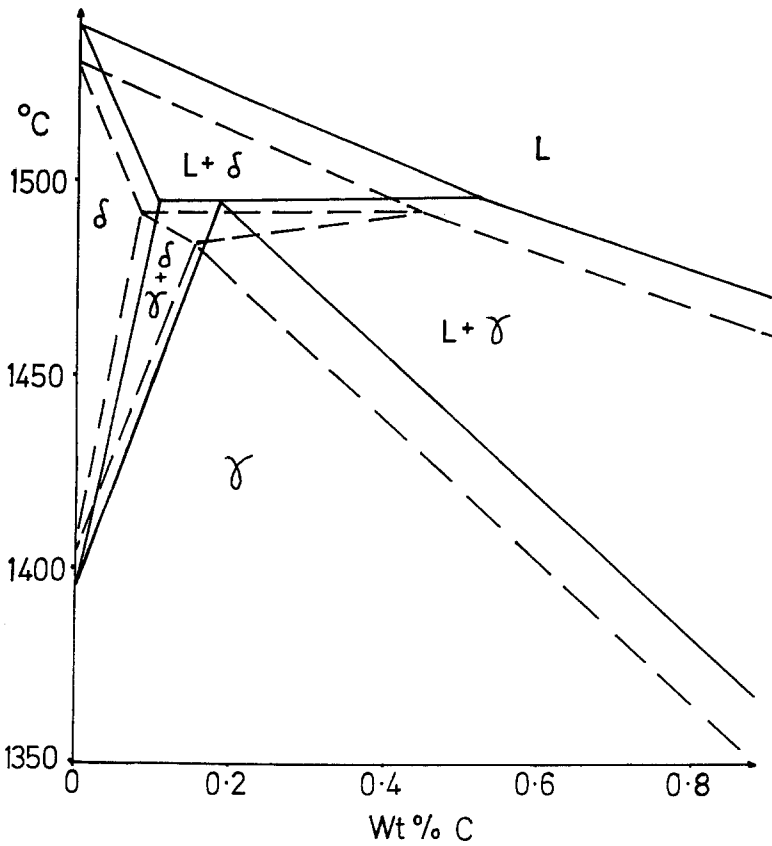
Fig. 1. Fe–C binary & pseudo-binary in multicomponent steel.

progress is dominated by rapidly diffusing carbon atoms. The back diffusion term, A_i, from the solute balance equation was restructured for carbon and nitrogen for progress through the peritectic, with uniform concentration in each phase. The expression thus generated is most readily understood from the schematic description, Fig. 2:

$$A_i = L \cdot \left(\frac{\mathrm{d} f^{\mathrm{bcc}}}{\mathrm{d} t} \cdot Cl_i \left(K_i^{\mathrm{fcc}} - K_i^{\mathrm{bcc}} \right) + \frac{\mathrm{d} Cl_i}{\mathrm{d} t} \cdot \left(K_i^{\mathrm{bcc}} \cdot f^{\mathrm{bcc}} + K_i^{\mathrm{fcc}} \left(f - f^{\mathrm{bcc}} \right) \right) \right)$$

where subscript 'i' is restricted to interstitial elements.

Modification consistent with that described at the end of section 2 may be required if the peritectic occurs or persists towards the end of solidification, but its incorporation for nitrogen is problematic. (The problem does not occur for carbon in the present, peritectic formulation because its liquid content is controlled independently of the equations employed for the other elements; neither does it affect the formulation for the other elements because its liquidus gradient, β, is zero during this process.)

Table 1. Carbon equivalent coefficients, E_i.

	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	V
Periectic	(1)	−0.123	+0.04	−	+0.06	−0.018	−0.05	+0.08	+0.075	−0.10
Eutectic	(1)	+0.31	−0.03	+0.33	−	*	−	+0.05		

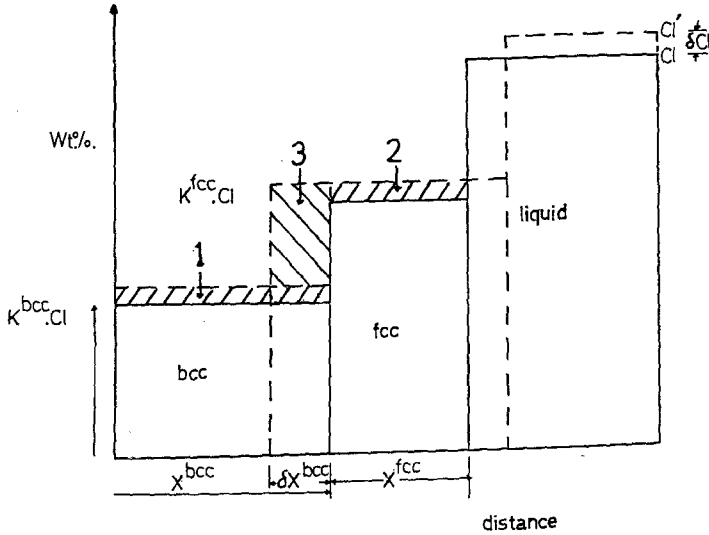$E_{Cr} = -0.015Cr + 0.00216Cr^2$ (ref. [2]).
$E = C + \Sigma E_i C_i$.

Fig. 2. Schematic representation of solute balance for interstitial elements during the peritectic reaction. Effective back-diffusion term in time δt comprises the three labelled areas, $1+2+3$: $\delta Cl \cdot (K^{bcc} \cdot X^{bcc}) + \delta Cl \cdot (K^{fcc} \cdot X^{fcc}) + \delta X^{bcc} \cdot Cl \cdot (K^{fcc} - K^{bcc})$. ———: position/concentration before solidification increment; — — —: position/concentration after solidification increment.

The diffusive behaviour of the 'slow' elements in substitutional solid solution is, at present, assumed to be unaffected by the solid state phase change, but superior formulations are being considered.

5. Initial operation and results

Some stability problems have been experienced with the program at high fractions solid. Depending on the composition, heat extraction rate and, notably, the mathematical description of the dendrite coarsening process, the program would not reliably achieve 100% solid under stable conditions. The schematic dendrite in Fig. 3 suggests that the greater inaccuracy in description of the dendrite should be at low fractions solid. The calculated results are, however, very insensitive to the morphological description at low fractions solid but surprisingly sensitive to representation of the coarsening process at completion of solidification. Further work is in hand to restructure or refine the iterative calculations under these conditions to make the program more robust in operation. It is hoped, for example, that the revised formulation described in section 2 will help in this respect. In the meanwhile, certain observations can be made but the program has yet to be proven and shown to be sufficiently reliable for confident application.

In steels of low, overall content of highly segregating species, the calculated solidus (an indicator of the "net" level of microsegregation) appears to be in
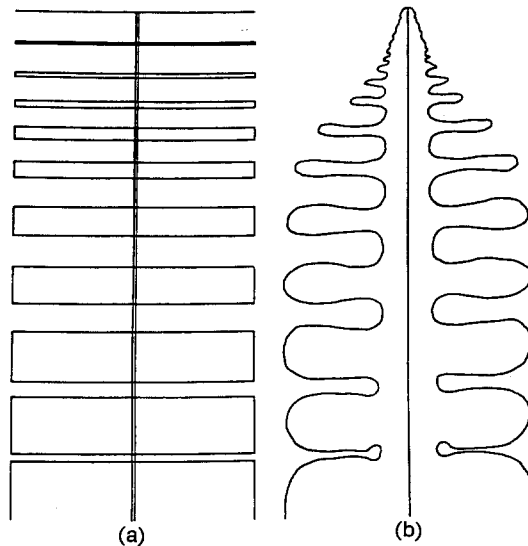
Fig. 3. Schematic dendrite structure implicit in 'MISEG' program. (a) *A 'MISEG' Dendrite*: Thickening and coarsening of secondary arms from a finite initial separation. No contribution from primary arms to solute redistribution. (b) *A More Realistic Representation*: Thickening and coarsening of secondary arms from zero length and separation at dendrite tip. Major contribution from primary arms to solute redistribution at early stages of solidification.

good agreement with that measured by thermal analysis experiments. Agreement is poor, however if significant amounts of strongly partitioning species such as carbon are present, in that the computed results fall substantially below such measurements, Table 2. (The experimental examples in Table 2 are taken from published work [5]) Indeed, the calculated results appear to reflect a real effect of persistent, highly segregated films of too small a volume fraction to be detected by thermal analysis. For example, several steels in reference [5] contained interdendritic austenite/carbide/phosphide eutectic which would only be encountered at well over 100 °C below the quoted, experimental solidus. Moreover, these films are now believed to be largely responsible for the total lack of measureable ductility down to temperatures previously described as substantially sub-solidus [6,7].

Table 2. Comparison of experiment [5] and computed solidification temperatures.

Temperature, °C	Steel 202 (low C)		Steel 310 (low C, high Cr)		Steel 205 (medium C)	
	Exp.	Comp.	Exp.	Comp.	Exp.	Comp.
Liquidus	1515	1514	1500	1498	1498	1498
Peritectic (max)	1475	1471	N/A	N/A	1480	1482
Solidus	1440	1447	1440	1438	1425	1392

The steel designations are those used in ref. [5], and are not international specifications.

The expected effects of manganese and sulphur on the solidus are observed, whereby a presence of manganese sufficient to remove the bulk of the sulphur from the residual liquid through precipitation of MnS markedly raises the calculated solidus temperature.

6. Conclusions

Significant progress has been made in the adaptation and extension of the Ogilvy-Kirkwood microsegregation model for multicomponent steels, allowing for eutectic termination and compound precipitation, and the peritectic phase transformation. The program is still under development in order to render it more 'robust' in operation, and requires more rigorously derived source data on multicomponent equilibria and the dendrite side-arm coarsening process. Initial results, however, are promising and it is expected that BSC will soon have a powerful, flexible tool for a quantitative understanding of the segregation process.

7. Acknowledgement

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