# Effect of Diffusion and Heat Transfer in Eutectoid Solidification

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## ABSTRACT

A theoretical model is formulated to describe the processes of diffusion and heat transfer that occur in eutectoid solidification. Radial as well as unidirectional solute diffusion are considered in this formulation. The resultant non-linear differential equation is then linearised with the aid of the *steady state* solution of the heat flow equation in the solid. Evaluation of the order of magnitude of parameters occuring in this equation indicates the radial contribution to be dominant in the growth of the secondary fiber eutectic(oid) phase. Separation of variables and perturbation solutions using a suitable small parameter are then used to evaluate the steady state solution. It is found that a boundary layer exists where the concentration varies rapidly from the interface to the steady state value in the fiber, within a very small distance, about 10 microns. The boundary layer thickness and concentration differential across it are evaluated for a typical case.

## INTRODUCTION

IN SEVERAL PREVIOUS publications, (1–3), the evaluation of a distribution coefficient and its refined estimates by consideration of constitutional supercooling and non-equilibrium solidification has been attempted. The usual method is to solve for $C_s/C_L$ where $C_s$ is the concentration of solute in the solid phase, and $C_L$ that in the liquid. Undercooling and nonequilibrium solidification are more of the norm than otherwise. Moreover, apart from the physical aspects of super cooling and solute build up at the interface caused by such rapid cooling, the steady state equilibrium value is usually reached at a distance away from the phase boundary. This 'boundary layer' can be obtained from a study of the distribution coefficient obtained by solution of the differential equations of diffusion and

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concentration with the appropriate boundary conditions. It has been found that such a length is of the order of $D/R$ and is the length where the concentration falls to $1/e$ of the interfacial value. For isotropic substances, this value is the same regardless of orientation or direction. However, when both axial and radial diffusion are concerned, the radial effects are by far predominant. For cylindrical or rod shaped precipitates the rates of axial and radial growth differ, whereas for spherical precipitates, radial growth is the only prevalent mechanism. *Even when* the physical parameters $D$ = diffusion coefficient and $R$ = rate of growth or solidification are taken as single valued or isotropic, it can be shown as is done subsequently in this paper, that the axial and radial rates of growth differ, causing non spherical agglomeration of secondary phases. Solidification kinetics in the non steady state thus would naturally influence subsequent steady state growth, where different mechanisms may become prevalent. That is to say, that the initial shape of the nucleating particle of secondary phase is determined by the non steady state parameters, and that subsequent steady state growth takes its boundary conditions from this initial solution. Even when the mechanisms of radial and axial growth differ subsequently, if the initial shape is non spherical, this tendency continues in the steady state where it is found the axial contribution to the diffusion mechanism is much less than that of the radial portion.

This phenomenonological or physical approach is to be contrasted with the alternative method of evaluation of equilibrium by the use of free energy curves. In this method, equilibrium is immediately obtained without consideration of *transients* in time by equating the chemical potentials of components of different phases, say liquid and solid, by means of the derivative of the free energy function. This free energy function is a well known entity and is a function of concentration, temperature, and chemical interaction parameters. The resulting compositions obtained by equating potentials give the result were the reaction allowed to complete under the influence of the driving potentials. Presumably the result of diffusion and heat transfer is caused by this factor, although the exact relation is not obvious.

In the following, an equation for solute enrichment in the development of a secondary fiber phase from pre existing fibers is solved. Radial as well as assumed axial growth is calculated for steady state with diffusion and heat transfer in the presence of an applied thermal gradient. A non linear equation is obtained which is solved by means of separation of variables and perturbation methods. Order of the parameters concerned indicates the radial growth mechanism to be predominant. A boundary layer is estimated at the interface and some typical parametric values used for the physical constants typical of metallic alloys, the thickness of the layer at the phase interface thus being evaluated.

## FORMULATION AND SOLUTION OF THE EQUATION

In *contrast* to earlier efforts at obtaining the distribution coefficient '$k$' the present analysis is more concerned with solid state diffusion for a solid solution



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quenched from eutectic liquid, and subsequent eutectoid decomposition whereby a secondary eutectoid phase separates from the matrix. The initial conditions as stated earlier depend on the transient solution. In the present, we assume the presence of pre-existing fibers given mathematically by certain boundary conditions. In the following, these are not our primary concern, the main effort here being towards the evaluation of the boundary layer(s) along the axial direction. Physical consideration leads to certain flux equations in the radial and axial directions for any given control element around a fiber. Upon combination of these equations and from the steady state heat transfer condition as derived in (4), the following is obtained:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) + D\frac{\partial^2 c}{\partial x^2} + R\frac{\partial c}{\partial x} \tag{1}$$

$$+ D'\left[c\left(-\frac{R}{K}\right)\alpha \exp\left(-\frac{Rx}{K}\right) + \left(\alpha \exp\left(-\frac{Rx}{K}\right)\frac{\partial c}{\partial x}\right]\right.$$

The following substitutions are effected to introduce the dimensionless perturbation small parameter $\epsilon$:

$$c = c_o C \quad , \quad r = a\bar{r} \quad , \quad x = L\bar{x} \tag{2}$$

$$\epsilon = \left(\frac{aR}{D}\right) = \left(\frac{a}{L}\right)^2 \quad \text{,where } L = \frac{D}{R} \tag{3}$$

Since $D$ is of order $10^{-6}$, $R$ being of order $10^{-3}$, '$a$' of order $10^{-8}$, it is seen that $\epsilon$ is of order $10^{-10}$, which is quite small and hence a suitable candidate for the perturbation solution.

Upon substitution in eq. (1), it reduces to:

$$\frac{\partial^2 C}{\partial \bar{r}^2} + \frac{1}{\bar{r}}\frac{\partial C}{\partial \bar{r}} + \left[\epsilon \frac{\partial^2 C}{\partial \bar{x}^2} + \frac{\partial C}{\partial \bar{x}}\right.$$

$$\left. + \left(-\frac{RC}{K} + \frac{\partial C}{L\partial \bar{x}}\right) \cdot \left(\alpha \frac{D'L^2}{D} \exp\left(-\frac{RL\bar{x}}{K}\right)\right)\right] = 0 \tag{4}$$

where the steady state is concerned, whence $dC/dt = 0$

It is immediately obvious that for the range of physical values considered and normally encountered that the radial solution is dominant, the terms in $\bar{x}$ being premultiplied by $\epsilon$, which when $\epsilon \longrightarrow 0$ become decreasingly small.

Consider now the equation in $\bar{x}$:

$$\frac{d^2 C}{dx^2} + \frac{dC}{d\bar{x}}\left(1 + a\frac{D'}{R}\exp\left(-\frac{D\bar{x}}{K}\right)\right) - \alpha\frac{D'D}{RK} \cdot C \exp\left(-\frac{D\bar{x}}{K}\right) = 0 \tag{5}$$

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where $L = D/R$ as in eq. (3).

In order to obtain the complete solution to eq. (4) which includes the $x$ component, the solutions are separated by using a separation constant. Let $C = X(x)R(r)$. , then

$$\frac{R''}{R} + \frac{1}{\bar{r}}\frac{R'}{R} = -A_n \tag{6}$$

$$\frac{X''}{X} + \frac{X'}{X}\left(1 + \alpha\frac{D'}{R}\exp\left(-\frac{D\bar{x}}{K}\right)\right) - \alpha\frac{D'D}{RK}\exp\left(-\frac{D\bar{x}}{K}\right) = \frac{A_n}{\epsilon} \tag{7}$$

where $A_n$ is the separation constant.

It may be remarked here, that as $\epsilon \longrightarrow 0$, from eq. (4) it is clear that the solution is one which exists in only the radial variable, i.e. $\bar{r}$.

From eq. (7) this corresponds to $A_n = 0$. Thus eq. (6), which is a Bessel equation of order 0, has the solution $J_o\ (A_n{}^{1/2}r/a)$ becomes $J_o\ (0)$, or a constant, since the complete solution involves the boundary condition premultiplying it, and also since $J_o\ (0) = 1$ as is well known. Choose now $\alpha D'/R = \bar{\epsilon}$, with $\bar{x} = X/\bar{\epsilon}$. (Eq. (7)) transforms to

$$\bar{\epsilon}\frac{d^2C}{dX^2} + \frac{dC}{dX}\left(1 + \bar{\epsilon}\exp\left(-\frac{DX}{\bar{\epsilon}K}\right)\right) - \frac{DC}{K}\exp\left(-\frac{DX}{\bar{\epsilon}K}\right) = \frac{A_nC}{\epsilon\bar{\epsilon}} \tag{8}$$

From ref. [5] the equation

$$\epsilon y''(x) + a(x)y'(x) + b(x)y(x) = 0 \tag{9}$$

has the solution at values $x = 0(\epsilon)$ as $\epsilon \longrightarrow 0$, where $y(0) = A$,

$$y(x) = A\exp\left(-a(0)\frac{x}{\epsilon}\right) \tag{10}$$

being the leading behaviour for $a(x)$ positive as $\epsilon \longrightarrow 0$

The boundary layer given by the leading term in eq. (10) is $C = \exp(-a(0)X/\bar{\epsilon})$ or $C = \exp(-x/D/R) = \exp(-xR/D)$ where $a(0) = 1$ to a first approximation. From an order analysis it is seen that the boundary layer is of thickness $(\bar{\epsilon})^{1/2}$ or $(\alpha D'/R)^{1/2}$

Thus when $x = \bar{\epsilon}^{1/2}$ in eq. (10), the concentration drops to $1/e$ of the boundary value.

The steady state solution of eq. (1) may then be obtained as per the transformed eq. (4) with the transformations made in variables $c,x,r$ as per eq. (2).

This solution becomes

$$c = c_oC = c_o\ (R(r)X(x)) = \sum_n B_nJ_o\ (A_n{}^{1/2}\frac{r}{a})\exp(-Rx/D) \tag{11}$$



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which expresses the radial and leading behaviour of the boundary layer solution in the transition region at the phase interface in the axial direction, this being the direction of growth. This approximation is probably all that is required considering the dominance of the radial solution and the structure of the axial equation.

The contribution of the second small parameter $\bar{\epsilon}$ is not immediately obvious as it appears as a secondary perturbation to the solution for eqs. (7, 8), and only appears in the second order and higher level perturbations. However, the thickness of the boundary layer at the interface, ($x = 0$) is determined by the value of this constant. The value is easily determined. Taking the following typical values for a eutectic alloy transformation as in ref. [4]: $D' = 3 \times 10^{-10}$ cm$^2$/sec., $^\circ K$., $\alpha =$ thermal gradient $= 3.5\ ^\circ K$/cm., $R = 10^{-3}$ cm./sec., $K = 0.2$ cm$^2$/sec., $\Delta T = 700\ ^\circ K$, where $\alpha = (R/K)\,\Delta T$. Upon substitution $\bar{\epsilon} = 10^{-6}$ and $(\bar{\epsilon})^{1/2} = 10^{-3}$. It is also seen that for $D = 10^{-6}$ cm$^2$/sec., the concentration drops to $1/e$ of the boundary value for a length equal to the boundary layer, 10 microns.

## DISCUSSION

The values of the separation constant $A_n$, and those of $B_n$ in eq. (11) are found from the boundary conditions and a knowledge of the eigenvalues of $J_o$ using orthogonality. Use of the perturbation expansion for $X(x)$ indicated that the leading term in eq. (11) given by eq. (10) is sufficient to determine the behaviour of the solution as the second term is premultiplied by $\bar{\epsilon}$ and the nth term by $\bar{\epsilon}^n$. Little variation occurs in the solution after a distance equal to the boundary layer is traversed, which depends on $\bar{\epsilon}$. The overall effect of the axial solution is also dependent on $\epsilon$. Thus two small parameters affect the solution.

The above equations and solution are based on the continuum assumption for isotropic solids. However, the parameters $D$, $D'$, and $K$ are physical constants which depend on the microscopic and atomic or discrete nature of the material., i.e. the crystalline structure. Thus although the continuum approximation is not valid in the atomic scale, the boundary layer length obtained from the continuum study is dependent on these constants and these parameters such as $D$ and $D'$ are strongly dependent on the atomic structure and interatomic spacing, mean free path, frequency of lattice vibration and of molecular vibration and so on. This boundary layer length may then be said to describe the region of influence of the atomic effects on the continuum properties of the phase transformation at the fiber matrix interface. A more exact description of the interface solution needs to account for the atomic motions and frequencies, as given in ref. [1], where statistical mechanics is used.

From a knowledge of the concentration of the fiber phase at the boundary, the effective partition coefficient can be found at the boundary layer, from eq. (11). Along the center line of the fiber, $r = 0$, and the partition coefficient diminishes by $1/e$ thus $k' = k/e$, which is the effective partition coefficient. The solute concentration at the interface for the fiber phase is then determined by this relation, $k$ being given by the phase diagram.



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## CONCLUSION

Much scope exists in development of new fiber reinforced composites. The available tools for analysis and prediction have also improved. The tendency, however, to rely too much on the continuum approximation in the sub microscopic region and molecular regime where much of the bonding and thus effectiveness of such composites is determined, is to be carefully rationalised. Limits in the present experimental techniques preclude the use of too much refinement and detail in the mathematical analysis and solution which after all are only means to an end in the practical design of such materials.

## NOMENCLATURE

| | |
|---|---|
| $a$ | lattice spacing |
| $\alpha$ | thermal gradient $^{\circ}K$/cm. |
| $c,C$ | conentation |
| $D$ | diffusion coefficient $cm^2$/sec. |
| $D'$ | thermal diffusion coefficient $cm^2$/sec. $^{\circ}K$ |
| $\epsilon, \bar{\epsilon}$ | perturbation small parameters |
| $K$ | thermal diffusivity $cm^2$/sec. |
| $^{\circ}K$ | degrees Kelvin, absolute temperature |
| $J_o$ | Bessel function of order zero |
| $L$ | length |
| $r$ | radial coordinate |
| $R(r)$ | separated solution in $r$ |
| $R$ | growth rate cm/sec. |
| $t$ | time variable |
| $T(t)$ | separated solution for transients in time |
| $\Delta T$ | temperature differential |
| $X(x)$ | separated solution for length, unidirectional coordinate |
| $x$ | axial coordinate |

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