

THE KINETICS OF CELLULAR SEGREGATION REACTIONS*

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Cellular segregation reactions, such as discontinuous precipitation and pearlite formation, often accomplish the segregation solely by diffusion along the cell boundary as it sweeps through the original unsegregated phase. Previous theories, which have assumed that the reaction is diffusion controlled, have been inadequate in describing many of its quantitative aspects.

If the diffusion is limited to the advancing cell boundary, the lamellae of the cells or nodules cannot reach equilibrium composition at any non-zero growth rate and for this reason the growth rate of the cells can no longer be determined by the diffusion rates alone. It is concluded that at least two controlling kinetic processes are required to describe such a complex reaction.

A simple model, which, in addition to diffusion control, assumes that the cell boundary moves with a velocity proportional to the net free energy decrease (taking into account the incompleteness of the segregation as well as the creation of lamellae surfaces), reproduces many of the observed features of these processes. Among these are the incompleteness of the segregation and the interlamellar spacing.

LA CINETIQUE DES REACTIONS DE SEGREGATION CELLULAIRE

Souvent les réactions de ségrégation cellulaire, telles que la précipitation des carbures et la formation de perlite, se produisent uniquement par diffusion le long de la frontière de la cellule lorsque celle-ci traverse la phase non ségréguée.

Les théories antérieures, qui admettaient que la réaction est contrôlée par la diffusion, sont incapables d'interpréter quantitativement de nombreux aspects de cette réaction.

Si la diffusion n'intéresse que la frontière de la cellule en mouvement, les lamelles des cellules ou nodules ne peuvent atteindre la composition d'équilibre pour toute vitesse de croissance non-nulle. Pour cette raison, la vitesse de croissance des cellules ne peut être déterminée en s'appuyant uniquement sur les vitesses de diffusion. Une telle réaction complexe ne peut donc être décrite que par l'intervention d'un minimum de deux mécanismes cinétiques.

Un modèle simple permet de reproduire la plupart des aspects observés et attribués à ces mécanismes. Ce modèle admet, outre l'action de la diffusion, que la frontière de la cellule se meut à une vitesse proportionnelle à la diminution d'énergie libre du réseau. On tient compte également de la formation de surfaces lamellaires ainsi que de l'état d'achèvement de la ségrégation.

DIE REAKTIONSKINETIK DER AUSSCHIEDUNG VON ZELLARTIGEN GEFÜGEN

Ausscheidungsreaktionen von zellartigen Gefügen, wie die inhomogene Ausscheidung und die Perlitbildung, laufen oft allein durch Diffusion entlang der Zellgrenze ab, während sich diese durch die ursprüngliche übersättigte Phase bewegt. Frühere Theorien, die angenommen hatten, dass die Reaktion durch die Diffusion bestimmt wird, reichen zur Beschreibung von vielen quantitativen Zügen nicht aus.

Wenn die Diffusion auf die vorrückende Zellgrenze beschränkt ist, können die Lamellen des Ausscheidungsgefüges bei einer endlichen Wachstumsgeschwindigkeit nicht die Gleichgewichtszusammensetzung erreichen, aus diesem Grund kann die Wachstumsgeschwindigkeit der Zellen nicht mehr allein durch die Diffusionsgeschwindigkeiten bestimmt sein. Daraus folgt, dass mindestens zwei bestimmende kinetische Vorgänge nötig sind, um solche eine komplexe Reaktion zu beschreiben.

Ein einfaches Modell, dem zugrunde liegt, dass die Reaktion durch die Diffusion bestimmt wird, und dass sich zusätzlich die Zellgrenze mit einer Geschwindigkeit proportional zur Abnahme der freien Energie bewegt (wobei sowohl die Unvollständigkeit der Ausscheidung als auch die Bildung von Lamellenoberflächen in Rechnung gesetzt wird) gibt viele der bei diesen Prozessen beobachteten Züge wieder. Unter diesen sind die Unvollständigkeit der Ausscheidung und die Abstände zwischen den Lamellen.

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‡ The distinction between eutectoid decompositions and precipitations is as follows. In eutectoid decomposition two new phases form alternate lamellae in a cell or nodule growing from the parent phase. In precipitation one of the two phases forming the cell lamellae has the same structure as the parent phase but differs in composition and orientation. Otherwise the morphology is the same.

INTRODUCTION

Many solid state segregation reactions such as precipitation and eutectoid decomposition,‡ result in a lamellar structure in which parallel plates of the final phases are grouped in nodules or cells. Most of the segregation occurs as the boundary of the growing nodules moves through the sample leaving behind the

segregated structure. In recent years it has become apparent that diffusion along the moving nodule boundary is often the only way that this mode of segregation can occur, and that little diffusion occurs in the lattice ahead of the boundary or in the lamellae after they have formed.^(1,2) Often the new phases in the nodules are formed at compositions which differ from the final equilibrium composition and can only approach equilibrium by means of slow lattice diffusion.⁽³⁾

This method of segregation has been called a pearlite reaction for eutectoid decompositions. For precipitations it has been known as cellular or discontinuous precipitation and occasionally as the recrystallization reaction. The mechanism for this type of process has been the subject of many papers. The approach of Zener⁽⁴⁾ for pearlite, which has been modified by Turnbull⁽⁵⁾ for precipitation, seems to have been the only one which has attempted to treat some of the quantitative relationships describing this process. It has been quite unsuccessful in predicting the spacing between lamellae of the same phase, since the predicted spacing is reported[§] to be smaller than that observed by a factor which ranges^(4,6) from 3 to 100.

For the iron-carbon eutectoid (pearlite) Zener assumed that carbon diffusion through the lattice, rather than along the pearlite boundary, controls the growth of pearlite. (The extrapolated carbon diffusion data are sufficiently high to account for the carbon segregation.⁽⁷⁾) Much evidence exists, however, to indicate that the rate of growth is not controlled by the carbon diffusion rate. For example, it is known that pearlite nucleates on a grain boundary but grows only into one of the adjoining grains. This cannot be consistent with the assumption that carbon diffusion through the lattice controls the rate, for then the pearlite would grow into both grains. Furthermore, alloy elements exert a strong influence on the growth rate without having a corresponding effect on the carbon diffusion rate. There is strong evidence that the alloy elements diffuse along the boundary,⁽⁸⁾ and it may be this diffusion which is important in controlling the growth rate.

Turnbull's modification (for precipitation) of Zener's treatment included the assumption that the process was grain boundary diffusion controlled. However, not all of Zener's original relations were consistently modified and there are some which still apply only to lattice diffusion.

The present paper is an attempt to develop a

model for these processes on the assumption that lattice diffusion is negligible compared with grain boundary diffusion. Two important modifications result. The first is that the cell can not segregate to equilibrium composition for any non-zero growth rate. This decreases the overall free energy change and places an upper limit to the growth rate for a given spacing. This upper limit results from the fact that at sufficiently high growth rates the segregation would be insufficient to give the thermodynamically required decrease in free energy accompanying cell formation.

The second important modification results from the fact that *any* growth rate smaller than the above mentioned upper limit is now possible and consistent with the diffusion rate. Another kinetic parameter is, therefore, needed to specify the process. In this paper, a model which assumed that the boundary moves with a velocity proportional to the net free energy decrease will be developed. It will be shown that the behavior of the cellular segregation reaction depends on the ratio of the mobility of the boundary to the diffusion coefficient along the boundary. Two simple systems will be treated; precipitation from dilute solution, and a symmetric eutectoid.

THEORY

Zener's model⁽⁴⁾ for pearlite assumed that carbon diffusion ahead of the interface controlled the rate of growth. The rate of this diffusion to the tips of the carbide lamellae (per unit area of the lamellae tip) is proportional to a driving force and inversely proportional to the spacing. This driving force was assumed to be proportional to the net free energy change ΔF accompanying the formation of carbide and ferrite of equilibrium composition, including the surface energy of the ferrite-carbide interfaces. Thus, per mole alloy

$$\Delta F = \Delta F_0 + \frac{2\sigma V}{S} \quad (1)$$

where ΔF_0 is the free energy change for the formation of a mole of equilibrium composition pearlite, σ is the carbide-ferrite surface free energy, V the molar volume of pearlite and S the interlamellar spacing. The growth rate, which is proportional to the flux to lamellae tips and hence also to $\Delta F/S$, is small for large spacings because of the large distance over which diffusion takes place. It is also small for small spacings because $-\Delta F$ becomes small as more energy is converted to surface free energy. ΔF and hence also the growth rate vanish for a critically small

§ See later section on ΔF_0 .

spacing S_0 given by

$$S_0 = -\frac{2\sigma V}{\Delta F_0} \quad (2)$$

The maximum growth rate is obtained for a maximum in $-\Delta F/S$ and occurs for a spacing equal to twice S_0 . Zener assumed that this spacing would be the observed spacing, but this prediction has not been verified. In view of this last assumption, this is not surprising, for the spacing could easily be governed not by the desire to maximize growth, but by any one of a number of quantities which the system might want to maximize, e.g. the rate of entropy production. Alternatively the ability of the cell to create new platelets might be the limiting factor. To eliminate this latter point the experiments on thermal cycling were carried out, and are reported later in this article.

When we now consider how Zener's model must be modified to take into account the assumption that all segregation occurs by diffusion along the advancing cell boundary we come to the following conclusions:

1. The system cannot reach equilibrium segregation. This has been shown experimentally for several systems⁽⁶⁾ and is a direct consequence of the diffusion assumption. The degree of segregation will be a function of the growth rate, spacing and diffusion coefficient.

2. Only a fraction, P , of ΔF_0 is realized if segregation is incomplete. The minimum possible spacings from purely thermodynamic reasons would correspondingly be larger by $1/P$. This fraction P is a function of growth rate, spacing, and diffusion coefficient and for precipitation has a form quite different from that for eutectoid decompositions. An examination of Fig. 1 shows that, for any small amount of precipitation, P is positive as long as the precipitate does not differ too drastically from the equilibrium composition. Hence a small amount of segregation, leaving the original phase only slightly changed in composition, will make P positive. For eutectoids, however, both new phases have to be reasonably close to the final composition for P to be positive, and hence a large amount of segregation must be accomplished.

3. The growth rate is no longer inversely proportional to S . The gradients are still inversely proportional to S , and so is the total flux to the lamellae, but the flux per unit area of lamellae tip, which is the quantity that determines its growth, is inversely proportional to both S and l (the thickness of the lamellae). If the degree of segregation is constant, l is proportional to S and we obtain the relationship derived by Turnbull⁽⁵⁾ that the growth rate is inversely

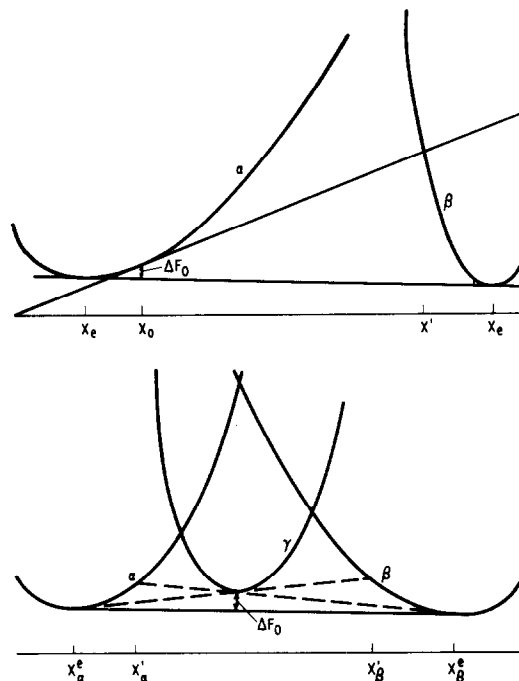


FIG. 1. Schematic free energy curves for a precipitating and eutectoid system. The chemical part of the free energy will decrease in a precipitating system as long as precipitate of a composition exceeding X' is formed, regardless of how little precipitates, and, therefore, of how little the α phase change in composition. For a eutectoid system none of the new phases can approximate the original phase in composition, and segregation to at least X_{α}' and X_{β}' must occur.

proportional to S^2 . But if the degree of segregation is not constant no such relationship will be obtained.

4. For a given spacing a range of growth rates is possible, resulting in different degrees of segregation. Therefore, another quantity must be specified. In Zener's treatment the spacing fixed the growth rate by the diffusion equation. Actually the diffusion equation provides only a relationship between spacing, growth rate, and the degree of segregation, and permits a range of growth rates for a given spacing within the limits imposed by thermodynamics. Another physical principle which relates these three quantities, growth, spacing and segregation is needed. Since within the limits imposed by thermodynamics, the boundary is free to move at any velocity, one can assume that it moves as an ordinary boundary under an applied pressure. The average pressure in this case is $\Delta F/V$ where ΔF now takes into account the fraction P of ΔF_0 realized due to incomplete segregation, as well as the retarding forces of the interlamellar surfaces.

$$\Delta F = P\Delta F_0 + \frac{2\sigma V}{S} \quad (3)$$

Any periodic variation in both driving pressure and boundary mobility will be smoothed out by a curving of the cell boundary if the surface tension of the

boundary is a sufficiently large fraction of $-P\Delta F_0 S/V$. Thus we can use the ΔF defined above and write for the growth rate G ,

$$G = -M\Delta F \quad (4)$$

where M is an average mobility of the boundary.

Since the growth rate in turn influences the degree of segregation through the diffusion equation and hence P , we have two simultaneous equations in the three unknowns. Thus, for a given spacing we can then determine the corresponding growth rate and degree of segregation.

What then determines the spacing? From the thermal cycling experiments we have good reason to believe that it is not the inability to create new lamellae, for a colony or nodule which had a spacing smaller than that usually observed for a given temperature rapidly changed over to the characteristic spacing. Let us assume that the spacing which the system chooses is that which maximizes the decrease in the free energy ΔF . Because of equation 4 this is also the spacing which maximizes both the growth rate, G , and the rate of decrease in free energy per unit area of cell boundary $G\Delta F_0/V$. It should be possible and would be desirable to justify this assumption on more basic grounds, but how this should be done has so far eluded the author.

For comparison it is interesting to note that in Zener's treatment the maxima in $-\Delta F$, G and $-G\Delta F/V$ do not coincide and give respectively for S/S_0 the values ∞ , 2 and 3 for bulk diffusion and ∞ , 3/2 and 2 for cell boundary diffusion. Zener and Turnbull both chose a maximum in G .

The diffusion equation

Of the available free energy change ΔF_0 , only the fraction P is realized during the segregation. P is related to the growth rate and the spacing by the diffusion equation which we will solve for two highly idealized cases. These illustrate some of the features of precipitation and eutectoid decomposition.

We will make the following simplifying assumptions:

(1) That the advancing boundary is plane. This will underestimate the effect of spacing, and result in a higher value of P .

(2) That no diffusion occurs except in the boundary and that the boundary can be represented by a slab of thickness δ , of material of concentration X_B having a diffusion coefficient D_B . D_B will be assumed independent of concentration and δ will be considered sufficiently small for there to be no concentration variation across the thickness.

(3) That the system has reached steady state, i.e. that the concentration in the advancing slab is stationary. We can then write the diffusion equation

$$D_B \delta \frac{d^2 X_B}{dZ^2} + G(X_0 - X_P) = 0 \quad (5)$$

where X_0 , X_P are the concentrations of the matrix and lamellae respectively and Z is the distance along the boundary normal to the lamellae. X_B and X_P are functions of Z , in other words the lamellae are allowed to vary in composition across their thickness.

(4) That X_B and X_P are related by some simple equation. This means that the local lamellae composition is related to the composition of the boundary ahead of it.

(5) That the phases are of equilibrium composition along the interface between lamellae.

Precipitation from dilute solution

Here we shall assume that X_P for the depleted parent phase is proportional to X_B where the X values represent the minor component. The diffusion equation is then easily integrated to give for the depleted parent phase

$$X_P = X_0 + A \cosh \left(\frac{kGS^2}{D_B \delta} \right)^{1/2} \frac{Z}{S} \quad (6)$$

where $k = X_P/X_B$, A is an integration constant, and Z is measured from the center of the lamella of the parent phase.

For precipitation from dilute solution the precipitate lamellae will be thin compared to the spacing. Hence in view of the fifth assumption we can set $X_P = X_e$ at $Z = S/2$ and thus evaluate A to obtain for the depleted parent phase lamellae

$$\frac{X - X_0}{X_e - X_0} = \frac{\cosh \left(\frac{kGS^2}{D_B \delta} \right)^{1/2} \frac{Z}{S}}{\cosh \frac{1}{2} \left(\frac{kGS^2}{D_B \delta} \right)^{1/2}} = \frac{\cosh \sqrt{\alpha} \cdot \frac{Z}{S}}{\cosh \frac{\sqrt{\alpha}}{2}} \quad (7)$$

The important parameter describing this process is

$$\alpha = \frac{kGS^2}{D_B \delta}.$$

The fraction of minor component precipitated is

$$Q = \frac{2}{(X_0 - X_e)} \int_0^{1/2} (X_0 - X) d(Z/S)$$

which upon integration becomes

$$Q = \frac{2}{\sqrt{\alpha}} \tanh \frac{\sqrt{\alpha}}{2} \quad (8)$$

For precipitation from slightly supersaturated solution the free energy curve can be approximated by a parabola, and we obtain as the fraction of the total free energy change released by cellular precipitation

$$P(\alpha) = 1 - \frac{2}{(X_0 - X_e)^2} \int_0^{1/2} (X - X_e)^2 d(Z/S)$$

which gives

$$P(\alpha) = \frac{3}{\sqrt{\alpha}} \tanh \frac{\sqrt{\alpha}}{2} - \frac{1}{2} \operatorname{sech}^2 \frac{\sqrt{\alpha}}{2} \quad (9)$$

If P is a function of α alone, the basic assumption that

$$-\Delta F = -P\Delta F_0 - \frac{2\sigma V}{S}$$

be maximized results in the following equation for α in terms of a new dimensionless parameter β

$$\beta = -\frac{kM\sigma^2V^2}{D_B\delta\Delta F_0} = \frac{\alpha^3P'}{P + 2\alpha P'} \quad (10)$$

where $P' = dP/d\alpha$. Equation 10 gives α as a function of the important parameter β which contains only terms that can be evaluated by independent measurement. Figure 2 gives the various quantities of interest in a precipitation process. P and Q are defined above as respectively the fraction of the available free

energy change released by precipitation, and the fraction of excess solute precipitated. $R = -2\sigma V/S\Delta F_0 - S_0/S = 2\alpha P'$ is the fraction of ΔF_0 converted to surface free energy, and can have any value from 0 (infinite spacing) to 0.49 which corresponds to a spacing slightly larger than Zener's predicted spacing. $(P - R)$ is the fraction of ΔF_0 available to exert pressure on the boundary and hence is equal to $G/(-M\Delta F_0)$.

The prediction is that, for a highly mobile boundary with a low diffusion constant, the precipitation is almost reversible in that all of the chemical energy released is converted to surface energy and the boundary goes as fast as is thermodynamically possible. At the other extreme of small β , the boundary is sluggish compared to its ability to accomplish segregation. The spacing can now be large and the segregation will still be sufficiently complete. Furthermore, a large spacing will reduce the drag due to surface tension on the sluggish boundary, permitting the full pressure of ΔF_0 to bear on it.

Decomposition of the symmetric eutectoid

Let us consider a symmetric eutectoid system with the eutectoid composition at $X_0 = 1/2$, the two new phases at $X_\alpha^e = X_e$ and at $X_\beta^e = 1 - X_e$ where $X_e < 1/2$. We will assume that the concentration of the minor constituent in either phase is proportional to its concentration in the boundary, i.e. $X_P/X_B = k$ for the alpha phase, and $(1 - X_P)/(1 - X_B) = k$ for the

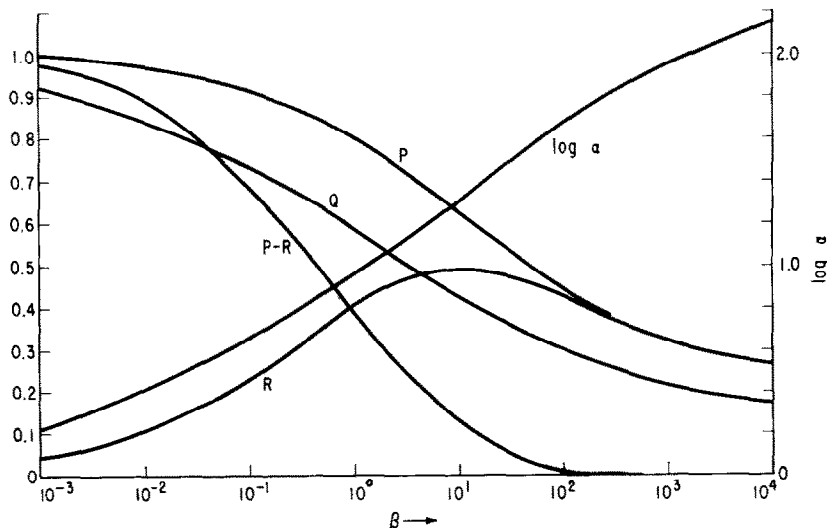


FIG. 2. Precipitation from dilute solution as a function of the parameter $\beta = -MV^2\sigma^2/D_B\delta\Delta F_0$

P the fraction of ΔF_0 realized.

Q the fraction of material precipitated.

R the fraction of ΔF_0 expended on surface energy.

$P - R$ the fraction of ΔF_0 exerting a pressure on the cell boundary $\beta = kGS^2/D_B\delta$

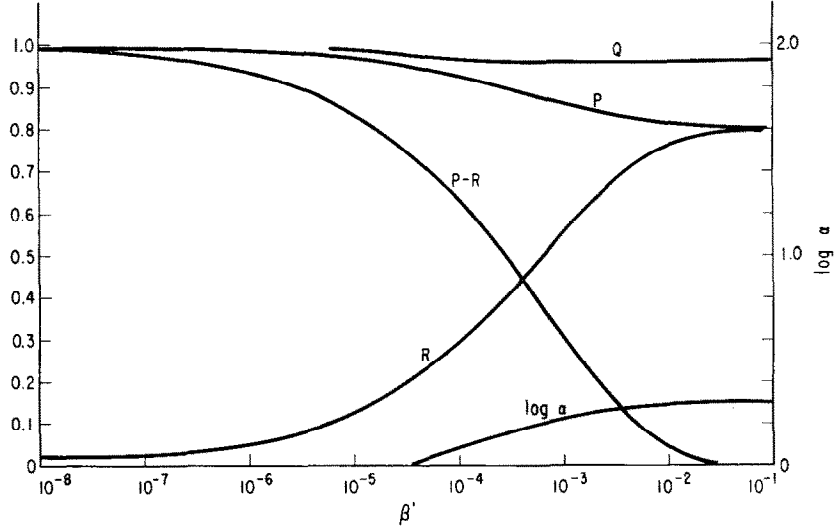


FIG. 3. Decomposition of the symmetric eutectoid as a function of the parameter $\beta' = MV^2\sigma^2/D_B\delta C$ for $\Delta F_0 = -0.010$.

β phase, where k is a constant. Then for the α phase

$$\frac{\frac{1}{2} - X}{\frac{1}{2} - X_e} = \frac{\cosh\left(\frac{kGS^2}{D_B\delta}\right)^{1/2} \frac{Z}{S}}{\cosh\frac{1}{4}\left(\frac{kGS^2}{D_B\delta}\right)^{1/2}} \quad (11)$$

and for the β phase

$$\frac{X - \frac{1}{2}}{X_e - \frac{1}{2}} = -\frac{\cosh\left(\frac{kGS^2}{D_B\delta}\right)^{1/2} \frac{(S/2 - Z)}{S}}{\cosh\frac{1}{4}\left(\frac{kGS^2}{D_B\delta}\right)^{1/2}} \quad (12)$$

From assumption (5) we obtain $k = 2X_e$.

We can define Q again as follows

$$Q = \frac{4}{(\frac{1}{2} - X_e)} \int_0^{1/4} (\frac{1}{2} - X) d(Z/S) \\ = \frac{4}{\sqrt{\alpha}} \tanh \frac{\sqrt{\alpha}}{4} \quad (13)$$

which is quite similar to the expression derived before (equation 8). In order to evaluate P we again assume a parabolic free energy curve for the two new phases. Hence the free energy ΔF of each phase relative to α and β in equilibrium with each other is

$$\left. \begin{aligned} \Delta F &= \frac{C}{(\frac{1}{2} - X_e)^2} (X - X_e)^2 \text{ for } \alpha \\ \Delta F &= \frac{C}{(\frac{1}{2} - X_e)^2} (X + X_e - 1)^2 \text{ for } \beta \end{aligned} \right\} \quad (14)$$

C is approximately temperature independent and is very much larger than $-\Delta F_0$. The ratio $-\Delta F_0/C$ varies approximately as the undercooling from the eutectoid temperature.

Using equation (14) we can write as before

$$P = 1 + \frac{4C}{\Delta F_0 (\frac{1}{2} - X_e)^2} \int_0^{1/4} (X - X_e)^2 d(Z/S) \\ = \left(1 + \frac{C}{\Delta F_0}\right) - \frac{C}{\Delta F_0} \left(\frac{6}{\sqrt{\alpha}} \tanh \frac{\sqrt{\alpha}}{4} - \frac{1}{2} \operatorname{sech}^2 \frac{\sqrt{\alpha}}{4}\right) \quad (15)$$

Again it is worth noting that, because $-C/\Delta F_0$ is large, α must be small in order that P be positive. This was mentioned before in connection with Fig. 1 and is apparent from the form of equation 15.

Since we are only interested in the region of positive P and hence small α , we can expand P in powers of α :

$$P(\alpha) = 1 + \frac{2C}{15\Delta F_0} \left(\frac{\alpha}{16}\right)^2 + \dots$$

Since P is again a function of α alone, we can apply equation 10 and obtain, by multiplying by $-\Delta F_0/C$,

$$\beta' = \frac{kM\sigma^2 V^2}{D_B\delta C} = -\frac{\frac{64}{225} \left(\frac{\alpha}{16}\right)^5}{\frac{\Delta F_0}{C} + \frac{2}{3} \left(\frac{\alpha}{16}\right)^2} \quad (16)$$

where $\beta' = -\beta\Delta F_0/C$ and has the advantage that it is approximately temperature independent for small undercooling. Similarly we obtain

$$R = -\frac{8C}{15\Delta F_0} \left(\frac{\alpha}{16}\right)^2 \quad (17)$$

In Fig. 3 the values of P , Q and R are plotted for

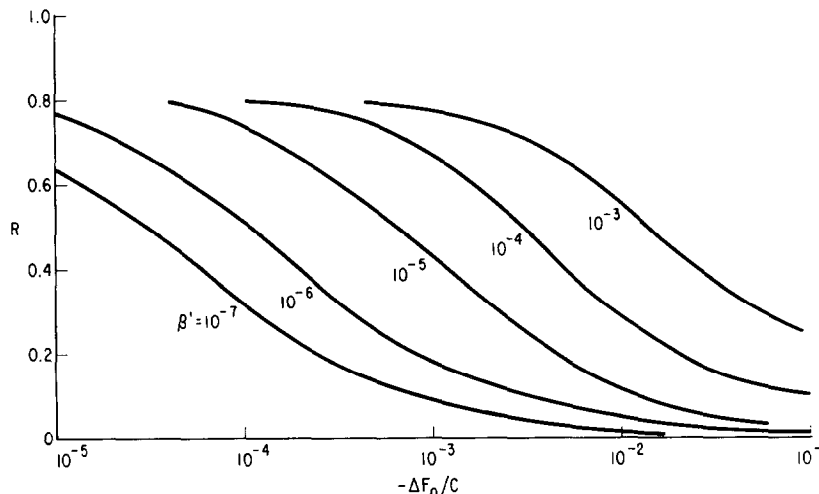


Fig. 4. The fraction R for a symmetric eutectoid as a function of ΔF_0 for various values of β' .

eutectoids with $\Delta F_0/C = -10^{-2}$ for comparison with Fig. 2. For small values of β' and β the behavior is quite similar, but for large values the behavior is different. For large β' equation (7) gives

$$\frac{\alpha}{16} = \left(-\frac{3\Delta F_0}{2C} \right)^{1/2}$$

and $P = R = 0.8$ for all values of $\Delta F_0/C$ for a symmetric eutectoid. Thus for large β' the eutectoid differs markedly from the precipitate. This is because in order to accomplish the thermodynamically required amount of segregation, a fine spacing is required. This fine spacing, in the limit, requires 0.8 of the available free energy.

In order to examine the behavior of the spacing with temperature for various systems, R is plotted against $\Delta F_0/C$ for various values of β' (Fig. 4).

The iron-carbon eutectoid

The iron-carbon eutectoid is of great practical interest. Unfortunately, the pure binary has never been systematically studied, and it is well known that small quantities of impurities or alloying elements exert a profound influence on the growth rate G .⁽⁷⁾ The high temperature carbon diffusion data can be extrapolated to the region in which pearlite occurs, and this gives a bulk diffusion coefficient which, within experimental error, could account for the observed growth rate. The fact that pearlite invariably grows into only one of the two grains must indicate that carbon diffusion through the bulk is not the rate determining step. Furthermore, the alloying elements which cannot diffuse rapidly through the bulk appear to segregate to a large extent and influence

the growth rate markedly without affecting the spacing by more than a factor of 2.⁽⁷⁾

Zener⁽⁴⁾ has pointed out that the impurities or alloy elements can not affect ΔF_0 markedly because of their low concentration. However, if the distribution coefficient between the boundary and the ferrite or cementite is small, they can be swept along by the boundary and thus reach a very high concentration. In this respect their effect on the driving pressure may not be negligible. If this is so a large degree of segregation of the alloy elements will be accomplished.

A more significant factor in the alloy effect might be in the marked dependence of grain boundary mobility on impurities. To a first approximation it seems that this would manifest itself mainly in the growth rate, since effects due to changes in the parameter β' could well be independent of impurity content. Even if β' changes, the ratios P , Q and R are relatively insensitive to β' and the more significant change in

$$G = -(P - R)M \Delta F_0$$

would come from changes in M . Since the spacing is given by

$$S = -\frac{2\sigma V}{R\Delta F_0}$$

it contains no quantities which would depend drastically on impurities.

The calculation of ΔF_0

The value of ΔF_0 is clearly defined here as the maximum available free energy change when one mole of alloy is decomposed to the ultimately stable phases. Some confusion exists because Zener introduced into his discussion both the free energy change ΔF_0 , and the chemical potential change $\Delta\mu$ of the minor

component (carbon). For his computation of the minimum possible spacing he correctly used ΔF_0 .

The chemical potential change is related by the Gibbs-Thompson equation to the minimum permissible radius of curvature at the tip of the lamellae. The free energy change is related to the minimum permissible spacing. It is possible from a knowledge of the various surface tensions, and the $\Delta\mu$ values for both components, to arrive at the minimum spacing by considering the curvatures of the cell boundary and the triangle of forces at the junction of two lamellae with this boundary. This gives an expression for the minimum spacing identical with equation (2).

When we are considering precipitation from a dilute solution, $\Delta\mu$, which is equal to $RT \ln (X_e/X_0)$, differs from ΔF_0 by a factor of $1/2(X_0 - X_e)$. The former varies as $(X_0 - X_e)$ whereas the latter varies as $(X_0 - X_e)^2$. Turnbull^(5,6) wrongly uses $\Delta\mu$ instead of ΔF_0 to compute his spacing.

$\Delta\mu$ is related to the minimum precipitate thickness, ΔF_0 to the minimum spacing. That this is self consistent may be seen as follows: If the supersaturation $(X_0 - X_e)$ is doubled, $\Delta\mu$ is doubled and the platelets may be half as thin. But twice as much will precipitate on these thinner platelets. Hence four times as many platelets are possible, resulting in a reduction in the minimum spacing by a factor of 4.

Turnbull and Treadwell⁽⁶⁾ report a spacing 100 times coarser than Zener's predicted spacing. This is however the result of confusing $\Delta\mu$ with ΔF_0 . In fact the Zener spacing as calculated by Turnbull would result in the thermodynamically impossible situation (in equation 1) where the surface energy term would be ten times the available free energy. Figure 5 is a plot, from their data, of $-S\Delta F_0/2V$ i.e. σ/R ($-S\Delta F_0/2V = 2\sigma$ if the Zener spacing exists). In order to evaluate ΔF_0 Henry's and Raoult's laws were assumed.

$$\Delta F_0 = NkT \left(X \log \frac{X_e}{X} + (1 - X) \log \frac{1 - X_e}{1 - X} \right)$$

X_e was taken from Stockdale's solubility data.⁽⁹⁾ The more recent solubility data of Borelius *et al.*⁽¹⁰⁾ was not used because its temperature dependence seemed inconsistent with recent calorimetric measurements of the heat of formation of the alloys.⁽¹¹⁾ Indeed preliminary results⁽¹²⁾ on the redetermination of the tin solubility, by observing resistometrically the temperature at which it is completely dissolved, indicates that Borelius' phase boundary is too high at the lower tin concentrations. The difference between Stockdale's and Borelius' data amounts to a factor of 2 in ΔF_0 in the region of interest for Fig. 5.

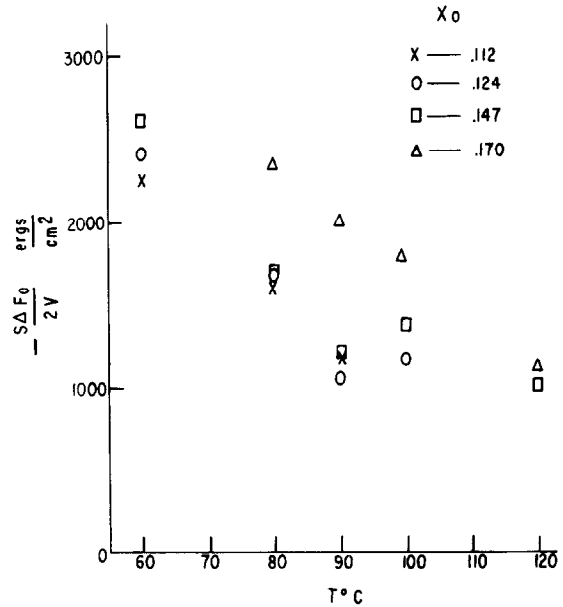


FIG. 5. The spacing data of Turnbull and Treadwell.⁽⁶⁾

Using a value of σ of 150 ergs/cm² we obtain a value of R ranging from 0.06 to 0.15, and thus the spacing is coarser than the Zener prediction by a factor ranging from 3 to 8 instead of the reported factor of 100.

Thermal cycling experiments

A plausible explanation for the failure to observe the spacing predicted by Zener is that it is difficult to nucleate or create the additional lamellae. It then becomes hard to understand the rapid creation, during a quench, of a band of fine pearlite so often observed on specimens of partially transformed isothermal pearlite. Similar observations exist for Pb-Sn precipitate nodules which continue growing, at room temperature, with the characteristic room temperature spacing with no discernable transition region. Down-quench observations like these could still be explained by rapid nucleation or multiplication of plates to within a certain factor of the Zener spacing. Up-quenches on the other hand force the specimen to start with a finer spacing than it normally would have, that is, a spacing closer to the Zener spacing. This should be a more nearly ideal spacing according to Zener, but not according to the present model. Accordingly two alloys, an SAE 1080 plain carbon eutectoid steel and a Pb-6.5 wt.% Sn, were partially transformed at a lower temperature to establish a fine spacing, and then permitted to grow at a higher temperature. In all cases the spacing coarsened within a short distance. Figures 6 and 7 are representative micrographs of the observed spacing change. The spacing predicted by Zener is therefore

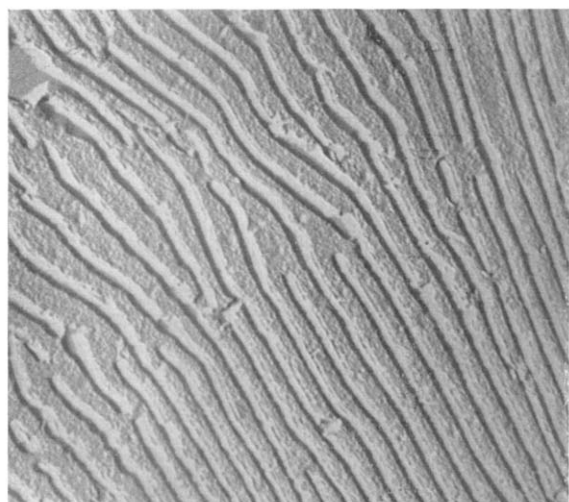


Fig. 6. Spacing change in a SAE 1080 plain carbon eutectoid steel during an up-quench from 660°C to 700°C. $\times 7812$.

not "an ideal but otherwise unattainable" spacing. The system will approach its characteristic spacing from perturbations in either direction.

DISCUSSION

It has been found necessary to describe the growth of a cellular segregation reaction by at least two independent rate processes: the diffusion along the cell boundary, and the mobility of the cell boundary in response to the driving pressure which results from the decrease in free energy when the boundary moves and accomplishes segregation. The model was evaluated for two highly idealized cases; precipitation from dilute solution and a symmetric eutectoid. It was found that for each case, two extremes occurred. The low-mobility high-diffusivity extreme resulted in a coarse interlamellar spacing and complete segregation. This is because, when the boundary is sluggish compared to the diffusion coefficient, much segregation can be accomplished even at large spacings.

The high-mobility low diffusivity extreme resulted in just enough segregation so that the free energy change was negative. The boundary rushed ahead as fast as it could within the limits imposed by the thermodynamics of the model. For eutectoids this resulted in an even finer spacing than that predicted by Zener, because much segregation must be accomplished before ΔF is negative. For precipitation this resulted again in a coarse spacing, and this time in little segregation.

Unfortunately none of the important kinetic parameters for a cell boundary is known. We are therefore limited to estimates and checks for internal consistency.

For instance there should be a relationship between spacing and degree of segregation which we can read off Fig. 2. From Turnbull's and Treafis' spacings data we estimate $R \sim 0.05-0.15$, which means a β of the order of 10^{-2} , which in turn should go along with a degree of segregation Q of 85-90%. From their resistance data Turnbull and Treafis⁽³⁾ estimate $Q = 0.6$. A recent calorimetric determination of the heat of formation of the alloy⁽¹¹⁾ can be combined with the reported heat of precipitation⁽¹³⁾ to give $Q = 0.6$. Both these estimates of Q are for room temperature, whereas the spacing was measured at higher temperatures. Since there is a large uncertainty in the estimation of R , owing to the estimation of ΔF_0 from an extrapolated phase boundary, the comparison is inconclusive. It would be useful to have simultaneous knowledge of the heat and free energy of formation, the heat of precipitation, the surface tension and spacing.

Another comparison with data comes from measured growth rates. Let us consider the case when β is small, that is, the low-mobility high-diffusivity extreme. Then $(P - R)$ is approximately constant and the growth rate is then proportional to ΔF_0 or the

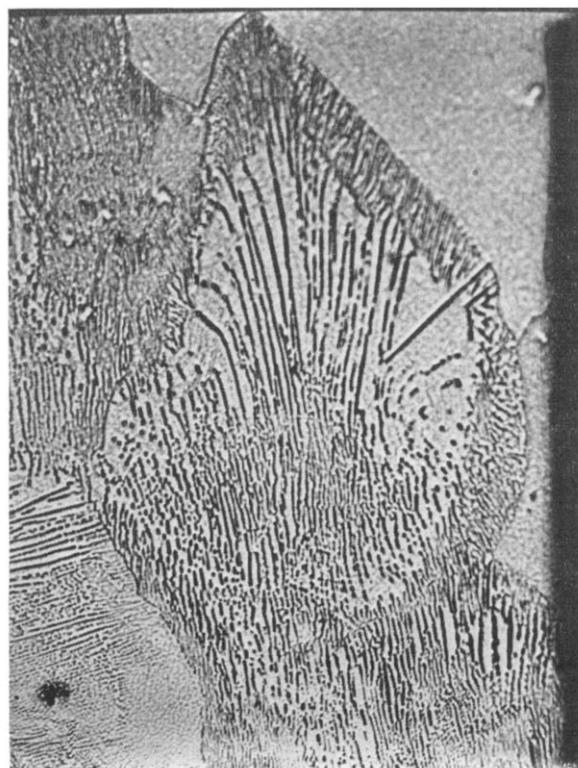


Fig. 7. Spacing change in a Pb-6.5% Sn colony started at 60°C, continued first at 80°C and then at room temperature. $\times 625$.

square of the supersaturation for small supersaturation. This is quite different from Turnbull's prediction that

$$G = \frac{X_0 - X_e}{X_0} \left(\frac{D_B \delta}{S^2} \right)$$

which, together with the spacing prediction, results in a fifth power dependence of growth on supersaturation. Table 1 gives a summary of growth data⁽⁴⁾ for Au-Ni in the small supersaturation region. The data seems to fit a square dependence, for which $(X_{500} - X_e)/(X_{100} - X_e) = 5^{1/2} = 2.2$, better than a fifth power dependence $5^{1/5} = 1.38$. This therefore permits a checking of the basic assumption of this paper.

The value of β of 10^{-2} estimated for Pb-Sn is smaller by a factor of 10^{-3} than would be estimated from the slab model of a boundary, if we assume isotropic mobilities in the slab and no barrier to the incorporation or removal of atoms into or from the crystal lattices. That β and M appear to be small by this factor is not therefore surprising. In an actual boundary the atomic mobilities may vary over a wide spectrum as one traverses normal to the boundary. The atomic mobilities which enter into the diffusion coefficient are heavily weighted in favor of the largest, while the reverse is true for the boundary mobility which will reflect the lower atomic mobility of the atoms which are in process of leaving or entering the boundary.

Most of the experimental observations of spacing fall in a very narrow range of undercooling, ΔT (a factor of 10), or supersaturation (a factor of 2). Over these ranges β and ΔF_0 would hardly change sufficiently to cause much variation in R , the fraction of free energy expended on lamellae surfaces. Indeed R appears to vary only slightly. The trend in R , as well as its value, are predicted by this model but require data on D_B and M .

Experiments on cellular precipitation in bicrystals, to determine growth rate, spacing and fraction precipitated as a function of misorientation, would be extremely useful, since the variations of M and D with θ can be estimated, and ΔF_0 remains constant. The one experimental observation available on growth rate only has been interpreted⁽¹⁵⁾ according to the Zener-Turnbull model. This keeps the spacing constant and therefore makes the growth rate proportional to D_B . Identical results would be obtained for the present model if the ratio of mobility to diffusion constant is independent of orientation. Then β is constant, resulting in a constant spacing and degree of segregation as well as a growth rate proportional to boundary mobility. Conversely, if the spacing is found not to be constant, one can predict

the change in β and hence in M/D_B . This, together with a knowledge of the angle of dependence of D_B , would enable one to predict M , G and Q .

In the case of the iron-carbon eutectoid, pearlite, it would be useful to examine the high purity alloy to see if spherical instead of hemispherical nodules begin to form, and in addition to assess the complete role of the impurities which have hitherto always been present.

Often general intragranular precipitation competes at higher temperatures with the cells, giving rise to what has been called the recrystallization reaction. By this term it has been implied that the general precipitation strains the grain, and that the cellular reaction has for its driving force the strain energy due to the general precipitation. That this is not so can be seen from the observations that the so-called recrystallization reaction often stops before it has consumed its grain. This can only mean that the driving force has disappeared. This would seem to rule out strain energy, and is strong support for a chemical driving force which has been diminished by general precipitation.

In summary the author would like to stress that the basic point of this paper is the need for at least two kinetic parameters to describe cellular segregation processes. The choice of the grain boundary diffusion coefficient and the grain boundary mobility was made here and is capable of experimental check. The assumption that the system chooses to maximize the free energy decrease proved to be useful, and it is felt that such an assumption should be derivable from more basic kinetic assumptions.

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TABLE 1. Composition (at % Ni) at which growth rate of 100 Å/sec and 500 Å/sec are observed in Au-Ni alloys (E. E. Underwood)

T (°C)	X_e	X_{100}	X_{500}	$\frac{X_{500} - X_e}{X_{100} - X_e}$
700	6.40	9.75	17.75	4.1
	66.75	58.5	50.25	2.0
600	4.25	5.90	8.50	2.6
	77.0	71.1	66.5	1.8
500	2.5	7.6	19.5	3.3
	84.0	77.5	64.5	3.0

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