

7.3 Scheil's Segregation Equation - a Model of Microsegregation

It is not possible to perform an exact calculation of df/dx in equation (2) at a mathematical treatment of the solidification process of such a complicated geometrical shape as the one in figures 2 and 3. In order to analyse the influence of various factors on the distribution of the alloying element we have to simplify the geometry considerably. For a mathematical treatment of the phenomenon microsegregation we choose the simplest possible geometry and consider the volume element given in figure 4 on page 7.

We assume that this volume element represents a small interdendritic area and make the following assumptions:

1. The length of the element equals half the dendrite arm distance, $\lambda/2$.
2. The volume element is so small that the temperature is the same within the element at any moment.
3. The solid and liquid phases have the same molar volume V_m .

If the last assumption is not fulfilled the solidification results in a change of the volume of the material. Pores are formed or melt flows into the volume element, which might cause macrosegregation. Here we will disregard such complications. Macro-segregation will be treated in chapter 11.

7.3.1 Scheil's Model for Microsegregation

In our first treatment of microsegregation we start with the following assumptions

- The convection and diffusion in the melt is so violent and rapid that the melt at every moment has an even composition.
- The diffusion in the solid phase is so slow that it can be completely neglected.
- Local equilibrium exists between the solid phase and the melt. The equilibrium can be expressed by the partition constant

$$k = \frac{x^s}{x^L} \quad (4)$$

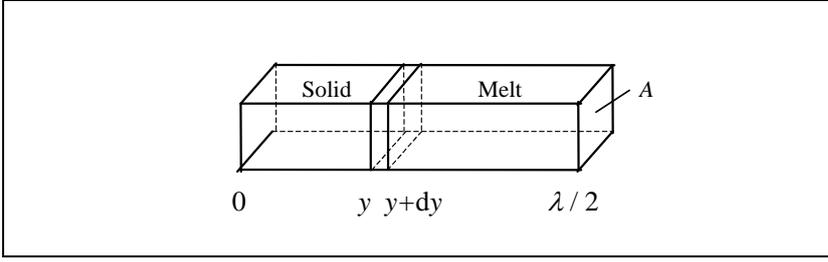


Figure 4.

Consider figure 4. The solidified material has reached a thickness y and grows with the amount dy during the time dt . Solidification of the slice $A dy$ requires a decrease of its concentration of alloying element from x^L to x^S . The amount $(x^L - x^S) \cdot A dy / V_m$ of the alloying element has to be moved into the melt. Its concentration increases then by dx^L .

This amount of alloying metal is brought to the volume of the melt $A \cdot (\lambda/2 - y - dy)$ from the solidified slice $A dy$ and its concentration increases from x^L to $x^L + dx^L$. A material balance for the alloying element gives

$$\frac{(x^L - x^S) \cdot A dy}{V_m} = \frac{A \cdot \left(\frac{\lambda}{2} - y - dy \right) \cdot dx^L}{V_m} \quad (5)$$

By reduction and by neglecting the product $dy dx^L$ equation (5) can be simplified to

$$\left(\frac{\lambda}{2} - y \right) \cdot dx^L = (x^L - x^S) \cdot dy \quad (6)$$

By introduction of k we can eliminate x^S . Integration of equation (6) from $y = 0$ to y and $x^L = x^0$ to x^L gives

$$\int_{x^0}^{x^L} \frac{dx^L}{x^L - kx^L} = \int_0^y \frac{dy}{\frac{\lambda}{2} - y} \quad (7)$$

where x^S is the initial concentration of the alloying element in the melt.

After integration we get

$$\frac{1}{1-k} \cdot \ln \frac{x^L}{x^0} = -\ln \frac{\lambda/2 - y}{\lambda/2} \quad (8)$$

Equation (8) is solved for x^L :

$$x^L = \frac{x^s}{k} = x^o \cdot \left(1 - \frac{2y}{\lambda}\right)^{-(1-k)} \quad (9)$$

The derivation of equation (9) is to little extent associated to the geometrical shape of the volume element. The formula is valid for any geometrical shape if $2y/\lambda$ is replaced by the more general variable f which represents the fraction of solidified material. f is called *degree of solidification* or *fraction of solid phase*. Equation (9) in its more general form be written

$$x^L = \frac{x^s}{k} = x^o \cdot (1 - f)^{-(1-k)} \quad \text{Scheil's equation} \quad (10)$$

Equation (10) is called *Scheil's segregation equation* after its originator. It is important to notice that x^L represents the instant concentration of the alloying element in the melt while x^s stands for the concentration of the alloying element in the last solidified material. Figure 5 shows how these two concentrations vary during the solidification process when f changes from 0 to 1 for the special case $k = 0.5$.

The dotted lines show the concentrations at three different occasions. At the first occasion the melt has a composition which slightly exceeds x^o . At the second and third occasion this concentration has increased exponentially and approaches infinity at the end of the solidification process.

Of course infinity is never reached in reality. A eutectic reaction may occur or there will be a homogenisation during the solidification process. The homogenisation process, which is known as back diffusion, will be discussed in section 7.5.1. Besides, Scheil's equation is only valid for small values of concentration of the alloying element because the partition coefficient k is constant only for low values of the concentration x .

During the treatment of the microsegregation during the solidification process above we have disregarded the time and temperature aspects. The solidification process is controlled by the rate of heat removal from the volume element. Normally the heat of solidification dominates and the degree of solidification, i. e. the fraction of solid phase can accurately be estimated from the amount of removed heat.

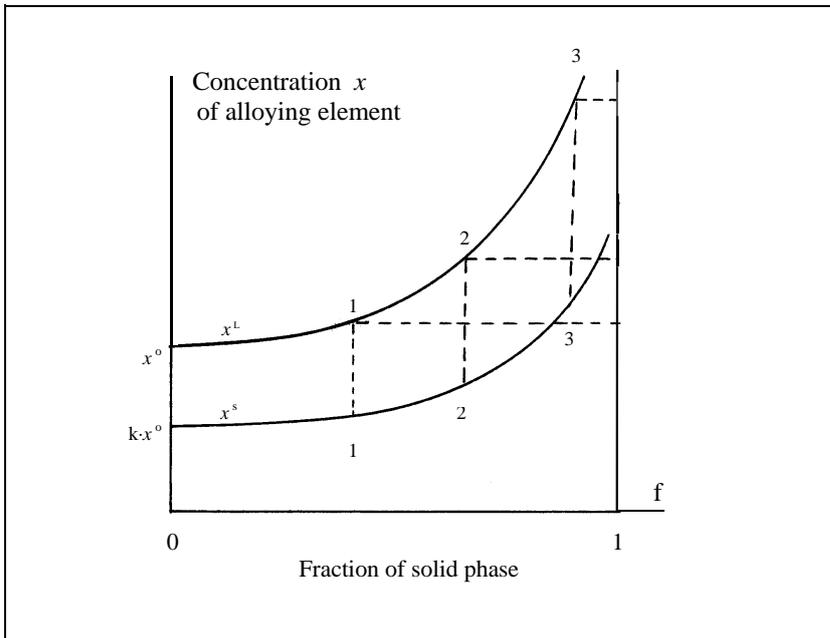


Figure 5. The concentrations of the alloying element in the melt respectively in the last solidified material during a solidification process for $k = 0.5$ as a function of the fraction solid phase.

The temperature represents a secondary variable, which automatically adopts the value required for the condition that the instant value of the concentration x^L of the alloying element shall lie on the liquidus line in the phase diagram of the alloy (figure 6).

However, there is an experimental method, called *controlled solidification*, where the temperature is determined from outside. It controls the solidification process by varying the temperature of the material according to a predecided temperature gradient (chapter 6, page 43).

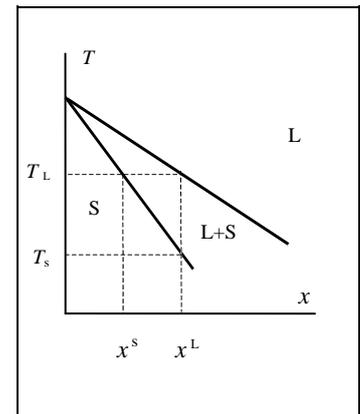


Figure 6. Phase diagram of a binary alloy.

Eutectic Solidification

When a molten binary alloy cools and starts to solidify the compositions of both the melt and the solid phase change gradually and follow the liquidus respectively the solidus lines in the phase diagram. As long as these lines are fairly straight the partition coefficient k is constant. This is the case for low concentrations of the alloying element.

We consider the case when Scheil's equation (equation (10) on page 8) is still valid at the eutectic temperature. At this temperature we get

$$x_E^L = x^o \cdot (1 - f_E)^{-(1-k_E)} \quad (11)$$

where

- x_E^L = concentration of the alloying element in the remaining melt at the eutectic temperature
- x^o = initial concentration of the alloying element in the melt
- k_E = partition coefficient of the alloying element
- f_E = fraction of solid phase at the eutectic temperature.

The fraction of remaining liquid f_E^L at the eutectic temperature equals $(1 - f_E)$. It is solved from equation (11):

$$(1 - f_E)^{-(1-k_E)} = \left(\frac{x^o}{x_E^L} \right)^{-1}$$

or

$$f_E^L = (1 - f_E) = \left(\frac{x^o}{x_E^L} \right)^{\frac{1}{1-k_E}} \quad (12)$$

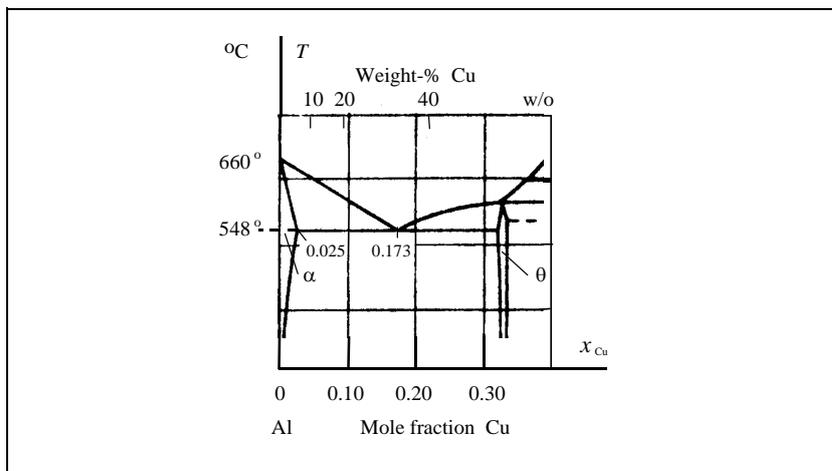
where

- f_E^L = the fraction of melt at the eutectic temperature, i. e. at the start of the eutectic reaction.

It is reasonable to assume that the melt, which remains at the eutectic temperature, will solidify with eutectic composition and structure. Thus the fraction $(1 - f_E)$ in equation (12) also represents the fraction of the solid, which has a eutectic composition, when the molten alloy has solidified completely.

Example 1.

As is seen from the phase diagram of the Al-Cu system the solid Al-phase has a maximum solubility of 2.50 at-% Cu at the eutectic temperature. The Cu-concentration is 17.3 at-% at the eutectic temperature.



Part of the phase diagram of the system Al-Cu.

According to the phase diagram a melt with an initial Cu-concentration of 2.50 at- % would be able to solidify to a homogeneous Al-phase with substitutionally solved Cu-atoms if microsegregation, leading to an uneven distribution of the Cu-atoms within the solid phase, could be disregarded. It cannot be disregarded, however.

Take microsegregation into consideration by applying Scheil's equation and calculate what fraction of the material, which solidifies with a eutectic composition and structure.

Solution:

It is reasonable to assume that the melt, which is left when the temperature has dropped to the eutectic temperature, will solidify eutectically. To calculate the desired fraction we only have to calculate the degree of solidification f_E from Scheil's equation when the melt has reached the eutectic composition. For application of Scheil's equation we have to know the partition constant k . An approximate value of this is

$$k = \frac{x^s}{x^L} = \frac{2.50}{17.3} = 0.1445 \quad (1)$$

Scheil's equation is applied on the eutectic melt:

$$x_E^L = x^0 \cdot (1 - f_E)^{-(1-k)}$$

or

$$0.173 = 0.0250 \cdot (1 - f_E)^{-(1-0.1445)} \text{ which can be reduced to}$$

$$1 - f_E = 0.1445^{1/0.8555} = 0.1023$$

At the eutectic temperature the fraction f_E is solid. The rest, i. e. the fraction $(1 - f_E)$, will solidify with eutectic structure.

Answer: 10 % of the alloy will solidify with a eutectic composition.

7.3.2 Validity of Scheil's Segregation Equation. Convection and Diffusion in Melts and Solid Metals. The Lever Rule

One of the conditions at the derivation of Scheil's equation was that the melt at every moment is homogeneous. This assumption is justified by the presence of convection and rapid diffusion in the melt.

Both these processes are time-dependent and the assumption is not fulfilled if the solidification process is rapid compared to the convection and the diffusion in the remaining melt. In order to understand the factors, which control the microsegregation, one has to examine the magnitudes of convection and diffusion.

Convection

Convection of importance is supposed to occur only in volumes with a thickness exceeding 1 mm. Interdendrite volumes have normally a thickness smaller than 1 mm. For this reason we will neglect convection in connection with microsegregation here. The influence of interdendritic convection on macrosegregations will be discussed in chapter 11.

Diffusion of Alloying Elements in Metal Melts

In order to examine the influence of diffusion on microsegregation we will use Einstein's relation for random walk:

$$l = \sqrt{2Dt} \quad (13)$$

where

- l = average diffusion distance of an alloying atom during the time t
- D = diffusion constant (m^2/s)
- t = diffusion time.

Equation (13) can be used for an estimation of the concentration distribution of the alloying element within a dendrite. If the total solidification time of the dendrite is chosen as the time t and we make the reasonable assumption that the diffusion constant is of the magnitude $10^{-10} \text{ m}^2/\text{s}$ or larger, the average diffusion distance can be calculated. The calculations show that an atom during this time is able to move more than half the dendrite arm distance during the solidification process.

The diffusion rate of an alloying element in a metal melt is normally of the magnitude $10^{-9} - 10^{-8} \text{ m}^2/\text{s}$ or $> 10^{-10} \text{ m}^2/\text{s}$. The diffusion constant of carbon, nitrogen, hydrogen and other interstitially solved atoms (foreign atoms between the crystal lattice atoms) have the same magnitude in steel alloys, i. e. both in austenite and ferrite for example. The conclusion is:

- No concentration gradients are likely to occur in the melt during the solidification process.

The diffusion in the *melt* is rapid enough to prevent such gradients. Probably there will be small concentration differences of interstitially solved elements in the *solid* phase, though. This matter will be discussed below.

Diffusion of Alloying Elements in Solid Metals

When we derived Scheil's equation we assumed that the diffusion in the solid phase could be neglected. For the *interstitially* solved elements carbon, nitrogen and hydrogen in both austenite and ferrite in iron-base alloys, no concentration gradients have been found.

For substitutionally solved alloying elements there are concentration gradients in some cases. The conclusion is that for these elements the assumption that the rate of diffusion in the solid phase can be neglected is not always true. The diffusion has to be taken into consideration.

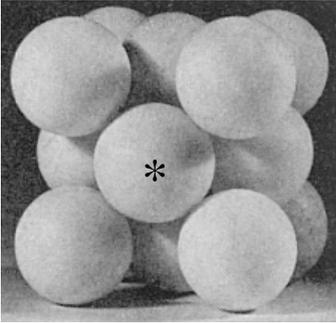


Figure 7.

FCC-structure.

There is an atom (marked with a star in the figure) in the centre of each lateral surface.

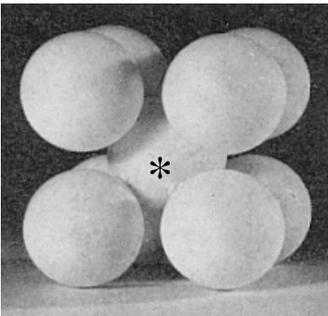


Figure 8.

BCC-structure.

There is an atom (marked with a star in the figure) in the centre of the unit cell.

In most metals with FCC-structure the diffusion constant is of the magnitude 10^{-13} m²/s or less for substitutionally solved elements (an alloying atom replaces a metal atom in the crystal lattice).

Examples of metals with FCC-structure are:

γ -Fe (austenite), Cu, Al and Pb.

In these cases there is probably a certain diffusion in the solid phase at the end of the solidification process. This occurs when the concentration gradient has become large.

The assumption that there is no diffusion in the solid phase is consequently comparatively good in the cases of FCC-metals.

The assumption is more uncertain if the solid phase has BCC-structure, which is the case for example for ferrite in steel and for the β -phase in copper alloys. In ferrite the diffusion constant for alloying metals is about 10^{-11} m²/s at 1400 °C. For sulphur in ferrite the diffusion constant is 10^{-10} m²/s.

Examples of metals with BCC-structure are:

δ -Fe (ferrite), β -brass, Li and V.

It is evident from the values of the diffusion constants, given above, that there are cases when the diffusion is rapid enough to smooth out the differences in composition, i.e. the concentration gradient, in the solid phase. If this occurs before the melt has disappeared completely, there will be an exchange of the alloying element between the melt and the already solidified material.

This phenomenon is called *back diffusion*. If back diffusion occurs after the solidification has been completed, the phenomenon is called *homogenisation*.

In the presence of back diffusion Scheil's equation (10) on page 8 does not describe the microsegregation properly but has to be modified. This case will be treated on page 31.

Lever Rule

In case of very rapid diffusion of the alloying element in the solid phase Scheil's equation can not be used at all. The rapid diffusion of the alloying element results in an even distribution of the alloying element in each phase, i. e. even compositions in the solid phase respectively in the melt.

Consider a mass element dm . The fraction f of the mass element has solidified and the rest, fraction $(1 - f)$, is molten. Instead of an even concentration x^o of the alloying element the concentration is x^L everywhere in the melt and x^S everywhere in the solid phase. A material balance of the alloying element will be:

$$f \cdot dm \cdot (x^o - x^S) = (1 - f) \cdot dm \cdot (x^L - x^o) \quad (14)$$

amount of the alloying
element removed from
the solid phase
amount of the alloying
element transferred to
to the melt

which gives by aid of equation (4) on page 4

$$x^L = \frac{x^S}{k} = \frac{x^o}{1 - f(1 - k)} \quad \text{Lever rule} \quad (15)$$

where

- x^o = initial concentration of the alloying element
- f = fraction solid phase in the mass element
- k = partition coefficient (x^S / x^L) of the alloying element.

Equation (15) is called the *lever rule*. It is valid at rapid diffusion of alloying elements in a solidifying melt.

Most practical cases are likely to be a hybrid between this extreme (rapid diffusion in the solid phase) and the extreme represented by Scheil's equation (no diffusion at all in the solid phase).

7.4 Solidification Processes in Alloys

Scheil's segregation equation (equation (10) on page 8) is independent of the cooling rate of the melt. As was pointed out on page 8, *time* has not been involved in the treatment of microsegregation so far.

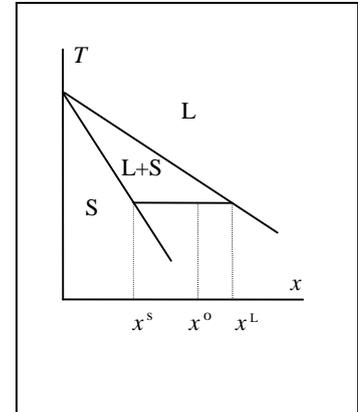


Figure 9.
Phase diagram of a binary alloy.

7.5 Influence of Back Diffusion in the Solid Phase on Microsegregation of Alloys

When we derived Scheil's equation and the lever rule, we did not consider the geometrical effects on the distribution of alloying elements at solidification.

As is seen from figure 4 on page 11 in chapter 6 the dendrite solidification structure is very complex. Primary and secondary arms grow simultaneously. During the growth process some of the secondary arms grow faster than other ones. The concentration distribution of the alloying elements in the solid alloy will thus contain a three-dimensional pattern of numerous concentration maximum and minimum.

For this reason it is difficult to specify a certain diffusion distance and calculate the back diffusion. Below we will discuss a method to handle this problem and derive an improved and successful model for microsegregation, which includes the effects of back diffusion. It was primarily derived by Flemings and is frequently used in metallurgical literature.

7.5.1 Scheil's Modified Segregation Equation

We consider the same volume element as in section 7.3.1 (figure 4 on page 7) when we derived Scheil's equation. If back diffusion is taken into consideration the basic material balance equation (6) on page 7 has to be completed on the right-hand side by a term, which represents the amount of alloying element, which is transported from the melt back into the solid phase.

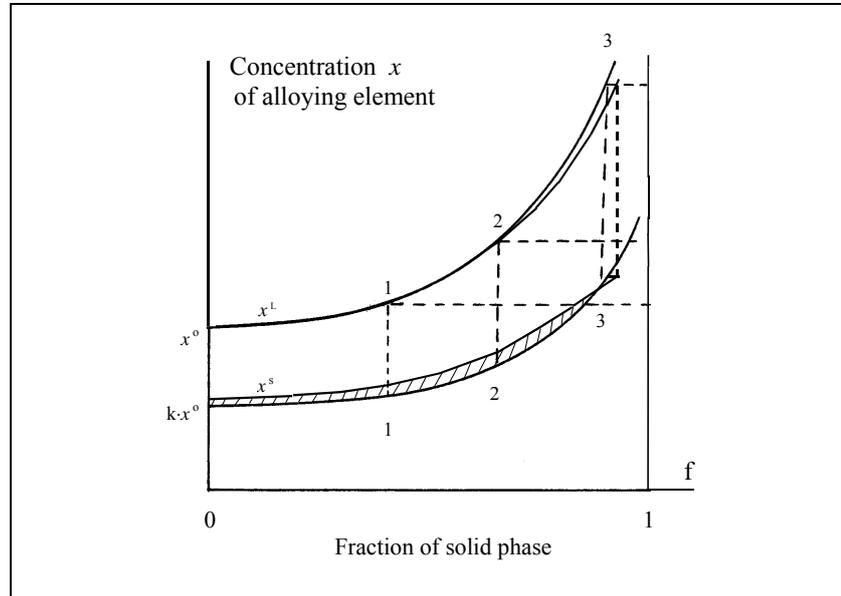
$$\text{Amount of alloying element} = \int_0^y \Delta x^s \cdot dy \quad (20)$$

If this term is included into equation (6) on page 7 and we assume that the molar volumes in the solid phase and the melt are equal, we get after reduction

$$\left(\frac{\lambda}{2} - y\right) \cdot dx^L = (x^L - x^s) \cdot dy - \int_0^y \Delta x^s \cdot dy \quad (21)$$

Increase of alloying element in the melt Addition of alloying element from the solidified volume Return of alloying element from melt to solid (back diffusion)

Figure 14.
The concentrations of the alloying element in the melt respectively the last solidified material during a solidification process for $k = 0.5$ as a function of the fraction solid with and without consideration to back diffusion.
The marked area represents the effect of back diffusion.



Equation (21) is to be compared with equation (6) on page 7. The shaded area in figure 14 represents the last term on the right-hand side in equation (21), i. e. the effect of back diffusion.

We have to find an expression for the concentration gradient in the solid phase close to the interface. This requires in principle application of Fick's second law on the whole solid phase and calculation of its concentration distribution. This is a complicated procedure, which has not been done analytically so far.

An approximate calculation can be performed if we assume that

$$dx^s = k \cdot dx^L \quad (22)$$

In addition, we set up a heat balance equation for the solidifying volume element. The amount of heat emitted from the volume element can be written

$$\frac{dQ}{dt} = A \rho (-\Delta H) \cdot \frac{dy}{dt} + A \rho c_p \cdot \left(-\frac{dT}{dt} \right) \cdot \frac{\lambda}{2} \quad (23)$$

where $(-dT/dt)$ is the cooling rate during the solidification process. The first term in equation (23) represents the heat of fusion and the second one is the amount of heat associated with

the temperature decrease. The last one is often small compared with the former one. Thus the second term on the right-hand side in equation (23) can be neglected.

We assume further that the amount of heat, which is removed per unit time (dQ/dt), is constant. As is seen from equation (23) dy/dt also becomes constant if we use these assumptions. We can replace dy/dt by $\lambda/2\theta$, where λ is the dendrite arm distance and θ is the *total solidification time*. This value is inserted into equation (21), which gives

$$D^s \frac{2\theta}{\lambda} \cdot k \cdot dx^L + \left(\frac{\lambda}{2} - y \right) \cdot dx^L = (x^L - x^s) \cdot dy \quad (24)$$

Integration and use of the relation $x^s = k \cdot x^L$ gives

$$\int_{x^o}^{x^L} \frac{dx^L}{x^L(1-k)} = \int_0^y \frac{dy}{D^s \cdot \frac{2\theta}{\lambda} \cdot k + \frac{\lambda}{2} - y}$$

$$\frac{1}{1-k} \ln \frac{x^L}{x^o} = -\ln \frac{D^s \cdot \frac{2\theta}{\lambda} \cdot k + \frac{\lambda}{2} - y}{D^s \cdot \frac{2\theta}{\lambda} \cdot k + \frac{\lambda}{2}}$$

which can be reduced to

$$\left(\frac{x^L}{x^o} \right)^{\frac{-1}{1-k}} = \frac{D^s \cdot \frac{2\theta}{\lambda} \cdot k + \frac{\lambda}{2} - y}{D^s \cdot \frac{2\theta}{\lambda} \cdot k + \frac{\lambda}{2}}$$

or

$$x^L = x^o \cdot \left(\frac{D^s \cdot \frac{2\theta}{\lambda} \cdot k + \frac{\lambda}{2} - y}{D^s \cdot \frac{2\theta}{\lambda} \cdot k + \frac{\lambda}{2}} \right)^{-(1-k)}$$

which can be transformed to

$$x^L = x^o \cdot \left(1 - \frac{\frac{2y}{\lambda}}{1 + D^s \cdot \frac{4\theta}{\lambda^2} \cdot k} \right)^{-(1-k)} = x^o \cdot \left(1 - \frac{f}{1 + D^s \cdot \frac{4\theta}{\lambda^2} \cdot k} \right)^{-(1-k)} \quad (25)$$

Equation (25) is a *modified form of Scheil's segregation equation*. A comparison between equations (25) and (10) shows that they differ by a correction term B in the denominator

$$B = \frac{4D^s \theta k}{\lambda^2} \quad (26)$$

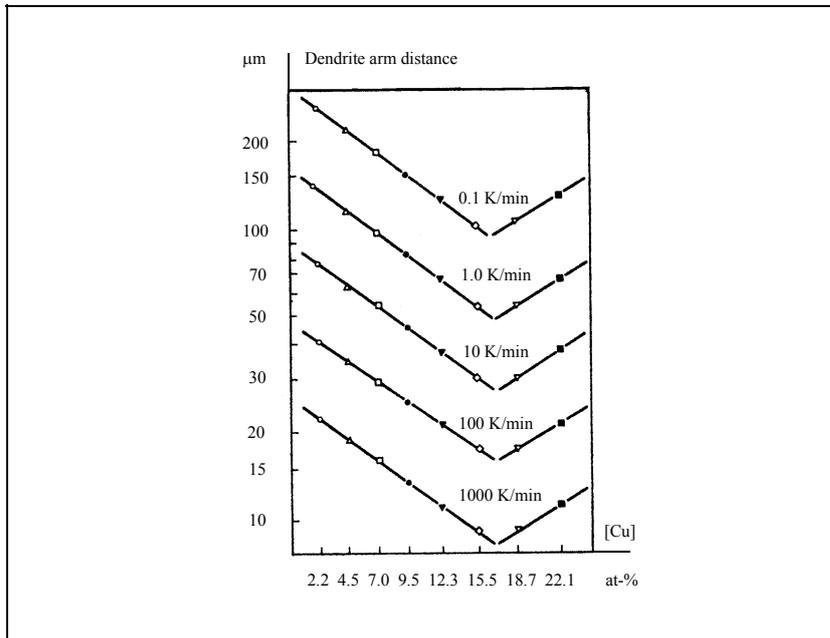
This correction term is caused by the *back diffusion*. The correction term is unimportant as long as it is $\ll 1$. It can be seen from equation (25), that the back diffusion becomes more and more important at the end of the solidification process, when f approaches the value 1.

More detailed calculations require knowledge of the value of the parameter B. It contains the solidification time, directly and indirectly, because the dendrite arm distance depends on the cooling rate. The parameter B contains the ratio $4\theta/\lambda^2$ and the dendrite arm distance decreases with increasing cooling rate. The total solidification time θ also decreases with increasing cooling rate. Thus the factors λ and θ counteract each other.

Example 4.

The figure below shows that the dendrite arm distance as a function of composition of the alloy and the cooling rate is known for a number of Al-Cu alloys. Use this knowledge to decide whether the importance of back diffusion in Al-Cu alloys increases or decreases with the cooling rate.

arm distance as a
 the concentration
 g element and
 te (parameter)
 of Al-Cu alloys.
 action occurs at
 . At higher Cu-
 s than 17.3 at-%
 precipitated, which
 curves, given in



Solution:

It is reasonable to assume that the heat flux is constant during cooling and solidification, which gives:

$$c_p^L \cdot \left(-\frac{dT}{dt}\right) = (-\Delta H) \cdot \frac{df}{dt} \quad (1')$$

The total solidification time corresponds to $f = 1$.

$$\theta = \frac{-\Delta H}{c_p^L \cdot \left(-\frac{dT}{dt}\right)} \quad (2')$$

Next we compare the correction terms, caused by the back diffusion for two different cooling rates.

$$B_1 = \frac{4D^s \theta_1 k}{\lambda_1^2} = \frac{4D^s \cdot k \cdot (-\Delta H)}{\lambda_1^2 \cdot c_p^L \cdot \left(-\frac{dT_1}{dt}\right)} \quad (2')$$

and

$$B_2 = \frac{4D^s \theta_2 k}{\lambda_2^2} = \frac{4D^s \cdot k \cdot (-\Delta H)}{\lambda_2^2 \cdot c_p^L \cdot \left(-\frac{dT_2}{dt}\right)} \quad (3')$$

Equation (2') and (3') are divided with each other, which gives

$$\frac{B_1}{B_2} = \frac{\left(-\frac{dT_2}{dt}\right) \cdot \lambda_2^2}{\left(-\frac{dT_1}{dt}\right) \cdot \lambda_1^2} \quad (4')$$

The figure shows that the faster the cooling rate is the smaller will the dendrite arm distance be. Quantitatively one can see that an increase of the cooling rate with a factor 10 000 leads to a decrease of the dendrite arm distance with a factor ≈ 12 , independent of the composition of the alloy.

The values $\frac{-\frac{dT_2}{dt}}{-\frac{dT_1}{dt}} = 10^4$ and $\frac{\lambda_2^2}{\lambda_1^2} = \frac{1}{12^2}$

both obtained from the figure in the text, are inserted into equation (4') which gives

$$\frac{B_1}{B_2} = \frac{10^4}{12^2} \quad \text{or} \quad B_2 = B_1 \cdot 0.014$$

The B parameter decreases when the cooling rate increases.

Answer: The importance of back diffusion in Al-Cu alloys decreases when the cooling rate increases.

If $\lambda = \text{const} \cdot \theta^{0.5}$ (see equation (10) page 12 in chapter 6) the back diffusion in Al-Cu alloys will be independent of the cooling rate according to example 2 above. In reality the exponent is lower than 0.5. The smaller the back diffusion is the larger will the microsegregation be. Thus we can conclude from

example 2 that the microsegregation will be stronger the larger the cooling rate is. A fast homogenisation after solidification can often compensate microsegregation. We will come back to this in section 7.6 and in next chapter.

We integrated equation (24) on page 33 under the assumption that the B-parameter was constant. This condition is well fulfilled in the many cases when the alloy has a narrow solidification interval. However, at broad solidification intervals the temperature dependence of D^s will be considerable. One also has to take the removal of cooling heat into consideration, which leads to a temperature decrease in the volume element.

Scheil's segregation equation (10) on page 8 shows that the first solidified material gets and keeps the composition kx^0 if the back diffusion is small.

In cases with strong back diffusion the first solidified material will smooth out its composition during the continued solidification. In these cases there are no simple approximate solutions but numerical calculations have been performed in special cases. One such case is the Al-Cu alloy described in figure 15.

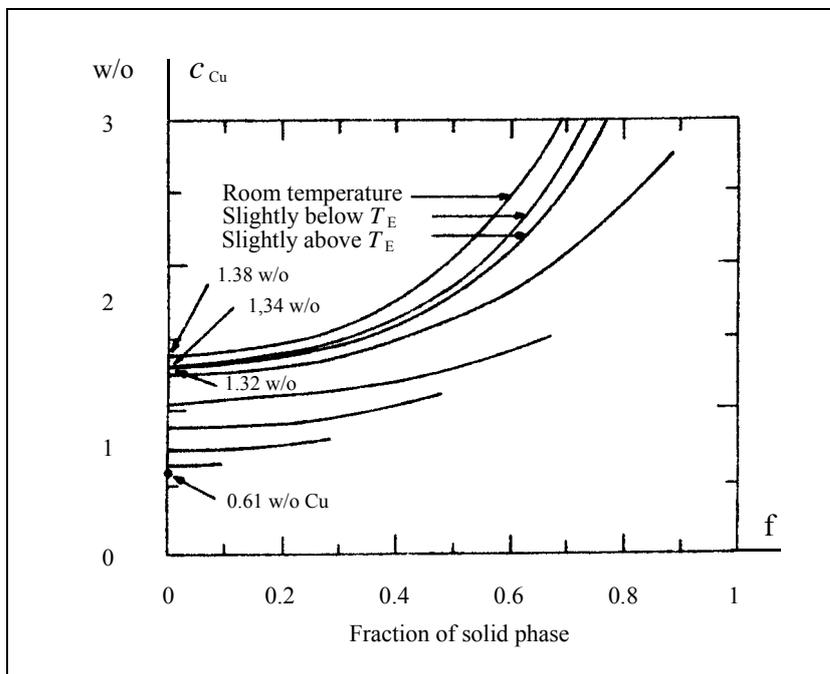


Figure 15.
Concentration distribution of Cu in an Al-4.5 w/o Cu alloy as a function of degree of solidification.

Figure 15 shows the result of such a numerical calculation for an Al-alloy with 4.5 w/o Cu. The calculated partition constant is $k = 0.136$. The first material will thus get the composition

$$c^s = kc^o = 0.136 \cdot 4.5 = 0.61 \text{ w/o Cu}$$

when it is formed. This value corresponds to the lowest point in the diagram in figure 15.

When the fraction of solid phase is 0.1 or 10 w/o, the Cu-concentration in the first solidified material has increased. This is illustrated by the short curve which ends at $f = 0.1$.

The higher curves show how the solidified layer grows and how its composition changes. The curves in figure 15 have been calculated by use of a B-value of $6.1 \cdot 10^6 \cdot D^s$. The diffusion constant was assumed to vary exponentially with the temperature.

7.5.2 Choice of Method to Calculate Alloy Composition

Calculation of the concentration of the alloying element as a function of the fraction solid phase $f = 2y/\lambda$ is performed as follows

- At *high* diffusion rates the lever rule is valid (equation (15) on page 15)
- At *low* diffusion rates Scheil's modified segregation equation is valid (equation (25) on page 33).
- Scheil's segregation equation (10) on page 8 is valid at solidification processes when more than 10 % of the structure is eutectic and the diffusion rate is low.
- When $D^s = 10^{-11} \text{ m}^2/\text{s}$ it is difficult to decide which relation one should use. The cooling rate is allowed to decide.

At *low* cooling rates the lever rule is valid.

At *high* cooling rates Scheil's modified equation agrees best with reality.

7.5.3 Degree of Microsegregation

By use of a microprobe microsegregation in a solidified material can be determined. A great number of such investigations have been performed on steel alloys. These investigations have shown that in most cases the concentration of the alloying elements at the centre of a dendrite arm is constant during the whole solidification process, provided that the material solidifies as austenite.

The reason for this is that homogenisation (page 14) occurs to a very little extent during solidification. The concentration distribution in the interdendritic areas are in such a case described by Scheil's modified segregation equation (equation (25) on page 33 when the primary precipitation is austenite.

Various alloying elements have very different partition constants and different tendencies of segregation. In order to describe the tendency of segregation the concept of *degree of segregation* has been introduced.

- Degree of micro-segregation = the ratio between the highest and the lowest measured value of the concentration of the alloying element in a dendrite crystal aggregate.

$$S = \frac{x_{\max}^s}{x_{\min}^s} \quad (27)$$

Because the relation $x^s = k \cdot x^L$ is always valid Scheil's modified segregation equation [equation (25)] can be used for calculation of the degree of segregation. The ratio of x_{\max}^L , when the segregation is highest ($2y/\lambda = f = 1$), and x_{\min}^L , when the segregation is lowest ($f = 0$), is formed:

$$x_{\max}^L = x^0 \cdot \left[\left(1 - \frac{\frac{2y}{\lambda}}{D^s \cdot \frac{4\theta}{\lambda^2} \cdot k + 1} \right)^{-(1-k)} \right]_{f=\frac{2y}{\lambda}=1} = x^0 \cdot \left(1 - \frac{1}{B+1} \right)^{-(1-k)} = x^0 \cdot \left(\frac{B}{B+1} \right)^{-(1-k)}$$

and

$$x_{\min}^L = x^0 \cdot \left[\left(1 - \frac{\frac{2y}{\lambda}}{D^s \cdot \frac{4\theta}{\lambda^2} \cdot k + 1} \right)^{-(1-k)} \right]_{f=\frac{2y}{\lambda}=0} = x^0$$

which gives

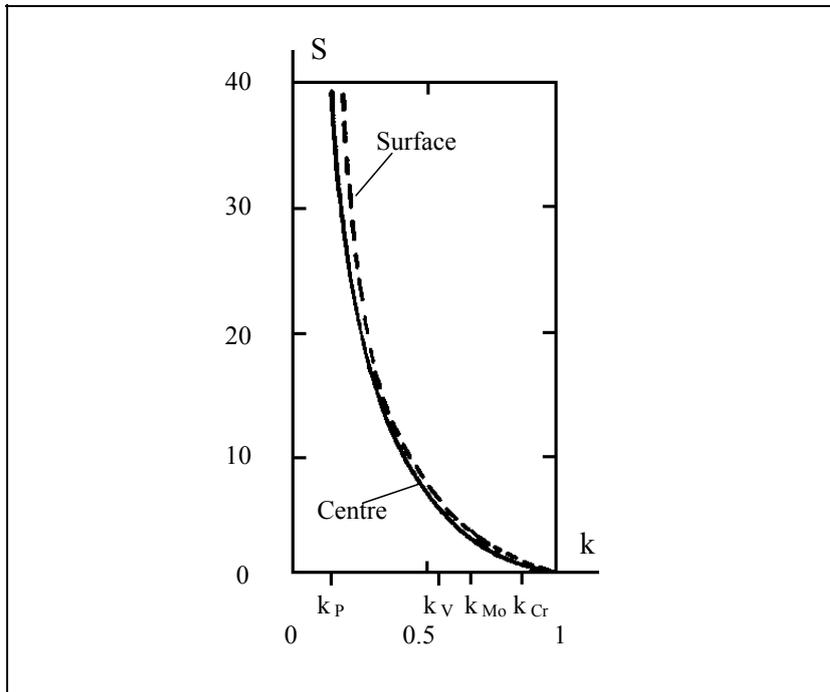
$$S = \frac{x_{\max}^s}{x_{\min}^s} = \frac{kx_{\max}^L}{kx_{\min}^L} = \frac{x_{\max}^L}{x_{\min}^L} = \left(\frac{B}{B+1} \right)^{-(1-k)} \quad (28)$$

It has been known for a long time that an increase of the carbon content in ternary Fe-Cr-C alloys increases the degree of segregation of chromium. The reason for this increase is that the partition constant of chromium between austenite and melt decreases with increasing carbon content. The result is that the segregation increases.

In steel alloys there are alloying elements or impurities, which have partition constants between austenite and melt close to 1 or slightly smaller, and substances, which have very small partition constants.

Because the degree of segregation S depends on the partition constant k according to equation (28) directly and indirectly (k is involved in B too), the degree of segregation can be expressed as a function of the partition constant. The result of such calculations for steel alloys, which solidify as austenite, is given in figure 16.

The calculations have been performed for two different cooling rates, which simulate the cooling rate, close to the centre respectively close to the surface zone in a 9 ton ingot.



calculations of the
segregation S of steel
function of the par-
tition coefficient k .
The solid line in the figure
corresponds to the centre
of the ingot. The dotted
line shows the degree of
segregation close to the sur-
face of the same ingot.

As expected low k -values correspond to very high values of the degree of segregation. For $k \geq 0.90$ the material becomes practically homogeneous. In figure 16 the approximate values of the partition constants of the most common alloying elements have been plotted. Phosphorous shows the highest degree of segregation.

The cooling rate is faster in the surface zone (dotted line) than in the centre. Figure 16 consequently shows that the degree of segregation increases with increasing cooling rate. This is compensated only too well by the fine structure, which facilitates an effective equalisation at the following heat treatment and machining.

In section 7.6 microsegregation and solidification processes in iron base alloys will be discussed more in detail because of their technical importance.

7.6 Solidification Processes and Microsegregation in Iron-Base Alloys

The solidification process in iron-base alloys starts with dendrite solidification and precipitation of either ferrite (δ) or austenite (γ).

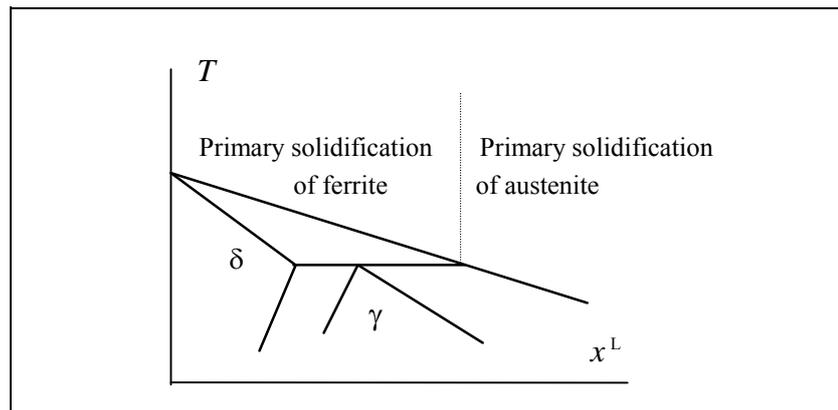


Figure 17.
Solidification reg
precipitation of f
respectively auste

The microsegregation in the two cases is completely different. The difference depends on two factors:

- the difference between the diffusion rates of the alloying element in ferrite respectively austenite
- the difference between the partition coefficients of the alloying element in ferrite respectively austenite.