Module 22

Solidification & Binary Phase Diagrams V

Lecture 22

Solidification & Binary Phase Diagrams V
**Keywords:** Effect of thermal gradient on solidification rate, evolution of microstructure during solidification, solid liquid interface, partition coefficient, constitutional super cooling, structure of an ingot, normal & inverse segregation, role of continuous casting to produce homogeneous alloys

**Introduction**

We are now familiar with phase diagrams of binary alloys. This is a graphical representation of the stability of various constituents in a binary alloy in a given temperature composition space. We have looked at a variety of phase diagrams having several intermediate phases, different types of invariant reactions involving 3 phases and allotropic transformations. A major limitation of phase diagram is that it ignores the effect of cooling rate. The predictions regarding the evolution of structure of an alloy are valid only if the alloy has been cooled very slowly. However to some extent assuming the concept of local equilibrium it is possible explain the origin of segregation (coring) within primary grains and the presence of unexpected constituents like eutectic in a terminal solid solution or unexpected primary phase even after peritectic reaction. This has been dealt with in details in the last lecture. The effect of departures from equilibrium cooling rate in cases of solid state transformation is likely to be even more complex. This will be taken up in one of the subsequent modules. In this lecture let us look at the stability of the solid liquid interface a little more critically.

**Effect of thermal gradient on the rate of solidification:**

The thermal gradient on the two sides of the interface is crucial in determining the whether the interface is likely to be planar. Heat extraction is a must for solidification to take place. The rate of heat transfer depends on thermal gradients on the two sides of a solid liquid interface. The heat always flows down the gradient. Figure 1 gives a schematic representation of the movement of the solidification front as the heat is being extracted from one side of a partially solidified metal. The heat flux per unit cross sectional area of the solid \( \dot{q}_s \) is given by \( \dot{q}_s = -k_s \left( \frac{dT}{dx} \right)_s \) where ‘\( k_s \)’ is the thermal conductivity of the solid and \( \left( \frac{dT}{dx} \right)_s \) is the temperature gradient within the solid. Heat can flow through solid only by conduction. However in liquid it can flow by conduction and convection. Let us assume that there is no agitation within the liquid and the change in the density of the metal due to the change in temperature is negligible. Under such a situation there will be little convection and hence the contribution due to convection can be ignored. Therefore the heat flux per unit cross sectional area of the liquid \( \dot{q}_L \) is given by \( \dot{q}_L = -k_L \left( \frac{dT}{dx} \right)_L \) where ‘\( k_L \)’ is the thermal conductivity of the liquid and \( \left( \frac{dT}{dx} \right)_L \) is the temperature gradient within the liquid. The S/L interface can move through a distance \( v \) in unit time if latent heat (= L /unit mass) released can flow through the solid. Let the cross section area of the S/L interface in fig 1 be unity and \( \rho \) be the density of the liquid. The heat released = \( LPv \). Therefore the relation between the two is as follows:

\[
\dot{q}_s = -k_s \left( \frac{dT}{dx} \right)_s = -k_L \left( \frac{dT}{dx} \right)_L + LPv \quad (1)
\]
\[ v = \left\{ k_S \left( \frac{dT}{dx} \right)_S - k_L \left( \frac{dT}{dx} \right)_L \right\} / L \rho \]  

(2)

It is evident from the above relation that the velocity of the solid liquid interface would primarily depend upon thermo-physical properties and thermal gradients within the solid and the liquid.

**Fig 1:** (a) Shows the direction of heat flow when it is dominated by higher thermal gradient within the solid. (b) Shows why any deviation from a planar interface is unstable in this situation. Since the liquid is at a higher temperature, the latent heat being released due to solidification must flow into the bulged region. This would raise the temperature of this region. Therefore help it to melt again. (c) Show thermal gradients at the two sides of a solid-liquid interface where the liquid is in a super cooled state. Here heat could flow out of the bulged region into the liquid as well. Therefore in this case bulge is stable. It can subsequently grow into a dendrite (a tree like structure).

**Effect of non-equilibrium cooling on the evolution of structure:**

We have looked at the evolution of structure in binary alloys when the cooling rate is extremely slow so that at every stage the composition of the solid and the liquid could change as predicted by the solidus and the liquidus. The composition of the solid can change only through diffusion whereas that of the liquid could change by diffusion as well as convection. Moreover the rate of diffusion in solid is an order of magnitude slower than that in the liquid. Therefore under normal rate of cooling the contribution of diffusion towards any change in the composition of the solid may be negligible. However within the liquid there can be two distinct situations; (i) there is enough convection current within the liquid so that its composition is the same everywhere (it is possible if the liquid is being continuously stirred or agitated) and (ii) there is no stirring within the liquid so that mixing could take place only by diffusion. Therefore we can visualize three distinct modes of solidification: (i) equilibrium or extremely slow cooling (ii) no diffusion in solid but perfect mixing in liquid (iii) no diffusion in solid but mixing by diffusion in liquid.

Non-equilibrium cooling is primarily responsible for segregation of solute atoms in an alloy. Slide 1 introduces the concept of segregation with respect to a hypothetical binary alloy. Let us consider the case of a terminal solid solution. The gross composition of the alloy is \( X_0 \). The solidification begins at a temperature \( T_1 \). Note that the solid that precipitates from the liquid has a composition \( kX_0 \) where \( k \) is known as the segregation (partition) coefficient. It is defined as the ratio of the composition of the solidus \( (X_S) \) and that of the liquidus \( (X_L) \) at a given temperature \( k = X_S/X_L \). Let us assume for simplicity
that $k$ is a constant (independent of temperature). This is why the liquidus and the solidus are shown as straight lines in the in slide 1. Note that the composition of the first solid that forms is $kX_0$ whereas the composition of the liquid that solidifies at the end is $X_0/k$.

Let us look at the effect of the three modes of solidification on the evolution of the structure on solidification of a terminal solid solution. The process for simplicity is being treated as one due to directional solidification and the main focus is on the growth or the movement of the planar S/L interface.
Equilibrium solidification: extremely slow cooling:

**Equilibrium solidification**

Allow sufficient time for solid state diffusion: only way composition of a solid can change

Conservation criterion: shaded area = amount of solute crossing the boundary

Let us consider the solidification of a terminal solid solution belonging to the binary alloy whose phase diagram is shown in slide 1. Consider the solidification of an alloy having $X_0$% B. The solid that forms at $T_1$ has $kX_0$ % B. The cooling rate is slow enough to allow sufficient time for the solute (B) to diffuse into the solid so that the composition of the solid formed earlier could follow that predicted by the solidus. At any intermediate temperature $T_2$, the compositions of the solid and the liquid are $X_S$ & $X_L$ respectively. The slide 2 gives the % solute as a function of distance from the surface of the mold at three different temperatures. The dotted line at $X_0$ gives the gross composition of the alloy. Note that at a temperature just below the liquidus ($T_1$) there is a large difference between the composition of the solid and the liquid. However within a particular zone the composition of the alloy is uniform (it is independent of distance). The composition of the liquid ($X_L$) is very close to $X_0$ when solidification just sets in (the first sketch in slide 1). The second sketch in slide 2 gives the distribution of B in the solid and the liquid at $T_2$. The third sketch in slide 2 gives the distribution of B in the solid and the liquid at a temperature a little higher than of the solidus ($T_3$). The area under the composition versus distance plot within the liquid is the net amount of solute that has moved (diffused) out from the liquid into the solid. The area under the plot within the solid gives the amount of B that has diffused into the solid from the liquid. The two should be equal. Note that although the sketches in slide 2 are schematic, an attempt has been made to keep the areas equal to highlight the principle of conservation of mass. The composition of the solid that forms from the liquid is uniform. Therefore the alloy on solidification is perfectly homogeneous.
No diffusion in solid but perfect mixing in liquid:

Slide 3 would help understand the evolution of the structure in a binary terminal solid solution during solidification in a situation where there is perfect mixing in the liquid state but no mixing (diffusion) within the solid. The sketch on the right gives a schematic phase diagram. The vertical dotted line at $X_0$ denotes the location of the alloy. The solidification begins at $T_1$ which is the liquidus temperature of the alloy. The composition of the solid that forms at this temperature is $kX_0$. Recall that $k$ is the partition coefficient. The first sketch on the left represents the partition of the solute between the solid and the liquid at a temperature just below $T_1$. The second sketch on the left represents the partition of the solute between the solid and the liquid at a temperature $T_2$. The composition of the solid that forms at this temperature is $X_S$ and the composition of the liquid is $X_L$. Since there is perfect mixing within the liquid the composition profile within this is represented by a horizontal line at $X_L$. Let us assume that the length of the whole rectangle is 1. The vertical line at $f_s$ is the interface between the solid and the liquid. The lengths of solid and liquid zones are $f_s$ and $(1-f_s)$ respectively. The vertical axis of the rectangle represents composition. The composition of the solid that forms at $T_1$ is $kX_0$ and that at $T_2$ is $X_S$. The line joining the two points describes the variation of the composition within the solid. Let us apply the principle of conservation of solute when the solid liquid interface moves through a very small distance $df$, towards the liquid. Look at the concentration profile within the liquid and the solid at $T_2$ given in slide 3. The concentration of B in the liquid over a distance $(1-f_s)$ is $X_L$. If it changes by a small amount $dX_L$ when the interface moves by a distance ‘$df$’, the amount of B that moves out of the liquid is $(1 - f_s) dX_L$.
\( f_S \) \( dX_L \). Note that the composition of the liquid & the solid at the interface are \( X_i \) and \( X_S \) respectively. Therefore the amount of B that moves into the solid when the interface moves by \( df_S \) is \( (X_L - X_S)df_S \). The mass balance gives the following relation between \( f_s \) (which is in fact the fraction solid at \( T_2 \)) and the composition of the liquid and the solid.

\[(X_L - X_S)df_S = (1 - f_s) dX_L \] (3)

Recall that the partition coefficient \( k \) is assumed to be constant. Therefore at any temperature the composition of the solid is given by \( X_S = kX_L \). On substitution of this in equation 3:

\[
\int \frac{df_S}{1-f_S} = \int \frac{dX_L}{X_L-X_S} + K = \frac{1}{(1-k)} \int \frac{dX_L}{X_L} + K 
\] (4)

\( K \) is the constant of integration. It can be evaluated from the initial condition that if \( f_S = 0; X_L = X_0 \).

The solution of equation 4 is given below:

\[-ln(1-f_S) = \frac{1}{(1-k)} lnX_L + K \] (5)

Substitution of the initial condition in equation 5, gives an expression for \( K \). This is as follows:

\[ K = \frac{lnX_0}{1-k} \]

The composition of the solidus and the liquidus under such a condition is given by the following sets of equations that are known as Scheil equation.

\[ X_L = X_0(1-f_S)^{(k-1)} = X_0(f_L)^{k-1} \] (6)

\[ X_S = X_0(1-f_S)^{(k-1)} \] (7)

\[ f_L = \left( \frac{X_L}{X_0} \right)^{\frac{1}{k-1}} \] (8)

Like lever rule the above set of equation has been derived by mass balance. This may be taken as the lever rule to estimate phase fractions under non-equilibrium rate of cooling. The dashed line (in slide 3) starting from the solidus at \( T_1 \) represents the solidus in such a situation. Note that in the case of a terminal solid solution even when the temperature reaches that of the eutectic there is still some amount of liquid left. This would solidify as a mixture of two phases (\( \alpha \) & \( \beta \)). This explains why under non-equilibrium rate of cooling such alloys would always have some amount of eutectic. It also predicts that during the solidification of a binary isomorphous system the last solid to form will be pure B (the constituent having the lowest melting point).
No diffusion in solid & mixing by diffusion in liquid:

Slide 4 explains the main features of solidification of a terminal solid solution when there is no mixing (diffusion) in the solid but there is limited mixing by diffusion within the liquid. The sketch on the right gives a typical phase diagram of the alloy. The dashed vertical line at $X_0$ is the composition of the specific alloy of our interest. The solidification begins at the liquidus ($T_1$) with the separation of solid having composition $kX_0$. At this stage the composition of the liquid is $X_0$. As the temperature drops the new solid becomes increasingly rich in B and the concentration of B at the interface start to build up from its initial concentration $X_0$. The mixing within the liquid is only due to diffusion. This is governed by the diffusivity of the solute within the liquid and the concentration gradient. The concentration of solute in the liquid at a distance far away from the interface is the same as that of the alloy. The initial gradient is less. This builds up with decreasing temperature until it reaches $T_3$ the solidus. At this stage the composition of the solid that forms is $X_0$ (this is exactly same as that of the alloy in our consideration) and that of the liquid is $X_0/k$. This is the condition at which there is a balance between the amount of B that diffuses into a thin layer of liquid at the interface and that needed to convert it into a thin layer of solid having $X_0$ amount of B. This may be visualized as a steady state growth of the solid. The amount of solute (flux per unit area per unit time) that enters into the thin layer of liquid at the interface is given by $-D \frac{dx}{dy}$ where $D$ is the diffusivity and $X_L$ is the amount of B in the liquid at a distance $Y$ from the interface.
interface. If $v$ is the velocity at which the solid liquid interface moves during the steady state growth, the amount of B needed is $= v(X_L - X_0)$. Equate the two to get an expression for $X_L$. The derivation is given below.

$$-D \frac{dx_L}{dy} = v(X_L - X_0) \quad (9)$$

**On integration:**

$$ln(X_L - X_0) = -\frac{v}{D} Y + K \quad (10)$$

$K$ is the integration constant. It can be evaluated from the initial condition that $Y = 0; X_L = \frac{X_0}{k}$. On substitution of the initial condition in equation in equation 10:

$$K = ln \left( X_0 \frac{1-k}{k} \right) \quad (11)$$

$$X_L = X_0 \left( 1 + \frac{1-k}{k} \ exp \left( -\frac{Y}{D/v} \right) \right) \quad (12)$$

These equations are valid only during the steady state stage of solidification. When the amount of liquid becomes extremely small a transient stage may again set in. The concentration of solute in the liquid could go beyond $X_0$ and may approach $X_E$ the eutectic composition.

The implications of equation 12 representing the solidification behavior of a terminal solid solution has been explained with the help slide 5. The sketch at the top represents how the composition of the liquid
is likely to vary with distance at \( T_3 \). Note that the composition of the liquid at a distance far away from the interface is equal to the gross composition of the alloy. Use these to estimate the temperature of the liquidus \( (T_L) \) from the corresponding phase diagram (see slide 4). This would vary from \( T_3 \) at the interface to \( T_1 \) where the alloy composition is \( X_0 \). The sketch at the bottom of slide 4 represents \( T_1 \) as a function of distance from the interface. If you draw a tangent to the composition versus distance plot given in the slide (represented by a dotted line) at \( Y = 0 \), it would meet the \( Y \) (distance) axis at \( X_c = X_0 \) at a distance equal to \( D/v \). This has the dimension of distance. It is also known as the characteristic width of the boundary layer at the solid liquid interface. The ratio of the temperature difference \( (T_3 - T_1) \) to the characteristic width is known as the critical temperature gradient. This is shown as a line ‘\( T_c \)’ in slide 5.

\[
\left( \frac{dT}{dy} \right)_{\text{critical}} = \frac{(T_3 - T_1)}{D/v}
\] (13)

If the slope of the temperature versus distance plot at the S/L interface is greater than the critical value described by equation 13, the interface is likely to be planar. Most often during solidification the temperature versus distance plot is like the one marked \( T_0 \) in slide 5. In such a situation the temperature of the liquid is lower than that of the liquidus \( (T_L) \). This is known as constitutional supercooling. It would make planar interface unstable and favor dendritic solidification.

The above analysis shows the importance of temperature gradient, diffusivity and velocity (or the rate of growth) on the evolution structures during solidification. If the gradient is higher than a critical value the solidification front is planar. This gives columnar grains. In the other extreme if the gradient is lower than the critical value final structure is dendritic. If the temperature gradient is initially higher than the critical value but during the process it becomes a little lower than the critical value the final structure becomes cellular. Here you have columnar grains but there is a thin boundary having eutectic structure. In alloys that solidify over a wide range of temperature the critical cooling rate is likely to be very high therefore such alloys are prone to dendritic solidification. It would be extremely difficult to maintain planar interface in such a system.
Fig 2: The stability of a planar interface depends on the temperature gradient in the liquid just ahead of the interface. (a) Planar interface is stable as heat can only flow through the solid and there is no supercooled liquid ahead of it. (b) Planar interface is unstable because of constitutional super-cooling.

Fig 3: Shows the structure of a metal after solidification in a mold. When the hot metal comes in contact with the mold surface it cools down. The temperature in this zone is very fine because of high nucleation rate. This is known as the chilled layer or zone, the thickness of this zone depends on the type of the mold. It is thicker in the case of metal mold because of its high thermal conductivity. As the zone becomes thick the rate of heat transfer drops, consequently the velocity of the interface becomes lower. The subsequent structure is determined by the temperature gradient ahead of the solid liquid interface. If it is greater than a critical value the interface remains planar. A few of the grains that are favorably oriented would grow into columnar grains. Note that lateral growth is not possible because there is no space for growth to take place. Towards the end when the temperature of the central zone becomes sufficiently super-cooled homogeneous nucleation occurs. They keep growing in all direction until impingement with the neighboring grains. Therefore these are equiaxed.

Fig 4 shows different stages of the progress of non-planar solidification front. Super-cooling is the primary condition for the stability of any deviation from a planar front. In alloys constitutional super-cooling helps satisfy such a condition. When this happens (a) solutes from the bulged region would migrate towards the neighboring liquid. This would bring down the liquidus temperature of this zone. This is why the region near the base of the bulge may melt back and the S/L front would look like the sketch shown in (b). The sketch (c) shows the boundary a little later than that in (b). When the temperature gradient is a little lower than the critical value for the planar interface the individual segments develop into a number of elongated columnar grains as shown in (d). The solute concentration in the liquid surrounding such grains can become equal to that of the eutectic. Therefore on completion of the solidification process these regions would have eutectic structure. The sketch in (e) shows a cross sectional view of the sketch in (d). This is a typical representation of a cellular structure.
Segregation:

We have looked at three distinct modes of solidification depending on the rate of heat extraction from the molten alloy. If the rate of heat extraction is extremely slow, the solute gets enough time to diffuse or move so that at every stage equilibrium is maintained at the solid liquid interface. As against this we can also visualize a hypothetical case where the rate of heat extraction is so fast that there is no time for the solute to move at all. In both the cases we expect the solid to be homogeneous. However under normal rate of cooling we do not expect an alloy even if it is supposed to be made of a single phase to be homogeneous immediately after solidification. The composition would vary from the surface to its core. The first solid to form has the highest melting and the one that solidifies last has the lowest melting point. Therefore in an ingot casting we expect the composition to vary from the surface to its core. If the solidification occurs by a process where there is no diffusion in the solid but perfect mixing in the liquid there will be a linear variation in composition from the core to its periphery. This represents the case of normal solidification. If the gross composition of the alloy is $X_0$, the concentration of the solute in the region near the surface is less than $X_0$, whereas that at the core (centre) is more than $X_0$. This is known as the normal segregation. It extends over a large distance. Often this is treated as macro-segregation.

If during solidification there is no diffusion within the solid and mixing within the liquid is only due to diffusion, it may result in formation of dendrites as a result of constitutional super-cooling. The composition in the core of the dendrite would vary from $X_0/k$ to $X_0$. However the concentration beyond this is likely to be uniform. The segregation within the dendrite may be considered to be microscopic. The last liquid to solidify often within the gaps between the dendrites is very rich in solute. If the alloy is a terminal solid solution of a binary eutectic system the last liquid within the dendritic channel always solidifies as eutectic.

![Fig 5](image)

**Fig 5:** (a) A schematic representation of a dendrite. It has a main trunk and several braches like a tree. They are known as primary, secondary and tertiary arms. The concentration of the solute within dendrites may not be uniform. (b) Shows composition contours with a dendrite. The central region is relatively pure. However beyond a certain distance the composition may be the same as the gross composition of the alloy.

Under certain conditions the segregation may exhibit an opposite trend. For example you expect that metals having higher melting point would segregate near the surface. Sometimes the solidified parts may have a trail of liquid left behind along fine channels. As it shrinks during solidification it may suck liquid that has relatively higher amounts of solutes. Thus on completion of solidification within the
relatively purer solid there may be pockets (regions) having higher solute concentration. This is known as inverse segregation. It is also encountered in large ingots. During solidification of molten metal in an ingot the fine tertiary arms may break and settle down at the bottom of an ingot because of gravity (solid is heavier than the liquid). This has higher concentration of metals with higher melting point. In general the central zone of an ingot is likely to have higher concentration of alloys having low melting point. However fine grains of solid having higher concentration of metals having high melting point might accumulate in this region due to difference in density. This is known as inverse segregation.

**Fig 6:** (a) A sketch showing normal & inverse segregation in an ingot mold. (b) A sketch to explain the origin of inverse segregation during solidification in a partially solidified casting.

**How to get homogeneous structure (alloys):**

Segregation is harmful in many applications. However under normal rate of cooling it is unavoidable in casting. Nevertheless it can be minimized by controlled solidification. Continuous casting is a possible option. The impurities accumulate within the liquid whereas the solid continuously coming out of the mold is relatively free from harmful solutes. This concept is used to make defect free transparent ice by a technique similar to that of continuous casting. Look at the ice cubes made in your freezer. These are not perfectly transparent. Whereas the ice cubes served with drinks in expensive restaurants are perfectly transparent. The central region of homemade ice cubes is translucent. This is due the presence of large numbers of tiny air bubbles. Water has dissolved gases. Water and air form a binary eutectic system. The initial layers of ice that form along the mold wall is pure therefore the periphery is transparent. During solidification air segregates to the central region and the composition of water approaches that of the eutectic. When this happens the central region solidifies as a eutectic. This is an intimate mixture of tiny air bubbles and ice crystals. This makes it translucent. If the setup could be so designed that the top remains as liquid where dissolved air segregates from the growing layers of ice could accumulate and later escape. The ice thus formed is likely to be transparent.
The other option is to subject a cast billet or an ingot to long hours of thermal exposure in a furnace. The process is known as annealing. At higher temperatures atoms in solid can diffuse faster. A rough estimate of the effective distance atoms could move within a span of time $t$ is proportional to $\sqrt{Dt}$ where $D$ is the diffusivity of the solute at a given temperature. Often the estimate is of the order of the grain size of the casting even if the temperature is very close to its melting point. This suggests that it can be used to eliminate micro-segregation. Removal of macro-segregation requires combined action of thermal exposure and large plastic deformation. Critical engineering components are made from alloys that are subjected to upset forging at high temperature after prolonged annealing.

**Summary:**

In this lecture we learned about the effect of cooling rate (heat extraction) on the evolution of structure during solidification of an alloy in a mold. The phase diagram can give an idea of the structure of an alloy on solidification under equilibrium rate of cooling. The structure of terminal solid solution immediately after solidification is likely to be homogeneous. However normal rate of cooling is rarely so slow. This leads to segregation of solutes in the casting. Solidification under two extreme cases has been explained in detail. If there is no diffusion in solid but perfect mixing within the liquid there is a large difference in the compositions of the solid that forms during the onset of solidification and the one that forms towards the end of solidification. This is often classified as normal segregation. If there is no diffusion in solid and the within the liquid is only due to diffusion there could be several variants of structure that could develop in the alloy. The shape of the solid liquid interface depends on the thermal gradient that develops within the liquid at the interface. If it is higher than a critical value it is likely to be planar. This gives rise to columnar grains. If it is lower the interface no longer remains planar. There could a region within the liquid having a temperature less than its liquidus. It is known as constitutional supercooling. This leads to the formation of dendrites. The core of dendrites or columnar grains is relatively purer than the periphery. If the gradient is initially a little higher than the critical value but gradually drops to favor constitutional super-cooling the structure tends to be cellular. These have been explained assuming the alloy to be a terminal solid solution of a binary eutectic system. The last liquid that forms in the two cases is eutectic. The problem associated with segregation has been highlighted. Methods of avoiding the same have been suggested.

**Exercise:**

1. Estimate the temperature gradient that is to be maintained within solid aluminum so that the planar solidification front moves into liquid aluminum maintained at its melting point at a velocity of 0.001m/s. Given thermal conductivity of aluminum = 225 W/mK, latent heat of fusion = 398 KJ/kg and density = 2700kg/m³.

2. What is partition coefficient? Derive Scheil equation for solidification of binary alloys. State the assumptions made during its derivation. What is the composition of the last solid that forms during solidification of a terminal solid solution of a binary eutectic system?
3. Use the equations derived in the previous question to plot how the compositions at the solid liquid interface keep changing as it moves while an Ag 5% Cu alloy is directionally solidified. Ag-Cu binary phase diagram has a eutectic reaction isotherm at 779°C where an alloy containing 28.1%Cu solidifies as a mixture of $\alpha$ having 8.8%Cu and $\beta$ having 92%Cu. The melting point of Ag is 960°C. The solidus and liquidus lines may be assumed to be straight lines. What is the amount of eutectic in the final structure?

4. What is constitutional super-cooling? When does this take place?

5. Derive an expression for solute concentration just ahead of a planar solidification front moving a constant velocity in a binary isomorphous alloy in absence of any convection current in liquid and diffusion in solid.

**Answer:**

1. Heat balance per unit area across a planar solidification front is given by $K_S T''_L = K_L T''_L + L_v V$ where $K$ is thermal conductivity. $T''$ denotes temperature gradient. Suffix S & L represent solid & liquid respectively. $L_v$ is latent heat of fusion / unit volume and $V$ is velocity of the planar front.

Since the temperature of liquid aluminum is constant $T''_L = 0$ and thus $V = \frac{K_S T''_L}{L_v} \therefore T''_L = \frac{398 \times 1000 \times 2700}{225} \times 0.001 = 4776 \text{ K/m}$

2. During solidification of an alloy solute gets partitioned between the solid and liquid. Partition coefficient ($k$) defines the extent to which it gets segregated between solid and liquid. It is given by $k = \frac{X_S}{X_L}$ where $X_s$ & $X_l$ denote composition of solid and liquid when both coexist. Derivation of Scheil equations are based on the following assumptions: (i) $k$ remains constant (ii) There is no diffusion within solid (iii) there is perfect mixing within liquid (there is no concentration gradient within liquid). Let us apply this to solidification of a terminal solid solution of a binary eutectic system given below. The figure on the left shows the position of solid liquid interface at a temperature $T_1$ when fraction of solid is $f_s$. As the interface moves by an infinitesimal distance corresponding to an increment of volume fraction solid by $df_s$ an amount of solute given by the shaded area within the liquid moves over to solid. Amount of solute that is added to solid is also shown by a shaded area within the solid.
Apply conservation of solute. Equate the filled in area: 

\( (X_L - X_S) \, df_s = (1 - f_S) \, dX_L \)

Note that \( X_S = kX_L \). The final expression obtained by integration

\[
\int \frac{df_s}{1-f_S} = \int \frac{dX_L}{(1-k)X_L} \\
\Rightarrow \quad -(1-k) \ln(1-f_S) = \ln(X_L) + C.
\]

Substitute initial condition: When \( f_S = 0 \); \( X_L = X_0 \) to evaluate the constant \( C \). This is given by \( C = -\ln(X_0) \). Thus \( X_L = X_0(1 - f_S)^{(1-k)} \) and \( X_S = kX_0(1 - f_S)^{(1-k)} \). These two give the amount of solid and liquid like lever rule in case of equilibrium solidification. These are known as Scheil equation.

Note that when \( X \_L \) approaches eutectic composition \( (X_E) \) still there will be some liquid left. This is given by:

\( f_L = \left( \frac{X_E}{X_L} \right)^{(1-k)} \). The last solid that forms has the same composition as that of the eutectic.

Note that the entries in first 3 columns give % solute in both solid and liquid at melting point and eutectic temperature. Partition coefficient \( k \) is estimated from these entries. The next 3 columns give fraction solid and solute concentrations in solid and liquid. \( f_L = 1 - f_S \).
### Directional solidification: no diffusion in solid & perfect mixing in liquid (stirring)

<table>
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The first row within columns 4-7 represents the initial condition when the alloy is totally liquid. The magnitude of \(X_L\) in this row is its initial composition. \(X_S\) is estimated by multiplying it with partition coefficient \(k\). The rest of the cells are evaluated using the expressions derived in the previous problem. Composition of the last liquid to solidify is the eutectic. % eutectic in this case is 6.9%
4. During solidification of an alloy solute gets partitioned between liquid and solid. As it cools the composition of liquid and solid keeps changing. While the composition of solid can change only by diffusion that of liquid can change due to both diffusion and convection current (stirring). The latter is much faster. If there is no convection or stirring concentration of solute builds up in the boundary layer. Its melting point becomes significantly lower than that of the liquid away from the interface. If the temperature gradient beyond the solid liquid interface is less than a critical value constitutional super cooling occurs. This promotes solidification. If the gradient is more than the critical value the solid liquid interface remains planar.

5. The following sketch shows a part of the phase diagram indicating the temperature range over which solidification takes place in an alloy having a given composition \((X_0)\). Here it takes place between \(T_1\) and \(T_3\). \(T_2\) is an intermediate temperature. Composition of solid & liquid at the interface within this range is given by the solidus and the liquidus. If partition coefficient is \(k\) composition of the first solid to form is \(kX_0\). Subsequent solid would have higher solute content. The composition profile as a function of the distance from the mold face is also shown in the next sketch. As the planar front moves the liquid too at the interface will become richer in solute. Therefore mass transfer within the liquid due to diffusion will keep increasing. This would continue until the temperature reaches \(T_3\). At this stage the composition of the liquid at the interface would be \(X_0/k\), whereas that of the solid should be \(X_0\). Hereafter the composition of the liquid and solid would not change even if the front moves. Velocity \((v)\) of the front would be determined by the rate at which solute would diffuse within the liquid. Since the concentration of solute would not change hereafter the velocity of the front should remain constant. This stage, called steady state would continue until the width of the remaining liquid becomes too small to maintain its steady state composition. In such a situation the final transient stage begins. The concentration starts building up. In case the alloy is a terminal solid solution of a eutectic system the last liquid to solidify would be eutectic whereas in case of an isomorphous system it would be pure B. During steady state the growth of solid layer needs to dispose of an additional amount of solute given by \(v(X_L - X_0)\). This has to diffuse through the stagnant liquid. The rate at which the solute would diffuse is given by \(-D \frac{dX_L}{dx}\) where \(D\) is diffusivity and \(x\) is the distance from the solidification front. The concentration of solute ahead of the interface could therefore be evaluated by equating these two.

\[-D \frac{dX_L}{dx} = v(X_L - X_0) \] or \[\int \frac{dX_L}{(X_L - X_0)} = -\int \frac{v}{D} \, dx + \text{constant}\]

Constant of integration is determined from initial condition that at \(x = 0\), \(X_L = X_0/k\). Thus we get \(X_L = X_0 \left( 1 + \frac{1-k}{k} \exp \left( -\frac{v}{D} x \right) \right)\).
The diagram illustrates the phase transitions in a system with stages labeled as (a) Initial stage, (b) Steady state, and (c) Final stage. The stages are characterized by specific temperature and concentration changes, denoted by $T_1$, $T_2$, and $T_3$, and concentration levels $X_0$, $X_0/k$, $X_l$, and $X_{0/k}$. The diagram shows the evolution of the system's state with respect to temperature and concentration.