Lecture 18-22:

Solidification of binary alloys: Solidification of binary alloys: limits of solubility, isomorphous system, lever rule, constitutional super cooling, effect of non equilibrium cooling, eutectic, peritectic, eutectoid & peritectoid system, complex phase diagram, ternary diagram, composition triangle, ternary eutectic, vertical & horizontal sections, structure of cast metal, segregation & porosity, iron-carbon diagram, steel & cast iron

Questions:

1. Nickel, Aluminium & Copper have face cantered cubic structure yet Ni is soluble in copper whereas Al has only a limited solubility. Explain why it is so?

2. Two metals A (melting point 800C) and B (melting point 600C) form a binary isomorphous system. An alloy having 35% B has 75% solid and rest liquid whereas an alloy having 55%B has 25% solid at 700C. Estimate the composition of solidus and liquidus at the above temperature.

3. Apply phase rule to the two phase field of a binary isomorphous diagram. What conclusion can be drawn?

4. A binary alloy having 28 wt % Cu & balance Ag solidifies at 779$^o$C. The soild consists of two pahses $\alpha$ & $\beta$. Phase $\alpha$ has 9% Cu whereas phase $\beta$ has 8% Ag at 779$^o$C. At room temperature these are pure Ag & Cu respectively. Sketch the phase diagram. Label all fields & lines. Melting points of Cu & Ag are 1083$^o$ & 960$^o$C respectively. Estimate the amount of $\alpha$ & $\beta$ in the above alloy at 779$^o$C & at room temperature.

5. A molten Ag-Cu (20%) alloy is allowed to cool slowly till room temperature. Refer to the diagram in problem 1 and plot its cooling curve. Estimate % $\alpha$ just after it has solidified at 779$^o$C & room temperature. Sketch its microstructure and find % Eutectic .

6. A diffusion couple consisting of Ag & Cu was kept at just below its euectic temperature. Show with the help of a schematic diagram the concentration profile along its length at different lengths of hold time. Assume that the couple is queched to suppress any transformation below its eutectic temperature.

7. Two alloys belonging to a binary system have the following microstructures. One having 25% B consists of 50% $\alpha$ & 50% eutectic and the other having 0.75%B has 50% $\beta$ & 50% eutectic. Microstructrural examination shows that eutectic is made of 50% $\alpha$ & 50% $\beta$. Estimate the composition of $\alpha$, $\beta$ & eutectic.

8. Draw the phase diagram for a binary alloy system having following features. Melting point of the two metals (A & B) are widely different. These are partially soluble in each other. There is one three phase reaction isotherm at a temperature higher than the melting point of B but lower

than that of A. Write down the equation representing the 3 phase reaction. What is it commonly known as?

9. Sketch a binary phase diagram showing 2 peritectic and 1 eutectic reaction isotherm. Assume both metal A & B have nearly same melting point & there are two & terminal two intermediate soild solutions.

10. Draw a binary phase diagram where A undergoes an allotropic transformation (but not B) and there are one eutectic and one eutectoid transformation.

11. Cooling curve of a binary alloy looks exactly similar to that of a pure metal. Is this possible?

12. The left hand side of a binary eutectic phase diagram is given below. The liquidus and solidus can be assumed to be straight lines.  Find out expression for segregation coefficient (ratio of solute concentration is solid to that in liquid) in terms of the parameters given in this figure.
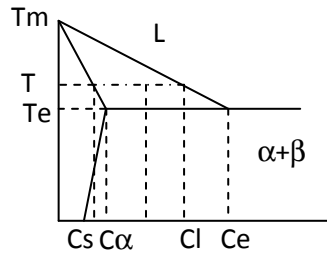


13. An alloy having solute concentration C is held at a temperature T within solid – liquid range and the liquid is filtered out. If this process is repeated by heating & filtering out the liquid will it ultimately give pure A? Is this a practical method of purification?

14. Sketch a phase diagram for a binary peritectic system with termial solid solutions and draw free energy composition diagrams at two temperatures (i) a little above peritectic reaction isotherm (ii) a little below peritectic reaction isotherm.

15. Estimate entropy change during solidification of the following elements and comment on the nature of the interface between solidifying crystal and liquid. The latent heat and melting point are given with brackets. (a) Al [10.67kJ/mole, 660C] (b) Si [46.44kJ/mole, 1414$^{\circ}$C]

16.  Microstructure of a cast Al-4.5%Cu alloy shows  some amount of eutectic when we know for sure that eutectic forms on solification of 33%Cu alloy giving a having 5.5%Cu and $Cu_2Al$. Give reason.

17. A binary alloy has a peritectic reaction isotherm at 500$^{\circ}$C given by $\alpha$ (10%A)+ L (60%B) = $\beta$ (45%B) Estimate % phases present just above & below the peritectic reaction isotherm in an alloy having 50%B under equilibrium cooling. If the alloy were cooled relatively fast what type of structure will you expect on completion of solidification.

18. Why the eutectic structure does not exhibit coring?

19. When would you expect planar solidification front? (a) When temperature gradient in solid $(T'_S)$ and in liquid $(T'_L)$ are both positive and $T'_S > T'_L$ (b) When the liquid is super-cooled $(T'_L < 0)$ and the solid is maintained at constant temperature. Assume temperature gradients in both liquid and solid to be constant. Give reasons.

20. 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.

21. 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?

22. 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 α having 8.8%Cu and β 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?

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

24. 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. Both the species must have same crystal structure, valence & nearly same atomic diameter. Ni & Cu have nearly same lattice parameter as well as valence. However lattice parameter of Al is longer, it also has higher valence. Therefore its solubility in Cu is limited.

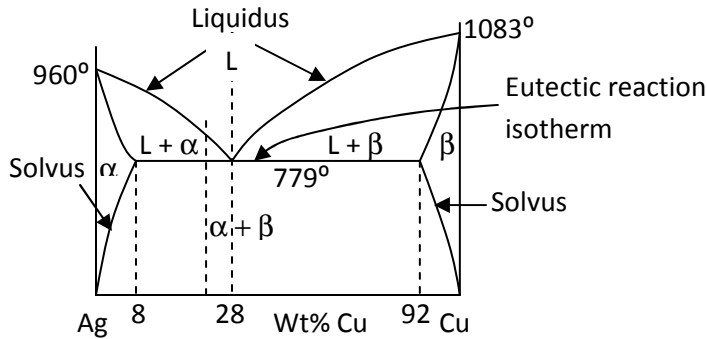2. A schematic binary phase diagram of this system is shown below:
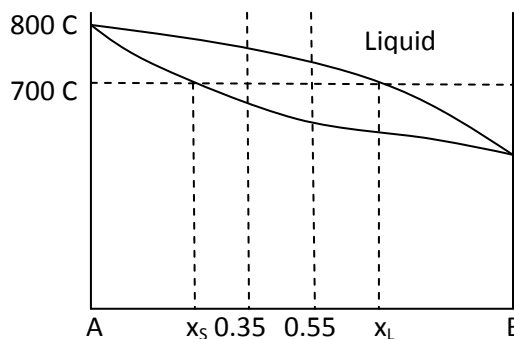


Apply lever rule to alloys with 35% B & 55%B $\frac{x_L - 0.35}{x_L - x_S} = 0.75$ and

$\frac{x_L - 0.55}{x_L - x_S} = 0.25$ Solve to get

$x_L = 0.65 \ \& \ x_S = 0.25$

3. Phase rule at constant pressure states P+F =C+2. In the two phase field P=2, it is a binary system therefore C=2. On substitution in the above expression F=1. It has only one degree of freedom. If temperature is constant compsitions of coexisting liquid & solid are fixed. This is given by the intersection of the tie line at the specified temperature. If you specify composition of solid the composition of coexisting liquid is fixed.

4. The process of solidification at 779°C can be represented as L = $\alpha + \beta$. This involves equlibrium between 3 phases. Such a system is known as eutectic. The phase diagram is as follows:

Liquidus

960°

1083°

Eutectic reaction isotherm

L

L + $\alpha$

L + $\beta$

$\beta$

Solvus $\alpha$

779°

Solvus

$\alpha + \beta$

Ag  8  28  Wt% Cu  92  Cu

28% Cu is a eutectic alloy. % phases are given by lever rule.

$\%\alpha = \frac{92-28}{92-8} \times 100 = 76\%$ at 779°C. At room temperature

$\%\alpha = \frac{100-28}{100-0} \times 100 = 72\%$

5. The cooling curve is as follows & refer to the diagram above.

Temp

L

Liquidus

Eutectic

$\alpha + L$

$\alpha$ + Eutectic

time
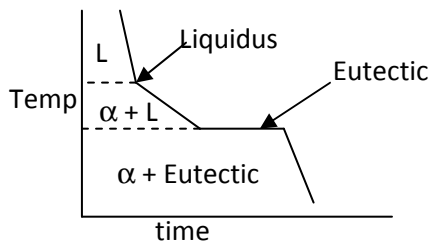
At 779°C: $\%\alpha = \frac{92-20}{92-8} \times 100 = 86\%$ Note that $\alpha$ is present as primary phase & within eutectic. At room temperature

$\%Eutectic = \frac{20-0}{28-0} \times 100 = 71\%$

The microstructure will consist of proeutectic $\alpha$ & eutectic.

6. Ag will diffuse into Cu & vice versa. The concentration profile will depend on hold time. These are given for different lengths of time assuming that length of both Ag & Cu are infinite.

Ag

Cu

100

% Ag

At time = 0

0

% Cu

100

0

Ag : $\alpha$

Cu: $\beta$

100

% Ag

At time =∞

0

% Cu

100

0
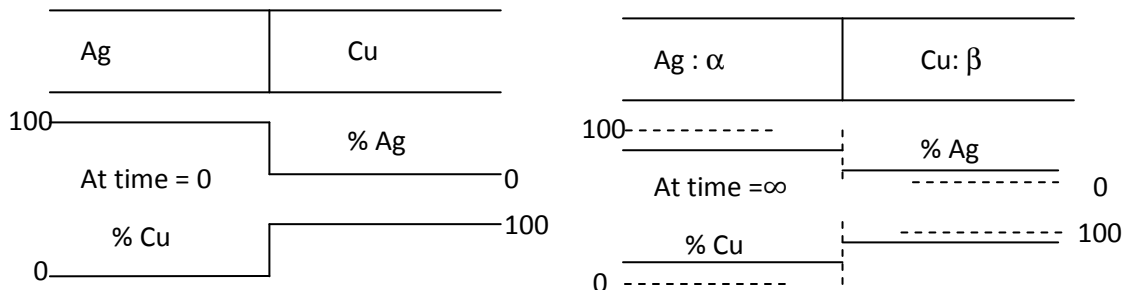
7. Let the eutectic reaction be represented as L (X1) = $\alpha$ (X2) + $\beta$ (X3). Composition of the three phases are given with brackets. The eutectic reaction isotherm is shown in the following

diagram. There are 3 unknowns. Therefore we need three equations to find these. These can be formulated as follows.

Alloy 1        Alloy 2



α                                β

X1   0.25    X2    0.75   X3
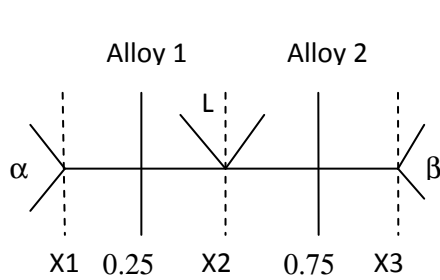
$For\ alloy\ 1: \dfrac{X2 - 0.25}{X2 - X1} = 0.5\ or;\ 2\ X1 + 2\ X2 = 1$

$For\ alloy\ 2: \dfrac{X3 - 0.75}{X3 - X2} = 0.5\ or;\ 2\ X2 + 2\ X3 = 3$

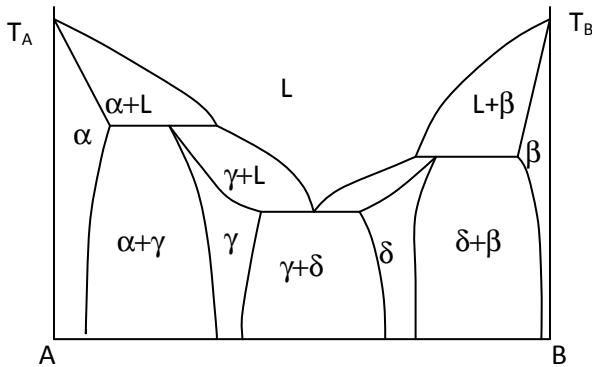$For\ eutectic: \dfrac{X3 - X2}{X3 - X1} = 0.5\ or;\ X1 - 2\ X2 + X3 = 0$

These equations can be solved by eliminating one after the other. Answer: X1 =0, X3 = 1 & X2= 0.5

8. The diagram is shown below. The 3 phase reaction in case must be L + α = β. This is called prectic reaction.
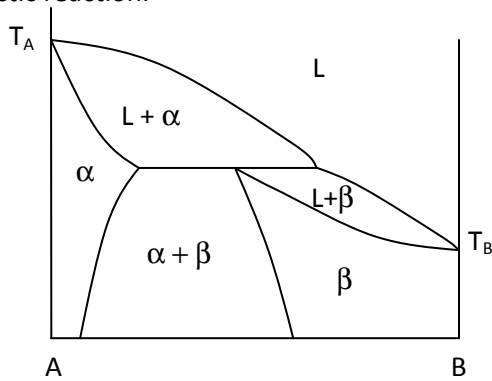


Note the melting points of the two metals are widely different. The peritectic isotherm lies between these two.
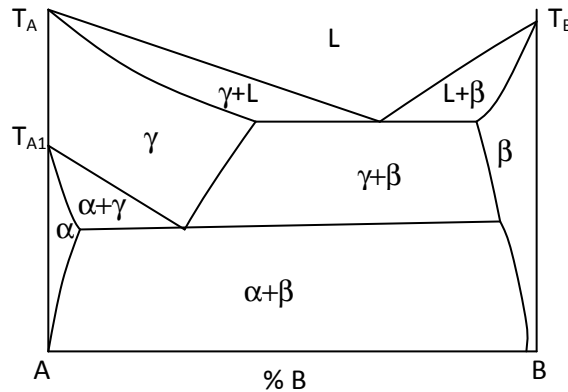
9.



Peritectic 1: α + L = γ

Peritectic 2: β + L = γ

Eutectic : L = γ + δ

10. The diagram is as follows:



Eutectic: L = γ + β

Eutectoid: γ = α + β

Allotropic transformation at : $T_{A1}$

11. Yes, if it is an eutectic alloy.

12. The equation representing the solidus is given by $\frac{Tm-T}{Tm-Te} = \frac{0-Cs}{0-C\alpha}$ & the line representing liquidus is given by $\frac{Tm-T}{Tm-Te} = \frac{0-Cl}{0-Ce}$ Thus segregation coefficient = $\frac{Cs}{Cl} = \frac{Ca}{Ce} < 1$ Clearly in this case it is a constant independent of temperature.

13. Let us look at an enlarged view of the phase diagram in problem 4. It is seen by holding the alloy at a temperature little above euectic temperature impurities could be partitioned into the liquid. If this is reapaeted composition of solid would tend to move towards purer A. In principle purification is possible. However since at every stage significant amount of liquid is rejected. The ultimate yield will be very small. This process of purification is not practical.
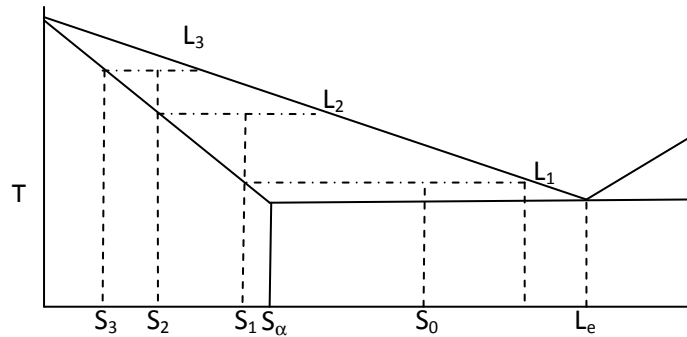
14.
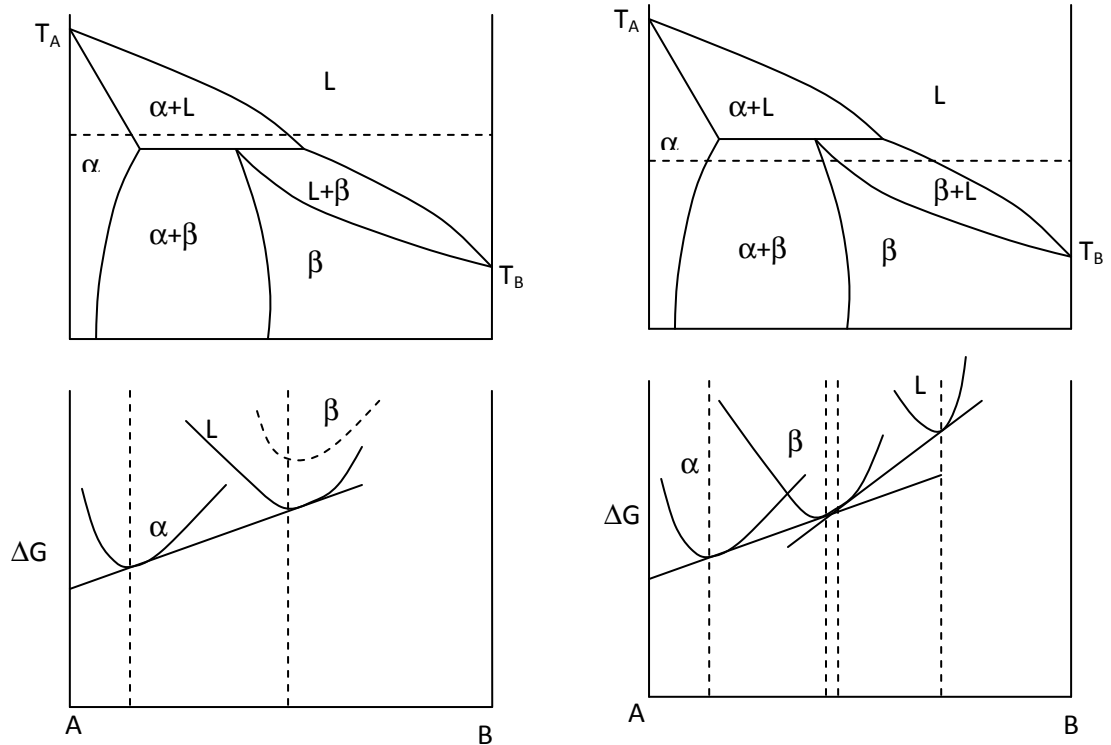


15. $\frac{\Delta S_m}{R} = \frac{\Delta H_m}{RT_m}$ is an indicator of the nature of the solid liquid interface.  Direct substitution of latent heat ($\Delta H_m$) melting point ($T_m$) & universal gas contant (R)  the above indicator for Al = 1.35 & for Si = 3.26. Therefore S/L interface wis planar for Al & faceted for Si.

16. Normal cooling is rather fast. The solid that forms during solidification changes with time. Diffusion in solid being slow the previously formed solid does not get enough time to change its composition. The average solid composition therefore follows a different path as shown in the following diagram. The eutectic reaction is given by  L (33%B) = $\alpha$ (5.5%B) +Cu$_2$Al ($\theta$).
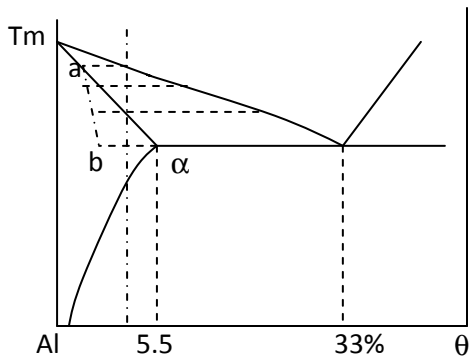


Under equilibrium cooling the alloy on solidification should consist of phase $\alpha$ only. There should be no eutectic. If cooling rate is fast composition of solid does not follow line a$\alpha$. Instead it follows line ab. This is because fast cooling does not give enough time for the solid to change its composition. Even at eutectic temperature some liquid is left behind. This is why we get some eutectic in the cast structure.

17. The phase diagram is as follows:

% α at just above peritectic temp = (60-50)/(60-10) = 0.20
balance 0.8 is liquid.

Just below peritectic temp: % β = (60-50)/(60-45)= 0.66
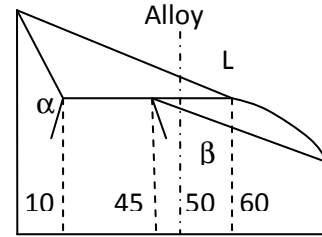


As the temperature drops below peritectic reaction isotherm there is a marked change in % liquid. It decreases from 80% to 33%. Phase β forms as a result of peritectic reaction at lquid / α interface. In the process α gets surrounded by a layer of β. B atoms from liquid must diffuse through β layer to α interface so that peritectic reaction could occur.Therefore due to non equilibrium cooling on solidification the alloy may have some amount of α retained. Final structure may consist of cored α dendrites surrounded by cored β. What is the composition of the last solid? (Answer: pure B)

18. Coring means composition gradient within a phase as a result of relatively fast cooling.  Eutectic transformation takes palce at a fixed temperature. It is a mixture of two phases of fixed compositions.  As per phase rule the degree of freedom is zero. This is why question of change in composition does not arise.

19. The temperature profile across the solid liquid interface in case (a) is given below. The arrow indicates the direction of heat flow. In case any a bulge develops on the solid liquid interface the direction of heat flow is changed. Bulge provides additional area through which heat could flow. Solidification is also accompanied by release of latent heat. Therefore temperature of this zone would rise and the bulge would shrink and disappear.
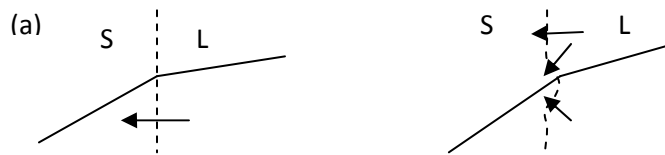


However in case (b) the situation is opposite. There being no temperature gradient in solid, heat cannot flow through it. It could only flow into super cooled liquid. In case a bulge forms the latent heat released can easily flow into super cooled liquid. Bulge provides additional area through which heat could flow. Unlike the previous situation it would grow. Such instability would exist all along the curved face. This would therefore promote dendritic solidification.
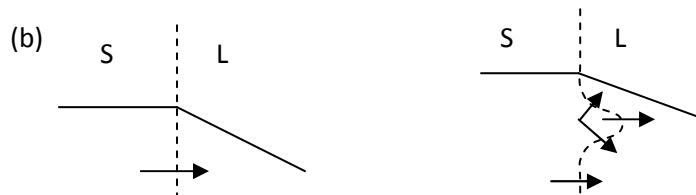
20. Heat balance per unit area across a planar solidification front is given by $K_S T_S' = K_L T_L' + L_v V$ where K is thermal conductivity. T' denotes temperature gradient. Suffix S & L represent solid & liquid respectively. $L_v$ is latent heat of fusion / unit volume and V is velocity of the planar front. Since the temperature of liquid aluminum is constant $T_L' = 0$ and thus $V = \frac{K_S T_S'}{L_v}$ $\therefore T_S' = \frac{398 \times 1000 \times 2700}{225} \times 0.001 = 4776 \ K/m$

21. 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.
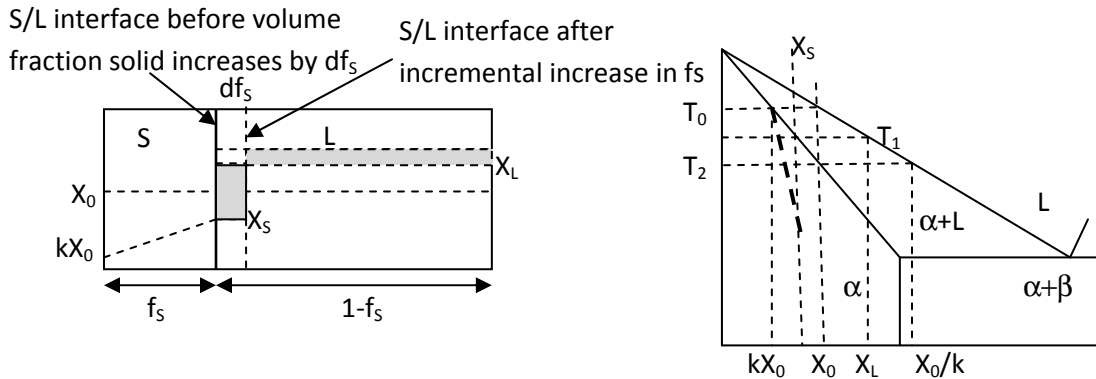


Apply conservation of solute. Equate the filled in area: $(X_L - X_S)df_S = (1 - f_S)dX_L$

Note that $X_S = kX_L$. The final expression in obtained by integration $\int \frac{df_S}{1-f_S} = \int \frac{dX_L}{(1-k)X_L}$

$\therefore -(1-k)ln(1-f_S) = ln(X_L) + C$. 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: $f_L = \left(\frac{X_E}{X_0}\right)^{(1-k)}$. The last solid that forms has the same composition as that of the eutectic.

22. The phase diagram is shown in the following sketch. The results are given in an Excel sheet.
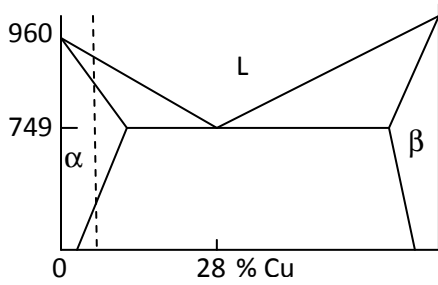


Note that the entries in first 3 columns give % solute in both solid and liquid at melting point and eutectic temperature. Partition coefficient k is estimated from these entries. The next 3 columns give fraction solid and solute concentrations in solid and liquid. $f_L = 1 - f_S$

| | | | | Directional solidification: no diffusion in solid & perfect mixing in liquid (stirring) | | | | |
|---|---|---|---|---|---|---|---|---|
| k | 0.314286 | | | $f_s$ | $X_S$ | $X_L$ | $f_L$ | |
| $X_S$ | T | $X_L$ | 0 | 0.014143 | | 0.045 | 1 | |
| 0 | 960 | 0 | 0.05 | 0.014649 | 0.046611 | | 0.95 | |
| 0.088 | 779 | 0.28 | 0.1 | 0.015202 | 0.048371 | | 0.9 | |
| | | | 0.15 | 0.01581 | 0.050305 | | 0.85 | |
| | | | 0.2 | 0.016481 | 0.05244 | | 0.8 | |
| | | | 0.25 | 0.017227 | 0.054813 | | 0.75 | |
| | | | 0.3 | 0.018062 | 0.057469 | | 0.7 | |
| | | | 0.35 | 0.019003 | 0.060465 | | 0.65 | |
| | | | 0.4 | 0.020075 | 0.063876 | | 0.6 | |
| | | | 0.45 | 0.02131 | 0.067803 | | 0.55 | |
| | | | 0.5 | 0.022749 | 0.072382 | | 0.5 | |
| | | | 0.55 | 0.024453 | 0.077805 | | 0.45 | |
| | | | 0.6 | 0.02651 | 0.08435 | | 0.4 | |
| | | | 0.65 | 0.029052 | 0.092438 | | 0.35 | |
| | | | 0.7 | 0.032291 | 0.102744 | | 0.3 | |
| | | | 0.75 | 0.036591 | 0.116427 | | 0.25 | |
| | | | 0.8 | 0.042641 | 0.135677 | | 0.2 | |
| | | | 0.85 | 0.05194 | 0.165264 | | 0.15 | |
| | | | 0.9 | 0.068589 | 0.218236 | | 0.1 | |
| | | | 0.931 | 0.088462 | 0.281469 | | 0.069 | |

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%

23. 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.

24. 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.

$$-D\frac{dX_L}{dx} = v(X_L - X_0) \ or; \int \frac{dX_L}{(X_L - X_0)} = -\int \frac{v}{D} dx + constant$$

Constant of integration is determined from initial condition that at $x = 0$, $X_L = X_0/k$. Thus we

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



(a) Initial stage

(b) Steady state

(c) Final stage