Module 18

Solidification & Binary Phase Diagrams I

Lecture 18

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Introduction

A pure metal is known for its ductility. It can be rolled down to thin foils or drawn into wires. Aluminum foils are used for packaging, copper & aluminum wires are used as electrical conductors, silver foils are used to decorate food products, gold foils find application in electroscope. These are applications where strength is not a major consideration. Wherever strength is a major consideration pure metals have little use. Strength of metals can be significantly improved by alloying it with other metals or nonmetallic materials. This is achieved by a process called mixing. In the last three modules we learnt about a mixing process that takes place in solid state called diffusion. However it is an extremely slow process. The rate of diffusion increases with temperature. We expect this to be much faster in a liquid state which is stable at a higher temperature. In a liquid besides diffusion the process of mixing can be further accelerated by agitation and / or convective flow. Therefore melting is the most common method of mixing different elements in a metal. Once each of the alloy additions dissolve in the liquid state it is allowed to solidify. In the next five modules we shall learn about the process of solidification of alloys. The topics to be covered include solidification of binary alloys, limits of solubility, isomorphous system, ideal & real solid solution, lever rule, effect of non equilibrium cooling, constitutional super cooling, three phase equilibrium such as eutectic, peritectic, eutectoid & peritectoid system, complex phase diagram, structure of cast metal, segregation & porosity, dendrite / columnar structure. Let us begin this module with the solidification of a binary alloy where the two components are soluble in each other in all proportions in both liquid and solid state. This is often referred to as an isomorphous alloy.

Binary isomorphous system:

Let the two metals in a binary system be A & B. They are soluble in each other in all proportion in both solid and liquid states. Both A & B have definite melting points. Since the two are soluble in all proportion in solid state they must have similar crystal structures, nearly the same atomic diameters and identical valence. Let us assume that the melting point of A is higher than that of B. If you monitor and later plot the temperature of molten pure metal as it cools you get cooling curves similar to that in fig 1 when the cooling rate is slow. In this case the number of component (C) is equal to one. As long as there is only one phase (P) the degree of freedom (F) as predicted by Gibb’s phase rule (P+F = C+1) is one. It means liquid or solid state may exist over a range of temperatures. However as solidification sets in both liquid and solid must coexist. In such a situation F = 0. This means two phases (liquid & solid) in a single component system at one atmosphere pressure can coexist only at a fixed temperature. This is why the temperature in fig 1 remains constant until the entire liquid gets transformed into solid at its freezing (or melting) point.
What should the cooling curve look like if the molten alloy were made of two components A & B? Since the two components are miscible in all proportions the liquid must be homogeneous. Its composition is the same at every location. Apply Gibb’s phase rule. Note that C = 2, P = 1, therefore F = 2. This denotes the number of independent variables. These are the temperature and the composition. It means at a fixed temperature the alloy can have a range of composition or an alloy can exist over a range of temperature. During solidification it must pass through a stage when both liquid and solid could coexist. In such a situation P = 1. Therefore F = 1. It means that two phases can coexist over a range of temperature. The cooling curve of such an alloy should be similar to the one given in fig 2.

An isomorphous alloy does not have a definite melting or freezing point. Such an alloy is characterized by a temperature where solidification begins and a temperature where it ends. Between the two temperatures both liquid and solid can coexist. If you find these two temperatures for a set of alloys having different compositions and plot these as a function of composition you would get a pair of lines as shown in fig 3. These are known as the liquidus and the liquidus solidus. Such a graph is known as the phase diagram of a binary isomorphous alloy. In the temperature region between the liquidus & the solidus the alloy is partly liquid and partly solid.

**Fig 1:** Shows a typical cooling curve of a pure metal. Note that liquid is stable above its melting point where as below its melting point it is solid. In this case P=1. Therefore F = 1. This is why both L & S exist over a range of temperature. Whereas both liquid (L) & solid (S) can coexist only at the melting (or freezing) point. Under an equilibrium rate of cooling both the melting & the freezing points are the same.

**Fig 2:** Shows a typical cooling curve of a binary isomorphous alloy. Note that liquid is stable above a temperature where solidification starts and solid is stable below a temperature where solidification ends. Whereas both liquid (L) & solid (S) can coexist over a range of temperatures. Unlike pure metal an alloy solidifies over a range of temperature.

**Fig 3:** Illustrates how to get the temperatures at which solidification begin and end from a normal cooling curve of an alloy. These are $T_S$ & $T_E$ respectively. The line denoting $T_S$ as a function of composition in the sketch on the left is called liquidus & the line denoting $T_E$ is solidus.
Let us analyze the process of solidification of an alloy of a given composition X as illustrated in slide 1. Draw a vertical line at \( N_B = X \) as shown. Solidification begins at a temperature where it intersects the liquidus. Draw a horizontal line through this point. Extend the same to intersect the solidus line. This gives the composition of the first solid to form in this case it is \( X_1 \). As the temperature drops the amount of solid keeps increasing. During the process the composition of the solid that forms keeps changing. At the same time composition of the existing solid should also change. The compositions of the liquid and the solid that can coexist at a particular temperature are given by the points of intersections of the horizontal line called tie line at this temperature with the liquidus & the solidus as shown in slide 1. How can the composition of the solid that has already formed change during solidification? The initial solid is rich in A whereas the new solid is rich in B. The composition of the old solid can change only if B atoms could diffuse through the solid. Diffusion in solid is a relatively slow process in comparison to that in the liquid. In addition convection current also helps the composition of the liquid to change as expected by the diagram. However for the composition of the solid to change sufficient time must be allowed during cooling. Therefore the alloy must be cooled very slowly so that at every stage there is an equilibrium between the solid and the liquid. Such a cooling rate is called equilibrium cooling rate. This is why often phase diagrams are called equilibrium diagrams.

**Slide 1:** The sketch shows a typical phase diagram of a binary isomorphous system. The composition can be denoted either as weight fraction (or %) or atom fraction. Let \( N_B \) denote the atom fraction of B in the alloy and \( X_i \) be the corresponding weight fraction. Alpha (\( \alpha \)) represents solid solution of B in A (or A in B). The line called liquidus gives the temperature at which solidification begins. It also gives the composition of the liquid. The solidus denotes the temperature & composition of solid during solidification.

**Slide 2:** Shows an equilibrium diagram of a binary isomorphous system made of two metals A & B. It gives the temperature range over which solidification takes place. Consider an alloy having a composition X. Let this denote either atom fraction or weight fraction B (\( N_B \)). Draw a vertical line at \( N_B = X \). It intersects the liquidus & solidus. These are the temperatures at which the solidification begins or ends. Draw a tie line at a temperature T. It is the dotted horizontal line. It intersects solidus & liquidus at \( X_1 \) & \( X_2 \).
Look at the diagram in slide 2. Note that the horizontal line tie line at a temperature $T$ intersects the solidus at $X_1$ which denotes the composition of the solid. The point $X_c$ denotes the composition of the liquid that coexists along with the solid. Let ‘$a$’ denote the weight fraction of the solid $\alpha$ and ‘$b$’ denote weight fraction of the liquid. The sum $a + b = 1$. The total amount of B in the alloy is distributed between $\alpha$ & liquid (L). The amount of B in $\alpha = aX_1$ and the amount of B in $L = bX_2$. The sum of the two gives gross composition of the alloy. Thus we have a second equation $aX_1 + bX_2 = X$. The two equations can be solved to get the weight fractions $\alpha$ & L. These are given by:

$$\text{Weight fraction of the solid } a = \frac{X_2-X}{X_2-X_1} \text{ and weight fraction of the liquid } b = \frac{X-X_1}{X_2-X_1} \; (1)$$

This set of equations is also known as the lever rule. The reason is explained in slide 3. It has a diagram that describes whether an alloy at a given temperature would exist in the form of a single phase (liquid or solid) or as a mixture of the two. It also helps estimating the amount of the liquid and the solid at a temperature where the phases could coexist. It is also useful in interpreting the evolution of the microstructure of the alloy during its solidification from the liquid state.

**Slide 3**: Illustrates the similarity between the equation set (1) and the lever rule. The point $q$ denotes the composition of the alloy ($q = X$). The point $p$ & $r$ are the compositions of the solid and the liquid that can coexist at this temperature. The mass balance between the two can be simulated as the moment balance in the case of a lever as shown in the sketch on the right. Therefore the ratio $(a/b)$ is given by $\frac{a}{b} = \frac{qr}{pq} = \frac{X_2-X}{X-X_1} \; ; \; a = \frac{X_2-X}{X_2-X_1}$

**Evolution of microstructure:**

This is illustrated in slide 4. The solidification of an alloy belonging to this system begins when the temperature of the molten alloy reaches its liquidus temperature. The solid that forms has a definite composition. It is given by the point of intersection of the tie line at the liquidus temperature with the solidus. The weight fraction of solid is given by the lever rule already derived as above. Obviously at the liquidus the weight fraction of solid is negligible. As the temperature goes down the amount of solid keeps increasing.

**Slide 4**: Illustrates how the solid forms from the liquid in an isomorphous alloy as it is cooled. Its composition is $X$. This is shown by the vertical dotted line at $X$. The solidification starts at the liquidus and it ends at the solidus. These are given by the points at which the vertical line at $X$ intersects the liquidus and the solidus. At any temperature between the two the system is partly solid and partly liquid. The composition of the solid is given by the point $p$ ($X_1$) on the solidus and that of the liquid is given by $r$ ($X_2$). The sketches on the right give the typical structures in the three different temperature regimes.
Solidification begins when the temperature of the alloy drops below its liquidus with the formation of a few tiny crystals. The ratio of the solid and the liquid keeps changing with decreasing temperature. This happens by the formation of new crystals and the growth of pre-existing ones. The compositions of the two coexisting phases (L & α) keep changing during this process. The new crystal that forms no doubt has a new composition but the composition of the crystals formed at higher temperatures must also change. This takes place by diffusion of B from the solid liquid interface into the pre-existing crystals. This is a relatively slow process. Let us assume that the alloy cools slowly so that there is enough time for the atoms to diffuse into the solid so that during solidification the composition of solid keeps changing. The progress of solidification is depicted by a set of sketches on the right in slide 4. Above the liquidus it is completely liquid. At any temperature between the liquidus and the solidus it is made of both liquid and solid. The ratio of the weight fraction solid to the weight fraction liquid is equal to $q_{r/pq} = \left(\frac{x_2-x}{x-x_1}\right)$. As the crystals grow in size some may meet along a boundary. This may be viewed as impingement. Consequently the growth in that direction stops. However the growth in other directions continues. Finally when the temperature reaches the solidus it is entirely made of a large number of crystals or grains of solid separated by distinct boundaries. Although every grain has identical crystal structure but the orientations are different. Note that the composition of the alloy at every location is the same as long as it is completely liquid (above liquidus) or solid (below solidus). However during solidification when it is partly liquid and partly solid, the compositions of the solid and the liquid are different. These are functions of temperature. The initial solid is rich in A. However as it cools % A goes down and % B goes up. The final composition of the solid is the same as the initial composition of the liquid. This is possible when the cooling rate is extremely slow. If it is not slow enough to allow the composition of the solid to change, what would happen then will be taken up in a later lecture.

**Thermodynamics of isomorphous alloy:**

A binary phase diagram of an isomorphous system depicts the relative stability of two phases in a temperature composition space. Gibb’s free energy gives a measure of phase stability. A phase having lower free energy is more stable at a given temperature. Two phases could coexist if the partial molar free energies (also known as chemical potential) of a solute in the two phases are equal. Let us use this concept to determine the phase diagram of a binary system made of two metals A & B. The two are
soluble in each other in both liquid and solid state in all proportion. The Gibbs free energy of a solution (or mixing) is a function of its composition and activities of the two constituents. In this case the two phases are L and α. The free energies of the two phases are given by the following equations.

\[ \Delta G^L = RT(N_A^L \ln a_A^L + N_B^L \ln a_B^L) \] (2)

\[ \Delta G^\alpha = RT(N_A^\alpha \ln a_A^\alpha + N_B^\alpha \ln a_B^\alpha) \] (3)

R is the universal gas constant and T is the temperature in °K. The superscripts denote phases L and α. The subscripts denote the constituents A and B. N denotes atom fraction and ‘α’ denotes activity. Let us assume that the liquid and the solid are ideal solutions where the activity of a constituent is equal to its atom fraction. This means that \( a_A^L = N_A^L; \ a_B^L = N_B^L; \ a_A^\alpha = N_A^\alpha; \ a_B^\alpha = N_B^\alpha \).

**Slide 5:** Shows the free energy composition diagram of a binary isomorphous system at a temperature higher than the melting points of both A & B. At this temperature the liquid is more stable than solid (α). Therefore the free energy of liquid is lower than that of the solid at all compositions. At a temperature lower than the melting point of B the solid is more stable. The lower curve would represent the free energy of the solid.

The slide 6 shows the trend exhibited by the free energy composition diagram at an intermediate temperature the alloy consists of solid only up to a certain amount of \( N_B \) and beyond a certain limit it is totally liquid. This is described by the intercepts of the common tangent to the free energy composition plots of the solid (α) and the liquid (L).

The intercepts of the tangent to the G versus \( N_B \) plot (in slide 6) denote chemical potentials (partial molar free energy). For example \( \mu_A^G = \) chemical potential of A in α. It is given by the intercept with the G axis at \( N_B = 0 \) and \( \mu_A^L = \) chemical potential of A in L. It is given by the intercept with G axis at \( N_B = 0 \). Since the slope of the G versus \( N_B \) plot of the solid at \( X_2 \) and that of the G versus \( N_B \) plot of the liquid at \( X_2 \) is given by a common straight line therefore \( \mu_A^G = \mu_A^L \). Similarly: \( \mu_B^G = \mu_B^L \). These are the conditions for

**Slide 7:** Shows how to find the compositions of solid (\( X_1 \)) and liquid (\( X_2 \)) that can coexist at a temperature T shown by the dotted line. For the ideal solid solution \( \alpha; \mu_A^G = \)
the thermodynamic equilibrium. Slide 7 shows how this concept can be used to find the compositions of the solid and the liquid that can coexist at this temperature.

The chemical potential of A in α can be equated to that of A in L provided the same standard state is used to find the same. The free energy of a species in its standard state is taken to be zero. Let us consider pure A in solid state at the temperature T to be its standard state. In order to find the chemical potential of A in the liquid, an additional energy is needed to convert pure solid A to pure liquid A at T. The second equation in slide 7 gives this. Therefore the chemical potentials of A in solid solution (α) and in liquid (L) are given by:

$$\mu_A^\alpha = RT \ln N_A^\alpha$$  \hspace{1cm} (4)

$$\mu_A^L = \frac{\Delta H_{mA}}{T_{mA}} (T_{mA} - T) + RT \ln N_A^L$$  \hspace{1cm} (5)

Since $\mu_A^\alpha = \mu_A^L$ ; $\therefore \ln \left( \frac{N_A^\alpha}{N_A^L} \right) = \ln \left( \frac{1 - N_B^\alpha}{1 - N_B^L} \right) = \frac{\Delta H_{mA}}{RT_{mA}} (T_{mA} - T) = F(A)$  \hspace{1cm} (6)

Similarly: $\mu_B^\alpha = \mu_B^L$ ; $\therefore \ln \left( \frac{N_B^\alpha}{N_B^L} \right) = \frac{\Delta H_{mB}}{RT_{mB}} (T_{mB} - T) = F(B)$  \hspace{1cm} (7)

The melting points and the corresponding enthalpies of melting are known. There are two equations and only two unknowns. Therefore the compositions of the two phases can be determined. The spreadsheet in slide 8 gives the data needed and the solutions. These have been used to construct the phase diagram in slide 9.
The above calculation has been done on the basis of the assumption that the two constituents of the binary alloy (A & B) form ideal solutions in both liquid and solid states. An ideal solution obeys Roult’s law. It states that the effective concentration of a species (commonly known as the activity) or a constituent in a solution is equal to its mole fraction ($a_A = N_A^e$; $a_B = N_B^e$). However, such systems are rare. Let us see what happens if there is a deviation from ideality.

**Non ideal solution:**

There are two possibilities. (i) Positive deviation: ($a_A^e > N_A^e$) or (ii) Negative deviation: ($a_A^e < N_A^e$). This is explained with the help of a set of plots in fig 4. In the case of positive deviation the activity is more than the atom (mole) fraction. Activity means effective concentration. If the activity of A in a solution is more than its atom fraction it means that atom A is surrounded by more number of A atoms (like atoms) than that corresponding to its concentration. In the case of negative deviation A is surrounded by more number of unlike atoms. The positive deviation means clustering of identical atoms and negative deviation means ordering.

**Fig 4:** It shows three different types of correlation between activity and mole (atom) fraction. In the cases of both positive and negative deviations you may find that as $N_B$ approaches 1 $a_B$ approaches $N_B$. At very low concentration of B, activity is proportional to mole fraction. This trend is true for both positive and negative deviation. The dotted lines show this trend. The trend shown at low
In cases of such deviations we do not expect the predicted phase diagram to match with those obtained experimentally. The deviations can be explained introducing the concept of activity coefficient. If the deviations are not large the predicted phase diagram may be similar. If the differences are large the types of phase diagram may be totally different. Some of these will be taken up in subsequent lectures.

**Summary:**

In this module we looked at the case of unlimited solubility of two metals in both liquid and solid states. An alloy belonging to this system does not have a definite melting point. Rather it solidifies over a range of temperatures. The temperature at which solidification begins is known as liquidus and the temperature at which this ends is known as solidus. The alloy consists of two distinct phases if the temperature lies between the liquidus and the solidus. The diagram where the liquidus and the solidus are plotted as functions of composition is known as phase diagram. This may also be looked at as a phase stability diagram. It gives the melting range of alloys belonging to this system. The principle of thermodynamic equilibrium has been explained. Free energy composition relationships can be used to determine or plot the phase diagram. This has been illustrated with an example for a system that consists of ideal solutions. The concept of deviation from ideality has been introduced in terms of the ways atoms are arranged in a solution.
**Exercise:**

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?

**Answer:**

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

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

3. Phase rule at constant pressure states P+F =C+1. 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 compositions 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 the solid the composition of coexisting liquid and the temperature are fixed.

![Binary Phase Diagram](image-url)