Module 20

Solidification & Binary Phase Diagrams III

Lecture 20

Solidification & Binary Phase Diagrams III
Keywords: Isomorphous system having an alloy that melts like a pure metal, common alloys belonging to isomorphous system, eutectic or peritectic system, determination of binary eutectic phase diagram from thermodynamic data, liquid immiscibility, monotropic, syntetic, eutectoid, peritectoid systems, complex binary phase diagrams having multiple 3 phase equilibrium

Introduction:

In the last two modules we have looked at the solidification behavior of binary alloys. If the temperature of an alloy is monitored during solidification and plotted against time we do get a change in its slope or a discontinuity in the form of a step on such a curve. These are the temperatures at which phase separation occurs in the alloy. However these temperatures are functions of composition. If these are plotted against composition we get a binary phase diagram. We have so far looked at isomorphous system where there is unlimited solubility in both solid and liquid state. Solidification in this case can be visualized as \( L = \alpha \). An alloy belonging to such a system has a characteristic phase diagram. If there is limited solubility in solid state there may be a range of compositions where the alloy on solidification will be made of two solids \( (\alpha + \beta) \). In such a case there will be a temperature at which three phases must coexist during solidification. In a binary alloy the degree of freedom of such equilibrium is zero. This means that the temperature and the compositions of the phases coexisting are invariant. We looked at two distinct examples. One is known as eutectic: \( L = \alpha + \beta \) and the other is called peritectic: \( L + \alpha = \beta \). Both of these have characteristic phase diagrams. We now know of three different types of hypothetical binary phase diagrams. However there are only a limited pairs of metals that have such phase diagrams. Most commercial metallic systems have a much more complex phase diagram. We shall learn about it in this module. Apart from experimental determination it is also possible to calculate such diagrams from available thermodynamic database. We have used this concept to calculate phase diagram of an isomorphous system. We would see how we can determine the phase diagram of a eutectic system. Binary phase diagrams can also have several other invariant reactions. We would learn about these as well. Although phase diagrams represent the state of equilibrium there are several instances where the thermo-physical properties of the liquid and the solids are such that the solidification and the subsequent transformations are very sluggish leading to the formation of meta-stable phases. We shall also learn about the characteristics of such phases and the restriction it imposes on the shape and the curvature of the lines separating a single phase regime from a two phase regime.

Isomorphous system:

Slide 1 gives a schematic phase diagram of a binary isomorphous system. The solidification behavior of alloys belonging to such system was discussed at length in the previous module. Slide 2 shows two other variants of isomorphous system. Here there is an intermediate composition which has a solidification characteristic that is exactly same as that of a pure metal. The intermediate alloy can have melting point which is either higher or lower than those of its constituents.
Isomorphous system

Slide 1 gives the phase diagram of a binary isomorphous system. Metals having nearly the same atomic diameters, identical crystal structure & valance are likely to have unlimited solubility in solid state. A few pairs of common metals do satisfy such conditions. Therefore they have phase diagrams similar to that in slide 1. A few of these are listed in slide 1. The room temperature microstructure of such alloys consists of several homogeneous grains (crystals) of phase \( \alpha \). Such alloys are ductile but their tensile strengths are higher than those of the metals of which the alloy is made.

Isomorphous system with intermediate maximum / minimum

Slide 2 shows two other variants of an isomorphous system where there are alloys that have a definite melting point. Their cooling curves are exactly same as that of a pure metal. The sketch on the left shows a case where the melting point of the intermediate alloy I has a melting point \( (T_{max}) \) higher than...
those of A & B (T_{max} > T_A > T_B). The sketch on the right shows a case where the melting point of the intermediate alloy I has a melting point (T_{min}) lower than those of A & B (T_{min} < T_A < T_B).

**Binary eutectic:**

Slide 2 shows a typical binary eutectic phase diagram between two metals A & B having limited solubility in solid state but unlimited solubility in liquid state. The terminal solid solutions are denoted as $\alpha$ & $\beta$. A few systems such as Ag-Cu, Al-Si & Pb-Sn have similar phase diagram. The eutectic in such alloys are intimate mixture of two phases. There are several ways the two distinct phases may be distributed within the eutectic. Two common types of eutectic microstructures are also shown in slide 2.

Slide 3 shows a typical eutectic phase diagram between two hypothetical metals completely miscible in liquid state but totally immiscible in solid state. Typical microstructures of hypoeutectic (A+E), eutectic
(E) and hypereutectic (B+E) alloys have been included in the diagram. There are some metallic systems whose phase diagrams are similar to that shown here. These are Cd-Bi & Sb-Pb.

**Determination of eutectic phase diagram from thermodynamic data:**

This is illustrated by estimating the eutectic temperature and composition of Bi-Cd system. These are soluble in liquid state but insoluble in solid state. The melting points & latent heats of fusion of Bi are 271°C & 10.89 kJ/mole and those of Cd are 321°C & 6.4 kJ/mole. Assume the liquid to be an ideal solution.

Slide 4 gives the derivation of the expressions for the liquidus as a function of composition. The sketch in the slide shows a schematic phase diagram. At a temperature indicated by the dotted line consider the equilibrium between solid A and the liquid L. Consider pure A (solid) at this temperature as its standard state. Its free partial molar free energy can be taken as zero. A set of equations on the top right of slide 4 shows how to estimate partial molar free energy of A dissolved in L. Since solid A at T has been taken as its standard state, the energy needed to melt it must be added to its partial molar free energy estimated on the basis of pure A in liquid state as its standard state. The list of symbols used in this slide 4 is as follows: $T_{mA}$ = melting point of A, $\Delta H_{mA}$ = latent heat of fusion of A, $T_{mB}$ = melting point of B, $\Delta H_{mB}$ = latent heat of fusion of B, $N_A^L$ = atom fraction of A in the liquid and $N_B^L$ = atom fraction of B in the liquid. The sum of the atom fractions of A & B in the liquid should be unity. Table 1 gives the output of a spreadsheet used to calculate the composition of the liquidus at different temperatures in terms of $N_B$. At every temperature there are two values of $N_B$ one denoting the composition of the liquid in equilibrium with A and the other denoting the composition of the liquid in equilibrium with B. At the eutectic temperature the two must be equal.

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Binary peritectic system:

Slide 5 shows a typical binary peritectic phase diagram. It is not as common as those of eutectic or isomorphous system. However, it is often a part of complex binary phase diagrams of many commercial alloys. Pt-Ag has such a phase diagram. Note that the melting points of the two are widely different. In principle all phase diagrams can be derived from thermodynamic database. The method has been illustrated assuming that the liquid & the solid obey Raoult’s law (ideal solution) in the case of an isomorphous system whereas in the case of a eutectic system the solids were assumed to be pure (with
no solubility) and the liquid to be an ideal solution. Various degrees of deviations from ideality in both solid and liquid states are responsible for different types of diagrams where there is limited solubility. We shall look at it a little more detail in a subsequent module.

**Invariant reactions (Three phase equilibrium):**

![Diagram of invariant reactions](slide6.png)

Real binary phase diagrams are rarely isomorphous, simple eutectic or simple peritectic. They often consist of several two phase regions & invariant reactions involving 3 phases even in a binary system. The common invariant reactions are classified into 2 groups. These are as follows: (i) a particular phase on cooling separates into two different phases as in the case of eutectic \((L = \alpha + \beta)\) (ii) two particular phases on cooling reacts to form a different phase as in peritectic \((L + \alpha = \beta)\).

Slide 6 gives three possible instances of 3 phase equilibrium under case 1. The first of the three named eutectic has been discussed in detail. The second invariant reaction called monotectic occurs in systems where there is immiscibility in liquid state. Whereas most metals are soluble in each other in liquid state there are cases (though very few) where there is immiscibility in the liquid state. One common example is that of Cu-Pb. The third invariant reaction called eutectoid occurs in many commercial binary alloys. The most common example is in the iron – carbon system where a high temperature solid phase called austenite decomposes at a fixed temperature into a mixture of two phases consisting of ferrite and iron carbide called cementite. This will be taken up in detail in one of the subsequent modules. All of these come under the category of invariant reactions because the degree of freedom for 3 phases to coexist or remain in equilibrium is zero.
**Two phases react to produce a third phase**

Peritectic: $\alpha + L = \beta$

Syntectic: $L_1 + L_2 = \beta$

Peritectoid: $\alpha + \gamma = \beta$

Slide 7 gives three possible instances of 3 phase equilibrium under case 2. The first of the three named peritectic has been discussed in detail. The second invariant reaction called syntectic occurs in systems where there is immiscibility in liquid state. Whereas most metals are soluble in each other in liquid state there may be cases (though very rare) where there is immiscibility in the liquid state. The third invariant reaction is known as peritectoid. All of these come under the category of invariant reactions because in a binary system the degree of freedom for 3 phases to coexist or remain in equilibrium is zero.

**Complex phase diagrams having multiple three phase equilibriums:**

Most phase diagrams may have several three phase equilibrium. A few examples of hypothetical phase diagram of two metals A & B are shown in the following slides. Slide 8 is a case where there are two 3 phase equilibrium (i) a peritectic and (ii) a eutectic. Note that the peritectic temperature is higher than that of the eutectic. Unlike eutectic transformation solidification here may still be partial even on completion of peritectic reaction. Also note that there is an intermediate phase $\gamma$. 
The phase diagram in slide 9 consists of a monotectic and a eutectic reaction. There is a miscibility gap in liquid state. The liquid L splits into two phases: L₁ & L₂ below a certain temperature. L₁ transforms into a solid α and L₂ at a given temperature. This is known as monotectic transformation.
The phase diagram in slide 10 consists of 3 three phase equilibrium: i) peritectic, ii) eutectic and iii) eutectoid. Note that the peritectic transformation occurs at temperature higher than that of the eutectic. There is an intermediate phase γ that forms due to the peritectic reaction. Subsequently it undergoes eutectoid transformation. The room temperature structure is made of two terminal solid solutions only.

The phase diagram in slide 11 consists of 3 three phase equilibrium: i) peritectic forming an intermediate phase γ, ii) eutectic consisting of a mixture of γ & β, iii) peritectoid forming a second intermediate phase δ. In this case both the intermediate phases are stable at room temperature.
The examples so far considered do not display the effect of allotropic transformations. There are several metals that may exist in more than one crystalline form. The cooling curves of such metals would exhibit additional steps. The most common example is that of iron. Pure iron on solidification is BCC. On further cooling it transforms into FCC and later again to BCC. Its cooling curve therefore has 3 discontinuities (steps). The sketch in slide 12 shows the effect of allotropic transformation on an equilibrium diagram.

Note that in this case metal A solidifies as $\delta$ at $T_A$. This is stable until the temperature reaches $T_{A1}$ where it transforms into $\gamma$. Subsequently at $T_{A2}$ it transforms into ‘$\alpha$’ which is the stable form of metal A at room temperature. Each of these transformations represents two phase equilibrium. Therefore these are invariants having zero degree of freedom. They appear as steps or discontinuities in the cooling curves. The metal B too undergoes allotropic transformation. It solidifies at $T_B$ as $\gamma$ which later at $T_{B1}$ transforms into $\beta$. The sketches in fig 2 describe the nature of such plots for metals A & B.

**Fig 2:** Cooling curves of the two metals whose phase diagram is given in slide 12. The sketch on the left is for A and that on the right is for B.
In all these examples given so far we have tried to draw the cooling curves for different alloys from the phase diagrams. This helps us understand the evolution of structures of metals on solidification. However most these have been obtained from the data collected from cooling curves. The principle of thermal analysis was introduced in module 5. Several commercial units for thermal analysis are available. Most of them use very small amount of metals. If the magnitude of latent heat of transformation is small it is likely that it may not get detected by normal cooling curves. However most of these units have facility to display differential plots. These are extremely sensitive to transformation temperatures even if the heat effects are small. Most of the phase diagrams available today have been obtained from thermal analysis. There are several other tools & techniques that can be used for experimental determination of phase diagrams. Measurement of physical or mechanical properties and examination of structures of alloys using various microscopes and X-ray diffraction have been extremely useful in compiling such diagrams.

Meta-stable state (Phase)

Binary phase diagrams represent the stability of various phases in a temperature composition space at a constant pressure. Bulk of the readily available phase diagrams for common binary alloys has been determined at 1 atmosphere pressure. The stable phases have the lowest free energy at a given temperature. However like pure metal a molten binary alloy too can also be super cooled to a temperature where it is not supposed to be thermodynamically stable. Such a state is known as meta-stable state. This is encountered in systems where the transformation is very slow or if the cooling rate is very fast. If a meta-stable phase is kept at a higher temperature it is expected to transform into a mixture of stable phases. There are several examples of meta-stable phases in binary alloys. The notable amongst these is iron carbide (Fe₃C which is also known as cementite). Carbon is soluble in molten iron whereas its solubility in iron at room temperature is extremely low. The most stable form of iron carbon alloy at room temperature is a mixture of ferrite (nearly pure iron having around 0.002% C) and graphite. However under normal rate of cooling carbon does not get enough time to form clusters of carbon atoms which could grow into crystals of graphite rather it combines with iron to form carbide (or a compound) having 75atomic % Fe and 25atomic % C. It is represented as Fe₃C.

The free energy of a meta-stable phase is always higher than that of the stable state. Therefore the concentration of solute in a meta-stable state should be higher than that of the stable state. This imposes certain restrictions on the shape (or curvature) of the solidus and the solvus of a phase diagram. This is illustrated with the help of a set of schematic diagrams in fig 3. Those in fig 3(A) have the correct curvatures for both solidus and solvus whereas fig 3(B) shows a diagram where the curvatures of the two are thermodynamically incompatible. The extended parts of the solidus and solvus have been represented by dashed lines to denote met-stable state. Note that at a temperature T₁ the meta-stable phase (α’) has a higher solute concentration than that of the stable phase (α) in fig 3(A) whereas in fig 3(B) the trend is just the opposite.
Fig3: Illustrates with schematic diagrams the correct shapes of the boundaries between different phase fields of a binary phase diagram. (A) Shows the correct shape of the solidus (abc) and solvus (dbe). Dashed portions of the two curves denote meta-stable equilibrium. The concentration of solute in the meta-stable state must be higher than that of the stable phase at a given temperature. This is evident from the points of intersection of the horizontal line at $T_1$ with dbe & abc and that at $T_2$ with abc & dbe. (B) Gives an example of thermodynamically incompatible shapes (curvatures) of the two phase boundaries abc & dbe. It suggests that the meta-stable states have lower solute content.

Summary:

In this lecture we looked at different types phase diagrams that you may come across in metallic systems. We started with isomorphous system exhibiting either a maximum or a minimum. Such systems have alloys whose cooling curves are similar to those of pure metals. We also looked at several binary alloy systems having either isomorphous, eutectic or peritectic phase diagrams. The method of determining eutectic phase diagram from thermodynamic data has been explained. An attempt has been made to find the liquidus and eutectic temperature isotherm of Bi-Cd system. Apart from eutectic & peritectic transformation phase diagrams may have several other forms of 3 phase equilibrium. All such transformations occur at definite temperatures since they are invariant. With the introduction of several such transformations the phase diagrams may look much more complex. A number of such cases have been considered. There are metals that may exist in several crystalline forms. The cooling curves of such metals must have additional invariant points. This too has been illustrated with a specific example. The curvature or the shape of the lines separating different regions of the phase diagram can also be explained in terms of the basic concepts of thermodynamics. The extended portions of these lines should be in the 2 phase regime. This gives the composition of a meta-stable phase. The concept has been explained with the help of a schematic binary phase diagram having terminal solid solutions.

Exercise:
1. 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 solid solutions.

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

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

1. The diagram is as follows:

   - Peritectic 1: \( \alpha + L = \gamma \)
   - Peritectic 2: \( \beta + L = \gamma \)
   - Eutectic: \( L = \gamma + \delta \)

2. The diagram is as follows:

   - Eutectic: \( L = \gamma + \beta \)
   - Eutectoid: \( \gamma = \alpha + \beta \)
   - Allotropic transformation at: \( T_{A1} \)

3. Yes, if it is an eutectic alloy.