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- When two or more metals combine to form alloys, a range of products may be obtained depending upon the temperature and composition of the constituent elements.
- Each of these products may display a different structure, and hence different mechanical properties. Therefore, it is imperative to know the relationship between these variables and resulting products for developing alloys with desirable properties.
- Phase diagrams (constitutional diagrams) exhibit pictorial representation of relationships and product description. They describe the areas where there is liquid, a solid solution, an intermetallic compound, etc.
- Phase diagrams show the equilibrium phases existing in an alloy at various temperatures. These diagrams are based on slow cooling of an alloy from molten state to obtain phases which are stable at room temperature.
- Phase diagrams vary according to the number of constituent elements. Binary diagrams represent two-element systems whereas ternary diagrams are for three-alloy systems.
- To understand and interpret such diagrams, it is helpful to learn how they are obtained. In this chapter, their construction will be considered followed by their interpretation. Finally, phase diagrams of the most important alloy system of steels will be discussed in detail.



- Component: unique chemical species that an alloy is composed, i.e. elements (Fe, C, Cu, B, N, ...) and compounds (Al₂O₃, H₂O, NaCl, ...)
- > Phase: homogeneous portion of a system with uniform physical and chemical characteristics
 - **Two distinct phases** in a system have distinct physical or chemical characteristics (e.g. water and ice). A phase may contain one or more components.
 - One-phase system is a homogeneous system. If there are more than one phase, then system is said to be heterogeneous (a mixture).
- > Solvent: major (host) component in a solution
- **Solute:** minor component in a solution
- Solubility Limit of a component in a phase: the maximum amount of component that can be dissolved in (e.g. alcohol has unlimited solubility in water, sugar has a limited solubility, oil is insoluble). The same concept applies to solid phases: Cu and Ni are mutually soluble in any amount (unlimited solubility) while C has a limited solubility in Fe.



- > When we combine elements, what is the equilibrium structure?
- > In other words, for a given composition and temperature:
 - How many phases do we get?
 - What is the composition of each phase?
 - How much of each phase do we get?





- **Components:** Elements or compounds that are mixed
- > Phases: Physically and chemically distinct regions resulting from mixture
- Composition: Amount of a component in a phase





- Solubility Limit: Maximum concentration for which only a solution occurs
- ► Example: The solubility of sugar (C₁₂H₂₂O₁₁) in a sugar-water syrup



Composition (wt%)



- Properties of an alloy depend not only on proportions of the phases but also on how they are arranged structurally at the microscopic level.
- Microstructure also depends on processing, heat treatment, etc.
- Phase diagrams are a guide for us to help understand, explain and predict microstructures of materials, as shown below.



Photomicrograph of a 0.38 wt% C steel having a microstructure consisting of pearlite and proeutectoid ferrite.

(Photomicrograph courtesy of Republic Steel Corporation)



Grey cast iron (Fe-3.2C-2.5Si wt%) containing graphite flakes in a matrix, which is pearlitic. The lamellar structure of pearlite can be resolved, appearing to consist of alternating layers of cementite (Fe₃C) and ferrite (BCC-Fe). <u>Courtesy of: http://www.msm.cam.ac.uk/phase-trans/2001/adi/cast.iron.html</u>

Unstable **Free Energy Metastable** Stable: Under constant temperature, pressure and composition; the system is chemically and structurally stable (not changing with time). Meta-Stable: Sometimes it will take too much time to achieve equilibrium due to

kinetics, thus a state along the path to

equilibrium may appear to be stable.

In thermodynamics, **the equilibrium** is described as the state of system that corresponds to the minimum of thermodynamic function **(free energy)**:

 Under constant conditions, the direction of any spontaneous change is toward a lower free energy.

• The state of **stable** thermodynamic equilibrium is the one **with minimum free energy**.

•Meta-stable system is trapped in a local minimum of free energy (that is not the global one).





Phase diagram is a graphical representation of the combinations of temperature, pressure, composition for which specific phases exist at equilibrium.





> Phase diagrams are classified according to miscibility of constituents in liquid & solid states:



Most common and important engineering alloy systems are binary systems exhibiting complete solubility in liquid state. They may show complete solubility or complete insolubility upon cooling to room temperature.



> There are few general rules governing construction and interpretation of phase diagrams:

 Phase diagrams are based on slow cooling of alloys to obtain structures that are thermodynamically stable at room temperature.

"Gibb's free energy" for transformation reaction is minimum, and is given by the expression:

$\mathbf{G} = \mathbf{U} + \mathbf{P} \bullet \mathbf{V} - \mathbf{T} \bullet \mathbf{S}$

- **G** : Gibb's free energy
- U : total energy
- **P** : pressure
- V : volume
- T: temperature
- **S** : entropy of the system

2. Condition of equilibrium for an alloy system is determined by a relation between number of coexisting phases, number of components and number of variables given by "Gibb's phase rule":

$\mathbf{P} + \mathbf{F} = \mathbf{V} + \mathbf{C}$

- **P** : number of phases
- C : number of components
- V : number of variables
- **F** : degree of freedom

The most common case:

Pressure is constant (atmospheric) and only temperature is variable, then V = 1 and the rule becomes:

P + **F** = 1 + **C**

- 3. Weight proportion of various phases in equilibrium at any temp. can be determined by difference btw composition of a phase at that temp. and the overall composition of alloy using "lever arm principle" in mechanics.
- Three phases cannot coexist at a time except at a constant temperature (e.g. eutectic or peritectic).
- **5. Two phases** are always apart by a two-phase region.



- > Upon further cooling, temperature of the metal does not change, but more solidification takes place because the heat energy released by the melt is used up in forming increasing amount of liquid-solid interface, and hence more solid is formed.
- > After the solidification is complete, further cooling reduces the temperature of the solid metal.
- In case of an alloy, unlike pure metal, the solidification does not take place at a constant temperature because more than one element is involved whose solidification temperatures would be different.
- Solidification begins when one of the elements begins to solidify and the temperature also continues to drop until the solidification is complete.

- As an example, phase diagram of copper-nickel (a binary system, completely soluble in liquid and solid states) will be constructed, as given below.
- A series of alloys containing different amounts of Cu & Ni will be made. Each sample is heated until molten and uniform in composition, then it is allowed to cool very slowly. Change in temperature by time is recorded.



- > First, pure Cu is cooled. Solidification starts (A) and finishes (B) at temperature of 1084 °C.
- Subsequently, alloys with various Cu-Ni composition are cooled from liquid state to obtain the solidification start (L) and finish (S) temperatures.
- ► Finally, pure Ni is cooled at the same temperature of C & D (1455 °C).
- > Then, the temperatures for each composition are plotted on a diagram, as shown below.



- > Lines through solidification start and finish temperatures are drawn to complete the diagram.
- The line joining points where solidification begins from liquid is called "liquidus" whereas the line joining points where solidification is complete is called "solidus".
- The region btw liquidus & solidus lines is in a mixed state where both solid & liquid phases are present. Thus, the two phases (solid & liquid) are separated by a two-phase region.



Construction of Phase Diagrams



- However, some binary systems having complete liquid and solid solubility do not have a continuous region of solid + liquid (e.g. Au-Cu, Au-Ni, Cr-Fe).
- In such systems, solidus & liquidus lines meet tangentially at a min. temperature ("X" in figure) which is below the melting point of both components.
- Alloy corresponding to this temperature is called "azeotropic alloy" which behaves like pure metal during solidification.



Interpretation of Phase Diagrams



- ➤ For given temperature (T) and composition (Co), we can use phase diagram to determine:
 - Nature of present phases
 - Compositions of phases
 - Relative fractions of phases
- Lets try on bismuth-antimony (Bi-Sb) phase diagram:
- Consider **alloy Z** with 50% Bi.
- It is a liquid composition with 50% Bi at temperatures above point x.



As it cools down to **Tx**, it begins to solidy. The first solid (**point a**) has 8% Bi (not 50%).

Further cooling to **Ti** results in more solid with 23% Bi (**point b**), and the remaining liquid has 73% Bi (point c).

Interpretation of Phase Diagrams

The reason for the increase in percentage of remaining liquid is that when first solids begin to solidify their compositions have less Bi (50-8=42% less). The overall Co of alloy Z is not changing, and thus the liquid becomes enriched in Bi.

Solidification is completed at Ty, and the solid has the same composition as the remaining liquid, i.e. 93% Bi (point d).



As cooling continues, the first and the last solids (with 8% & 93% Bi) homogenize with each other due to high temp. diffusion, and a uniform composition of 50% Bi prevails in the solid. This is the ideal case. In practice, however, areas of segregation of alloying elements are observed (known as coring).

Interpretation of Phase Diagrams

Another example:

- > Phase diagram: Cu-Ni system
- System: binary (two components: Ni & Cu)
 isomorphous (complete solubility of one component in another)
- Consider: microstuctural changes
 (Co = 35% Ni)



Cored Structure vs Equilibrium Structure





Interpretation of Phase Diagrams – Lever Rule

- Relative weight fractions of two phases (liquid & solid) can also be obtained from diagram at any temperature using "lever arm principle (lever rule)".
- To determine the weight fraction, a horizontal line (tie line) is drawn at Ti, which constructs line mn passing through point i.
- ► Then, line segments (**mi**, **in**, **mn**) are determined from diagram: $mi = C_o - C_L = 50 - 23 = 27\%$ $in = C_a - C_o = 73 - 50 = 23\%$ $mn = C_a - C_L = 73 - 23 = 50\%$
- Thus, the weight fractions of solid and liquid phases are calculated: wt % of solid = (in/mn)*100 = 46% wt % of liquid = (mi/mn)*100 = 54%



Systems Insoluble at Solid State

- For binary alloys that are completely insoluble in solid state, the diagram looks like that of bismuth-cadmium (Bi-Cd), as shown in figure.
- > All the rules described previously are also applicable to this type of system.
- But, there is a significant difference: alloy Y (in figure) behaves like a pure metal as solidification is concerned.
- This alloy solidifies at constant temp.
 (Tc), just like pure metal.
- Unlike pure metal, the solidification product is not a single phase.
- In fact, it is a mixture of two phases (solid-Bi & solid-Cd), and they are completely insoluble in each other.



Systems Insoluble at Solid State

- > The two phases exist side-by-side with various structures, as shown in figure.
- The nucleation of phase Bi produces a plate. The liquid next to it becomes enriched in Cd since nucleation of Bi changes liquid composition, as explained before. Due to enrichment of Cd, the liquid next to Bi solidifies as Cd in the plate form.
- Sequence of events continues until all of the liquid is transformed to solid at constant temperature (Tc).
- Such transformation is "eutectic transformation", the temperature (Tc) is "eutectic temperature", and the alloy Y is "eutectic alloy".
- At eutectic, one phase (liquid) decomposes to produce two phases (Bi & Cd).

Eutectic: Easy to melt (in Greek)



Systems Insoluble at Solid State

- An alloy (other than alloy Y) would solidify to produce either pure-Bi or pure-Cd followed by eutectic lamellar structure.
- For instance, consider alloy X cooling from 300 °C in liquid state. At point a, it starts to solidify and pure-Bi begins to form. At point b, more Bi is formed and liquid composition is given by point m', which is 30% Cd.



Weight fraction of pure-Bi at point b is determined by lever rule:

wt % =
$$\frac{bm'}{T_bm'} = \frac{30-20}{30-0} * 100 = 33\%$$

- Above point c, the liquid composition is 40% Cd (eutectic composition). This remaining liquid will solidify as a lamellar eutectic structure at constant temperature (Tc).
- Alloy Z will also solidify to give pure-Cd followed by lamellar structure.

This is the most common alloy system (involving steel) where two metals are partially soluble in solid state. Silver-Copper (Ag-Cu) system is an example (as shown below).

Systems Partially Soluble at Solid State

➤ At temperatures below eutectic, solubility decreases as cooling continues. This gives rise to precipitation of new solid solutions, which is the basics of "age (precipitation) hardening".

Typical Binary-Eutectic System:

- Diagram: Cu-Ag system
- Phases: 3 single-phase regions (L, α, β) separated by two-phase regions
- Solubility: Limited (partial)
 - α : mostly Cu
 - β : mostly Ag
 - α + β : mixture
- ► Eutectic Transition: $L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$







Let us examine: 40% Sn – 60% Pb alloy **at 150 °C**

- **1.** the phases present: $\alpha + \beta$
- 2. compositions of phases:

 $C_{o} = 40 \text{ wt\% Sn}$ $C_{\alpha} = 11 \text{ wt\% Sn}$ $C_{\beta} = 99 \text{ wt\% Sn}$

3. relative amount of each phase:

$$W_{\alpha} = \frac{B}{A+B} = \frac{C_{\beta} - C_{0}}{C_{\beta} - C_{\alpha}} = \frac{99 - 40}{99 - 11} = 67 \ wt\%$$
$$W_{\beta} = \frac{A}{A+B} = \frac{C_{0} - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{40 - 11}{99 - 11} = 33 \ wt\%$$



Proof of calculations (Co of Sn):

 $C_{0} (Sn) = C_{\alpha} \cdot W_{\alpha} + C_{\beta} \cdot W_{\beta}$ = 0.11 \cdot 0.67 + 0.99 \cdot 0.33 = 0.40 \rightarrow 40%



Let us examine:

- 40% Sn 60% Pb alloy **at 220 °C**
- **1.** the phases present: $\alpha + L$
- 2. compositions of phases:

 $C_o = 40 \text{ wt\% Sn}$ $C_\alpha = 17 \text{ wt\% Sn}$ $C_L = 46 \text{ wt\% Sn}$

3. relative amount of each phase:

$$W_{\alpha} = \frac{B}{A+B} = \frac{C_{L} - C_{O}}{C_{L} - C_{\alpha}} = \frac{46 - 40}{46 - 17} = 21 \text{ wt\%}$$
$$W_{L} = \frac{A}{A+B} = \frac{C_{O} - C_{\alpha}}{C_{L} - C_{\alpha}} = \frac{40 - 17}{46 - 17} = 79 \text{ wt\%}$$



Microstructures in Eutectic Systems

Pb-Sn System

C_o < 2 wt% Sn

- at extreme ends
- Polycrystal of α grains
 (i.e. only one solid phase)



Microstructures in Eutectic Systems



Pb-Sn System

- 2 wt% Sn < C_o < 18.3 wt% Sn
- initially: L + α
- then: only α
- finally: two phases
 - 1) α polycrystal
 - 2) fine β -phase inclusions



Pb-Sn System

C_o = C_E = 61.9 wt% Sn

- eutectic (lamellar) microstructure
- alternating layers (lamellae) of α and β crystals



Arrows indicate the directions of diffusion of Pb & Sn atoms. Pb atoms diffuse toward α -phase layers (Pb-rich). However, the direction of diffusion of Sn is in the direction of β -phase layers (Sn-rich). Thus, eutectic structure forms in these alternating layers as atomic diffusion of Pb & Sn occur over only relatively short distances.

50 u.m



Microstructures in Eutectic Systems

HYPOEUTECTIC & HYPEREUTECTIC



Microstructures in Eutectic Systems



The tin-lead equilibrium diagram

The microstructures indicated are those obtained under non-equilibrium conditions of solidification.

Isothermal Reactions



- > Transformation reactions (at T_{cst}) in a binary system in liquid or solid states are as follows:
- **1. Eutectic:** the reaction whereby a liquid changes to two solid phases at a constant temp. (e.g. Fe-C): $L \rightarrow \alpha + \beta$
- 2. Eutectoid: the reaction whereby a solid changes to two different solid phases at a constant temp. (e.g. Fe-C), which is essentially the same as eutectic except that all phases in reaction are solids: $\gamma \rightarrow \alpha + \beta$
- 3. Peritectic: the reverse of eutectic whereby solid and liquid phases are combined to produce another solid phase (e.g. Fe-C), which occurs when the solidification temp. of two phases has a large difference: $L + \alpha \rightarrow \beta$
- 4. Peritectoid: the same reaction as peritectic except that it is a solid state reaction (e.g. Ni-Zn and Fe-Nb): $\alpha + \beta \rightarrow \gamma$



- **5.** Monotectic: the reaction similar to eutectic except that on cooling whereby one liquid transforms to a solid phase and another liquid phase (e.g. Zn-Pb and Cu-Pb): $L_1 \rightarrow L_2 + \alpha$
- 6. Monotectoid: the same as monotectic except that it is in solid state (e.g. Al-Zn), however the use of this term is not widespread as it seems to be eutectoid: $\alpha_1 \rightarrow \beta + \alpha_2$
- **7. Syntectic:** the reaction of peritectic type in which two liquids combine to form one solid (e.g. Na-Zn): $L_1 + L_2 \rightarrow \alpha$



Isothermal Reactions

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- An improvement in properties of a binary alloy is frequently gained by adding a third element. Two commercial examples are: addition of nickel (Ni) to steel (Fe-C) to improve toughness, and addition of lead (Pb) to brass (Cu-Zn) to improve machinability.
- ➤ The presence of third element, however, alters the binary phase diagram. In principle, use and interpretation of ternary phase diagrams are the same as binary diagrams, and phase rule and lever arm principle are valid. In practice, however, ternary systems are more complex than binary systems.
- Constant pressure ternary systems are three-dimensional (Fig. a). They consist of an equilateral composition triangle while temperature is plotted vertically.
- To facilitate such interpretation, 2D plots are obtained by sectioning diagram at constant temperatures (isothermals, Fig. b) or at constant ratio of compositions (isopleths, Fig. c). Although they do not provide true compositions, they are useful in predicting the changes expected on heating or cooling.







Property Variation with Solubility

> The properties of an alloy depends upon two factors:

1.The properties of the phases of which it is composed

2. The manner in which the several phases are associated

- A general idea of how the properties will vary within a given system can be secured from the phase diagram.
- A system in which the components are completely soluble in solid state will exhibit a variation in hardness and conductivity as depicted in Fig. a.
- However, as seen from Figs. b & c, presence of small amounts of solute atoms has a tremendous influence in decreasing conductivity.







Q: Determine the weight percentages of **austenite** (γ), ferrite (α) and pearlite (α+Fe₃C) upon slow cooling of 0.4% C steel from 900 °C to room temperature.

- (a) At 900 °C, the steel is composed of austenite only.
- (b) Upon cooling, it intersects line A₃ where ferrite begins to form. Just before line A₁, austenite contains 0.83% C. Weight fractions of ferrite and austenite are determined by lever arm principle: $W_{\alpha} = (0.83 - 0.4) * 100/(0.83 - 0.025) = 53.4\%$ $W_{\gamma} = (0.4 - 0.025) * 100/(0.83 - 0.025) = 46.6\%$
- (c) Upon further cooling, austenite decomposes into ferrite & cementite (pearlite) with fractions below (note that γ-composition is 0.83% C, not 0.4% C):

 $W_{\alpha} = (6.67 - 0.83) * 100 / (6.67 - 0.025) = 87.9\%$ $W_{Fe_{3}C} = (0.83 - 0.025) * 100 / (6.67 - 0.025) = 12.1\%$

Total fraction of ferrite in the final microstructure: Proeutectoid ferrite = 53.4% Eutectoid ferrite = 87.9% of 46.6% = 40.9% Total ferrite = 53.4% + 40.9% = 94.3%



EXAMPLE (1)

Q: In Fe-C diagram, austenite-pearlite reaction can only take place at a constant temperature whereas austenite-ferrite reaction can take place at a range of temperatures. Why?

A: The answer lies beneath the Gibb's phase rule (where V=1 for atmospheric pressure):

 $P + F = V + C \rightarrow P + F = 1 + C$

(a) Lets consider austenite-ferrite reaction: The number of components in the system is two (i.e. Fe & C, so C=2) and the number of phases is also two (i.e. austenite & ferrite, and so P=2):

 $2 + F = 1 + 2 \rightarrow F = 1 \rightarrow$ Temperature is variable

(b) For austenite-pearlite reaction:

The number of components in the system remains the same, but the number of phases is three (i.e. austenite and ferrite & cementite, and so **P=3**):

 $3 + F = 1 + 2 \rightarrow F = 0 \rightarrow$ Reaction must take place at a cst temp.





Q: Determine the weight percentage of carbon in cementite.

- A: Cementite is **iron carbide**, which is **Fe₃C**.
- ➤ It consists of **3 atoms of iron (Fe)** and **1 atom of carbon (C)** in its molecule.
- The total atomic weight of Fe₃C is calculated as:

Atomic weight of $\text{Fe}_3\text{C} = 3*(\text{atomic weight of Fe}) + 1*(\text{atomic weight of C})$ = 3*(56) + 1*(12)= 168 + 12= 180

➤ Therefore, weight percentage of carbon in Fe₃C is:

$$\frac{\text{Weight of C}}{\text{Weight of Fe}_{3}\text{C}} * 100 = \frac{12}{180} * 100 = 6.67\%$$

Q: Consider slow cooling of **plain carbon steels (1040, 1080, 1120)** from austenite to room temperature. Draw the microstructures of the transformation products in each region.

EXAMPLE (4)

A: Microstructures of each steel in each region upon their cooling are presented below. Note that 1080 is an eutectoid steel while 1040 and 1120 are hypoeutectoid and hypereutectoid steels, respectively.

