Chapter 9.

Phase Diagrams

9.1 Introduction

- Good understanding of phase diagrams will help engineers to design and control heat treatment procedures: some properties of materials are functions of their microstructures, and hence of their thermal histories.
- The development of microstructure of an alloy is related to the characteristics of its phase diagram. Phase diagrams provide valuable information about melting, casting, crystallization, and other phenomenon.
- Topics to be discussed are: terminology of phase diagrams and phase transformations, interpretation of phase, simple binary phase diagrams, and development of equilibrium microstructures upon cooling.

Definitions and Basic Concepts

- “Components”: pure metals and/or compounds of which an alloy is composed (Ex.: solute and solvent in Cu-Zn brass).
- A “System”: a specific body of material under consideration (Ex.: ladle of molten steel) or a series of alloys consisting of the same components but without regard to alloy composition (Ex.: the iron-carbon system).
- “Solid solution”: consists of atoms of at least two different types; the solute atoms (minor component) occupy either substitutional or interstitial positions in the solvent lattice (host or major component).

9.2 Solubility Limit

- Solubility limit is the maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution at a specific temperature. Adding more solute in excess of this limit results in forming another solid solution or compound with different composition.
- Consider sugar-water ($\text{C}_{12}\text{H}_{22}\text{O}_{11} - \text{H}_2\text{O}$) system. As sugar is added to water $\rightarrow$ sugar-water solution (syrup). Adding more sugar $\rightarrow$ solution becomes more concentrated until solubility limit is reached (solution is saturated with sugar). Further additions of sugar simply settle to the bottom of the container $\rightarrow$ system now consists of two separate substances: a sugar + water syrup liquid solution and solid crystals of undissolved sugar.
- Figure shown indicates that the solubility limit depends on the temperature of water; temperature verses composition in weight percent. Solubility increases slightly with rising temperature.
- Note at 20° C the maximum solubility of sugar in water is 65 wt%.
9.3 Phases
- A phase is a homogeneous portion of a system that has uniform physical and chemical characteristics. Every pure material is considered to be a phase. Every solid, liquid, and gaseous solution may be considered a phase.
- In above example: sugar-water syrup solution is one phase. The solid sugar is another phase.
- If two or more phases present in a given system, a boundary separating the phases will exist across which there will be a discontinuous and abrupt change in physical and/or chemical characteristics (liquid solution and solid sugar); one type of properties is sufficient (water and ice; identical in chemical make up).
- One-phase system is termed “homogeneous”. Systems with two or more phases are termed “heterogeneous”, or “mixtures” which is the case of most metallic alloys, but also happens in ceramics and polymers.
- A two-component alloy is called binary. One with three components is called ternary.

9.4 Microstructure
- In metal alloys, microstructure is specified by the number of phases present, their proportions, and the manner in which they are distributed.
- The microstructure of an alloy depends on variables such as the alloying elements present, their concentrations, and the heat treatment of the alloy (temperature, heating time, and rate of cooling).
- Different phases may be distinguished by polishing it to a mirror finish, etching it (components etch at a different rate) and observing the surface under a microscope (light and dark for two-phase alloy; uniform texture for single phase).

9.5 Phase Equilibria
- Free energy is defined as a thermodynamic quantity which is a function of the internal energy of a system and the randomness or disorder of the atoms (or molecules).
- A system is at equilibrium if its free energy is at a minimum under some specified combination of temperature, pressure, and composition. At macroscopic level, this means that the characteristics of the system do not change with time but persist indefinitely; that is, the system is stable.
- Phase equilibrium refers to equilibrium as it applies to systems in which more than one phase may exist:
  - Example: suppose that the sugar-water syrup is contained in closed vessel at 20° C; if the system is in equilibrium, the composition of the syrup is 65 wt% sugar and 35 wt% water, and the amounts and compositions of the syrup and solid sugar (2 phases) will remain constant with time. If the temperature is suddenly raised to 100° C; solubility limit is increased to 80 wt% sugar and 20 wt% water. Thus some of the solid sugar will go into the solution in the syrup. This will continue until the new equilibrium syrup concentration is established at the higher temperature.
- Phase equilibrium illustrated above used liquid-solid system, but phase equilibrium may involve solid phases. In this regard the state of the system is reflected in the characteristics of the microstructure, which necessarily include not only the phases present and their composition but, in addition, the relative phase amounts and their spatial arrangement or distribution.
- Often, especially in solid systems, a state of equilibrium is never completely achieved, because the rate of approach to equilibrium is extremely slow; such a system is said to be in a nonequilibrium or metastable state.
- A metastable state or microstructure may persist indefinitely, experiencing only extremely slight and almost imperceptible (hardly noticeable) changes as time progresses.
Much of the information about the control of microstructure (or phase structure) of a given alloy system is displaced in what is called a phase diagram (equilibrium or constitutional diagram).

Many microstructures develop from phase transformations (changes occur between phases when temperature is changed, ordinarily cooling). This may involve the transition from one phase to another or the appearance or disappearance of a phase.

**Equilibrium phase diagrams** represent the relationships between temperature and the compositions and quantities of phases at equilibrium. In the present discussion we will study these diagrams for binary alloys. A binary alloy is one that contains **two components**.

External pressure is another parameter that influences the phase structure and sometimes diagrams are given with pressure as one of the variables. However, in practice, pressure remains constant in most applications. In the phase diagrams we will discuss, pressure is assumed to be constant at one atmosphere (1 atm).

The diagrams discussed here do not indicate the dynamics when one phase transforms into another.

### 9.6 Binary Isomorphous systems

Consider the binary phase diagram for copper-nickel system, as shown. The abscissa ranges from 0 wt% Ni (100 wt% Cu) to 100 wt% Ni (0 wt% Cu).

**Three different phase regions** (or fields) appear in the diagram: an $\alpha$ field, a liquid ($L$) field, and a two-phase $\alpha + L$ field.

The liquid $L$ is a homogeneous liquid solution composed of both copper and nickel.

The $\alpha$ phase is a substitutional solid solution consisting of Cu and Ni atoms and having FCC crystal structure.

Below temperature $\sim$1080°C copper and nickel are mutually soluble in each other in the solid state for all compositions. Both Cu and Ni have FCC crystal structure, nearly identical atomic radii and electronegativities, and similar valences.

The Cu-Ni system is called **isomorphism** because of this complete liquid and solid solubility of the two components.

Note solid solutions are commonly designated by $\alpha, \beta, \gamma, \ldots$.

The line separating the $L$ and $\alpha + L$ phase fields is termed **liquidus** line. The line separating the $\alpha$ and $\alpha + L$ phase fields is termed **solidus** line. In the figure, these lines intersect at the two composition extremities that represent the melting temperatures of Cu (1085°C) and Ni (1453°C). These melting points represent solid-to-liquid transformations.

<table>
<thead>
<tr>
<th>Component</th>
<th>Crystal Structure</th>
<th>Electroneg</th>
<th>r (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>1.9</td>
<td>0.1246</td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>1.8</td>
<td>0.1278</td>
</tr>
</tbody>
</table>
For any compositions other than pure components, melting occurs over the range of temperatures between the solidus and liquidus lines; both \( \alpha \) and \( L \) phases will be in equilibrium within this temperature range.

**Example:** When heating alloy composition 50 wt% Ni – 50 wt% Cu (see figure), melting begins at 1280° C; the amount of liquid phase continuously increases with temperature until about 1320° C, at which the alloy is completely liquid.

### 9.7 Interpretation of Phase Diagrams

- For a binary system of known composition and temperature that is at equilibrium, at least three kinds of information are available: (1) phases that are present, (2) the compositions of these phases, and (3) the percentages of fractions of the phases.

#### 9.7.a Phase Present

- Establishment of what phases are present is relatively simple. **Just locate the temperature-composition point** on the diagram and observe the phase(s).

**Examples:**
- Consider an alloy 60 wt% Ni – 40 wt% Cu at 1100° C. From figure this will be located at point \( A \) \( \rightarrow \) single \( \alpha \) - phase alloy.
- Consider an alloy 35 wt% Ni – 65 wt% Cu at 1250° C. From figure this will be located at point \( B \) \( \rightarrow \) alloy consist of both \( \alpha \) and \( L \) phases at equilibrium.

#### 9.7.b Determination of Phase Compositions

- To determine the phase compositions (in terms of the concentrations of the components) we first locate the temperature-composition point on the phase diagram:
  - For **single-phase region**: the composition of this phase region is simply the same as the overall composition of the alloy.
- For **two-phase region**: to compute the equilibrium concentrations of the two phases, we use the **tie-line method**:
  1. Construct a tie line (horizontal line called an isotherm) across the two-phase region at the temperature of the alloy.
  2. Intersections of the tie line are noted and perpendiculars are dropped to the horizontal composition axis, from which the composition of each of the respective phases is read.

**Example:**
- Consider an alloy 35 wt% Ni – 65 wt% Cu at 1250° C; located at point \( B \) and lying within the \( \alpha + L \) region phases at equilibrium. The intersection of the tie line with the liquidus line meets the composition axis at 31.5 wt% Ni – 68.5 wt% Cu which is the composition of the liquid phase \( C_L \). The intersection of the tie line with the solidus line meets the composition axis at 42.5 wt% Ni – 57.5 wt% Cu which is the composition of the \( \alpha \) solid-solution phase \( C_\alpha \).
9.7.c Determination of Phase Amount

The relative amounts (as fraction or percentage) of the phases present at equilibrium may also be computed with the aid of phase diagram.

Again we first locate the temperature-composition point on the phase diagram:

- For single-phase region: the alloy is composed entirely of the phase identified; the phase fraction is 1 or the percentage is 100%.
- For two-phase region: here we use the tie line in conjunction with the lever rule:
  1) Construct a tie line across the two-phase region at the temperature of the alloy.
  2) The overall alloy composition is located on the tie line.
  3) The fraction of one phase is computed by taking the length of the tie line from the overall alloy composition to the phase boundary for the other phase, and dividing by the total tie line length.
  4) Repeat step (3) for the other phase.
  5) Multiply fractions by 100 if percentages are desired.

Let $C_o =$ overall composition, $W_L =$ fraction of liquid phase, $W_\alpha =$ fraction of solid phase.

Using the lever rule:

$$ W_L = \frac{S}{R+S} \quad (9.1a) $$

Substituting compositions we write:

$$ W_L = \frac{C_{\alpha} - C_o}{C_o - C_L} \quad (9.1b) $$

Similarly, we define

$$ W_\alpha = \frac{R}{R+S} \quad (9.2a) $$

$$ W_\alpha = \frac{C_o - C_L}{C_\alpha - C_L} \quad (9.2b) $$

Note: the fractions are inversely proportional to the length to the boundary for the particular phase. If the point in the diagram is close to the phase line, the fraction of that phase is large.

Example:

Consider an alloy 60 wt% Ni – 40 wt% Cu at 1100° C (point A). At this composition and temperature, only the $\alpha$ phase is present, so the alloy is completely or 100% solid $\alpha$.

Again consider 35 wt% Ni – 65 wt% Cu alloy at 1250° C; located at point B and lying within the $\alpha + L$ region phases at equilibrium (see figure). So $C_o = 35$ wt% Ni; and from above computations $C_\alpha = 42.5$ wt% Ni and $C_L = 31.5$ wt% Ni.
Thus

\[
W_L = \frac{C_a - C_L}{C_a - C_L} = \frac{42.5 - 35}{42.5 - 31.5} = 0.68
\]

\[
W_\alpha = \frac{C_a - C_L}{C_a - C_L} = \frac{35 - 31.5}{42.5 - 31.5} = 0.32
\]

Same answers will be obtained if we used wt% of copper instead of nickel.

- **Not to be confused:**
  a) **Phase compositions** are expressed in terms of weight percents of the components (Ex. wt% copper wt% nickel). For alloys with single phase: the composition of that phase is the same as the total alloy composition. For alloys with two phases: the tie line must be employed, the extremities of which determine the compositions of the respective phases.
  b) **Fractional phase amounts** (Ex. mass fraction of the \( \alpha \) or \( L \) phase): when a single phase exists: the alloy is completely that phase. For a two-phase alloy: the lever rule is used by which a ratio of the tie line segment length is taken.

- For multiphase alloys, it is often more convenient to specify relative phase amount in terms of **volume** fraction rather than mass fraction; volume fractions can be determined from examination of the microstructure and, furthermore, the properties of the multiphase alloy may be estimated on the basis of volume fractions.

### 9.8 Development of Microstructure in Isomorphous Alloys

#### 9.8.1 Equilibrium Cooling

- Assume that cooling occurs **very slowly** in which phase equilibrium is continuously maintained.
- Consider Cu-Ni system shown. Consider an alloy composition 35 wt% Ni - 65 wt% Cu as it is cooled moving down:
  1. At 1300\(^\circ\) C, **point a**, alloy is completely liquid (35 wt% Ni - 65 wt% Cu) with microstructure represented by circle shown noted as \( L \) (35 Ni).
  2. As cooling begins, no microstructural or compositional changes will be realized until we reach the liquidus line **point b** - 1260\(^\circ\) C. At this point, the **first solid \( \alpha \) begins to form** with composition 46 wt% Ni - 54 wt% Cu [noted as \( \alpha \) (46 Ni)], using tie line. The composition of \( L \) is still approx. the same 35 wt% Ni - 65 wt% Cu, \( L \) (35 Ni).

With continued cooling, both compositions and relative amounts of each of the phases will change: compositions will follow liquidus and solidus lines. The fraction of the \( \alpha \) phase will increase with continued cooling. Note that the overall alloy composition (35 wt% Ni - 65 wt% Cu) remains unchanged during cooling even though there is a redistribution of copper and nickel between phases.
3. At 1250°C, point c, the compositions of the L and α phases are 32 wt% Ni - 68 wt% Cu [L(32 Ni)] and 43 wt% Ni - 57 wt% Cu [α (32 Ni)], respectively.

4. At 1220°C, point d, the solidification is almost complete, the solid α is approximately 35 wt% Ni - 65 wt% Cu (overall alloy composition) while that of the last remaining liquid is 24 wt% Ni - 76 wt% Cu.

5. Upon crossing the solidus line, remaining liquid solidifies; the final product is a polycrystalline α-phase solid solution that has a uniform 35 wt% Ni - 65 wt% Cu composition point e [α (35 Ni)]. Subsequent cooling will produce no microstructural compositional changes.

9.8.8 Nonequilibrium Cooling

- Conditions of equilibrium solidification and development of microstructures are realized only for extremely slow cooling rates: there must be readjustments in the compositions of the liquid and solid phases with changes in temperature. Such readjustments are accomplished by diffusions in both solid and liquid phases and also across the solid-liquid interface, so sufficient time must be allowed at each temperature for the approximate compositional readjustments. Diffusion rates are low for solid phases and decrease with diminishing temperature. In almost all practical solidification situations, cooling rates are much too rapid to allow these compositional readjustments and maintenance of equilibrium, thus, microstructures other than those described above develop.

- Consider the isomorphous alloy with composition 35 wt% Ni - 65 wt% Cu (same as above) as it is cooled moving down as shown (assume that diffusion rates in the liquid phase are sufficiently rapid such that equilibrium is maintained in the liquid):

1. At 1300°C, point a', alloy is completely liquid (35 wt% Ni - 65 wt% Cu) with microstructure represented by circle shown noted as L(35 Ni). As cooling begins, no microstructural or compositional changes occur.

2. At point b' - 1260°C, α-phase begins to form with composition 46 wt% Ni - 54 wt% Cu [noted as α (46 Ni)], using tie line. The composition of L is still approx. the same.

3. Cooling to point c' - 1240°C, liquid composition shifts to 29 wt% Ni – 71 wt% Cu and the α phase that solidified is 40 wt% Ni – 60 wt% Cu [α (40 Ni)]. However, since diffusion in the solid α phase is relatively slow, the α phase that formed at point b' has not changed composition appreciably (it is still about 46 wt% Ni) and the composition of the α grains has continuously changed with radial position, from 46 wt% Ni at grain centers to 40 wt% Ni at the outer grain perimeters. Thus at point c', the average composition of the solid α grains that have formed would be some volume weighted average composition, lying between 46 and 40 wt% Ni. Assuming this average to be 42 wt% Ni – 58 wt% Cu [α (42 Ni)]. Using the
lever rule, there is a greater proportion of liquid is present for this non-equilibrium condition than for equilibrium cooling. This non-equilibrium solidification phenomenon implies that the solidus line on the phase diagram has been shifted to higher Ni contents; presented by the dash line in the figure. No similar case for the liquidus line because it is assumed that equilibrium is maintained in the liquid phase during cooling sufficient rapid diffusion rates.

4. At point d' - 1220° C and for equilibrium cooling rates, solidification should be completed. However, for this non-equilibrium situation, there is still an appreciable proportion of liquid remaining, and the phase that is forming has a composition of 35 wt% Ni [α (35 Ni)]; also the average α-phase composition at this point is 38 wt% Ni [α (38 Ni)].

5. Non-equilibrium solidification finally reaches completion at point e' - 1205° C. Composition of this last α phase to solidify is about 31 wt% Ni; the average composition of the α phase at complete solidification is 35 wt% Ni.

6. The inset at point f' shows the microstructure of the totally solid material.
   - Degree of displacement of the non-equilibrium solidus curve from the equilibrium one depends on the rate of cooling. The slower the rate of cooling, the smaller this displacement. Furthermore, if the diffusion rate in the solid phase is increased, this displacement will be diminished.
   - As discussed above, for isomorphous alloys under non-equilibrium solidifications, the distribution of the two elements within the grains is nonuniform called segregation; concentration gradients are established across the grain; see figures above and below. The center of each grain is rich in high-melting element (Ni), whereas the concentration of the low-melting element increases with position from this region to the grain boundary cored structure.

   - Cored structure gives rise to less than the optimal properties.
   - Coring may be eliminated by a homogenization heat treatment carried out at a temperature below the solidus point for the particular alloy composition. During this process, atomic diffusion occurs, which produces compositionally homogeneous grains.

9.9 Mechanical Properties of Isomorphous Alloys
   - For all temperatures and compositions below the melting temperature of the lowest-melting component, only a single solid phase will exist. Therefore, each component will experience solid-solution strengthening (section 7.9), or an increase in strength and hardness by additions of the other component.
Part a shows tensile strength versus composition for the copper-nickel system at room temperature which passes through max. at 60 wt% Ni.

Part b shows the ductility-composition behavior which is opposite to part a, where ductility decreases with additions of the second component. The curve exhibits a minimum.

![Graphs showing tensile strength and ductility](image)

9.10 **Binary Eutectic Systems**

- Figure below shows a binary alloy for the copper-silver (Cu-Ag) system; called a binary eutectic phase diagram. Features:
  - **Three single-phase regions**
    - \( \alpha \), \( \beta \), and **liquid L**. The \( \alpha \) phase is a solid solution rich in copper; it has silver as the solute component and an FCC crystal structure. The \( \beta \) phase solid solution also has an FCC structure, but copper is the solute. The \( \alpha \) and \( \beta \) phases are considered to include pure copper and pure silver, respectively.
  - The solubility limit for the \( \alpha \) phase is the boundary line CBA between the \( \alpha/(\alpha + \beta) \) and \( \alpha/(\alpha + L) \) phase regions. It increases with temperature to a maximum (with 8.0 wt% Ag at 779° C) at point B and decreases back to zero at the melting temperature of pure copper at point A (1085° C). Below 779° C, the solubility limit line BC is termed **solvus** line. The boundary AB is the **solidus** line.
  - For the \( \beta \) phase, similarly, the line HG is **solvus** and the line GF is the **solidus** line Maximum solubility of copper in \( \beta \) phase is at point G (8.8 wt% Cu at 779° C).
Horizontal line \( BEG \) (connects max. solubility positions) may be considered as a solidus line. It represents the lowest temperature at which a liquid phase may exit for any copper-silver alloy that is at equilibrium.

There are also three two-phase regions: \( \alpha + L \), \( \beta + L \) and \( \alpha + \beta \). The tie line and lever rule can be used for these phases.

Also, single-phase regions are always separated from each other by a two-phase region that consists of the two single phases that it separates.

When adding silver to copper, the temperature at which alloys become totally liquid is lowered; \( line \, AE \rightarrow \) melting point of copper is lowered by addition of silver. Same can be said for silver \( \rightarrow \) \( line \, FE \). These two liquidus lines meet at point \( E \) which also passes the horizontal isotherm line \( BEG \). Point \( E \) is called an invariant or eutectic point (liquid and two solid phases exit in equilibrium), which is designated by the composition \( C_E = 71.9 \, \text{wt\% Ag} \), and temperature \( T_E = 779^\circ \text{C} \).

An important reaction occurs for an alloy composition \( C_E \) as it changes temperature in passing through \( T_E \):

\[
L(C_E) \xrightarrow{\text{Cooling}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})
\]

Upon cooling, the liquid phase is transformed into the two solid (\( \alpha \) and \( \beta \)) phases at the temperature \( T_E \); the opposite reaction occurs upon heating. This is called a eutectic reaction (eutectic means easily melted), and \( C_E \) and \( T_E \) represent the eutectic composition and temperature, respectively. \( C_{\alpha E} \) and \( C_{\beta E} \) are the respective composition of the \( \alpha \) and \( \beta \) phases at \( T_E \).

For the copper-silver system, the eutectic reaction may be written as:

\[
L(71.9 \, \text{wt\% Ag}) \xrightarrow{\text{Cooling}} \alpha(8.0 \, \text{wt\% Ag}) + \beta(91.2 \, \text{wt\% Ag})
\]

Often, the horizontal solidus line at \( T_E \) is called the eutectic isotherm.

Note that the solid product of eutectic solidification is always two solid phases, whereas for a pure component only a single phase forms; why we call above diagram eutectic phase diagram!

In binary phase diagrams, one or at most two phases may be at equilibrium within a phase field; true for eutectic. However, for eutectic system, three phases may be in equilibrium, but only at points along the eutectic isotherm.

Another common eutectic system is that for lead and tin with phase diagram very similar to that of copper-silver.

Three single-phase regions are \( \alpha, \beta, \text{and liquid } L \). The \( \alpha \) - phase is a solid solution tin in lead. The \( \beta \) - phase is a solid solution of lead in tin. The eutectic invariant point is located at 61.9 wt\% Sn and at 183\(^\circ\) C. Maximum solubility compositions and melting temperatures are different from that of copper and silver.

Low-melting-temperature alloys are occasionally prepared with near-eutectic compositions. A familiar example is the 60-40 solder, containing 60 wt\% Sn and 40 wt\% Pb.
9.11 Development of Microstructure in Eutectic Alloys

- Depending of the composition and assuming slow cooling, different types of microstructures are possible:
- **Case 1**: between pure component to solid solubility or that component at room temperature; lead-rich alloys containing 0-2% wt Sn (for \(\alpha\) - phase ss) and also approx. 99-100 wt% Sn (for \(\beta\) - phase ss).

Consider alloy composition \(C_1\) as shown. Slowly cool from 350°C along line \(ww'\).

Alloy remains liquid until we cross the liquidus line at 330°C, where the solid \(\alpha\)-phase begins to form with composition based on liquidus and solidus boundaries. Solidification continues until as \(ww'\) crosses the solidus line. The resulting alloy is polycrystalline with a uniform composition \(C_1\), and no further changes will occur upon cooling to room temperature.
**Case 2**: between room temperature solubility limit and maximum solid solubility at eutectic temperature; from about 2% - 18.3 wt% Sn (lead rich alloy), also from about 97.8 % - 99 wt% Sn (tin rich alloy). Consider alloy composition $C_2$ as shown. Slowly cool along line xx'. Down to the intersection of xx' and the solvus line, changes that occur are similar to case 1 (see insets at points d, e and f). Crossing the solvus line, $\alpha$ solid solubility is exceeded which results in forming small $\beta$-phase particles (inset at point g). These particles increase in size as cooling continues and mass fraction of $\beta$-phase increase slightly as temperature decreases.

**Case 3**: involves solidification of the eutectic composition 61.9 wt% Sn, as shown. Consider an alloy with composition $C_3$ is cooled from temperature 250°C down the vertical line yy': As temperature is lowered, no changes occur until we reach the eutectic temperature 183°C. Upon crossing the eutectic isotherm, the liquid transforms to the two $\alpha$ and $\beta$ phases, represented by the reaction:

$$L(61.9 \text{ wt\% Sn}) \xrightarrow{\text{Cooling}} \alpha(18.3 \text{ wt\% Sn}) + \beta(97.8 \text{ wt\% Sn})$$

(9.9)

In which the $\alpha$- and $\beta$-phases compositions are dictated by the eutectic isotherm end points. During this transformation a redistribution of the lead and tin components necessarily occur. The redistribution is accomplished by atomic diffusion where the produced solid microstructure consists of alternating layers (lamellae) of the $\alpha$ and $\beta$ phases that form instantaneously during transformation (see inset at point i), this microstructure is called a eutectic structure. A photomicrograph of this lamellar structure for the lead-tin eutectic is shown (375X).
Continue cooling of the alloy from just below the eutectic to room temperature will result in only minor microstructural alternations.

The microstructural change that accompanies this eutectic transformation is represented schematically in the figure; where the \( \alpha - \beta \) layered eutectic growing into and replacing the liquid phase. The redistribution process of lead and tin occurs by diffusion in the liquid just ahead of the eutectic-liquid interface. Colored and black arrows indicate the directions of diffusion of lead and tin atoms.

- **Case 4**: includes all compositions within the eutectic isotherm except eutectic composition. Consider alloy composition \( C_4 \) as shown. **Slowly cool** along the vertical line \( zz' \):
  - **Starting** at point \( j \), the microstructure between \( j \) and \( l \) is similar to that for case 2. Just prior to to crossing the eutectic isotherm (point \( l \)), the \( \alpha \) and \( L \) are with compositions approximately as indicated by the insets, determined by the appropriate tie line.
  - **As temperature** is lowered to just below the eutectic, the liquid \( L \) phase (of eutectic composition) will transform to eutectic structure \( \rightarrow \) alternating \( \alpha \) and \( \beta \).
  - Insignificant changes will occur with the \( \alpha \)-phase that formed in the \( \alpha + L \) region (see inset at point \( m \)). So, the \( \alpha \) phase will be present both in eutectic structure (called eutectic \( \alpha \)) and also as the phase that was formed during cooling through the \( \alpha + L \) region (called primary \( \alpha \)).
The photomicrograph shows the microstructure of a lead-tin alloy of composition 50 wt% Sn – 50 wt% Pb. **Large dark regions are primary α** (lead rich) present within a lamellar eutectic structure consisting of a tin-rich β phase and a lead-rich α phase (light layers), 400X.

- It is sometimes convenient to use the term **microconstituent** an element of the microstructure having an identifiable and characteristic structure. For inset above, there are two microconstituents: primary α and eutectic structure (distinct lamellar structure).

- To compute the **relative amounts** of both eutectic and primary α microconstituent:

**Example:**
Consider the alloy of composition C₄ shown in the figure.

**Just above TE:**
The fraction of the eutectic microconstituent $W_e$ is just the same as the fraction of the liquid $W_L$ from which it transforms

$$W_e = W_L = \frac{P}{P+Q} \quad (9.10)$$

The fraction of **primary α** is just the fraction of the α phase prior to eutectic transformation or

$$W_α' = \frac{Q}{P+Q} \quad (9.11)$$

**Just below TE:**
The fractions of the total α, both eutectic and primary, (Just below TE) and also of the total β are determined by use of the lever rule and a tie line that extends entirely across the α + β phase field.

Again for an alloy having composition C₄:

$$W_α = \frac{Q+R}{P+Q+R} \quad (9.12)$$

$$W_β = \frac{P}{P+Q+R} \quad (9.13)$$

$$= \frac{97.8 - C_4'}{97.8 - 18.3} = \frac{97.8 - C_4'}{79.5}$$

$$= \frac{C_4' - 18.3}{97.8 - 18.3} = \frac{C_4' - 18.3}{79.5}$$
Analogous (to case 4) transformations and microstructures result for alloys having compositions to the right of the eutectic (between 61.9 wt% Sn and 97.8 wt% Sn). However, below the eutectic temperature, the microstructure will consist of the eutectic and primary $β$ microconstituents (coming from $β + L$ region).

Note that for case 4, conditions of equilibrium are not maintained while passing through the $α + L$ and $β + L$ regions, the following will be realized for the microstructure upon crossing the eutectic isotherm: (1) grains of the primary microconstituent will be cored (nonuniform distribution of solute across the grains), and (2) the fraction for the eutectic microconstituent formed will be greater than for equilibrium situation.

9.12 Equilibrium Diagrams Having Intermediate Phases or Compounds (not covered)

So far, eutectic binary diagrams have only two solid phases $α$ and $β$; these are sometimes called terminal solid solutions because they exist over composition ranges near the concentration extremities of the phase diagram.

For other alloy systems, intermediate solid solutions (intermediate phases) may be found at other than the two extremes. See the copper-zinc system. It looks horrible: it has many invariant points and reactions. It has 6 different solid solutions: 2 terminal ($α$ and $η$); 4 intermediate ($β, γ, δ, and ε$). The $β'$ phase is termed an ordered solid solution $→$ copper and zinc atoms are situated in an ordered arrangement within the unit cell. Some phase boundary are dashed to indicate that their positions have not been exactly determined (diffusion rate are very slow at low temperature and need long times to attain equilibrium). Only single- and two-phase regions are found. Same rules (discussed above) are used to determine compositions and amounts.
For some systems, discrete intermediate compounds rather than solid solutions may be found on the phase diagrams; for metal-metal systems, they are called intermediate compounds. Consider the magnesium-lead (Mg-Pb) system shown. The compound Mg$_2$Pb has a composition of 19 wt% Mg – 81 wt% Pb; represented as a vertical line on the diagram, rather than a phase region of finite region; hence, Mg$_2$Pb can exist by itself only at this precise composition. Other characteristics: (1) The compound Mg$_2$Pb melts at about 550°C at point M, (2) Solubility of Mg in Pb is rather extensive (large composition span) for the $\alpha$-phase field; but, solubility of Mg in Pb is extremely limited (very narrow) for the $\beta$-phase terminal solid-solution region, and (3) this diagram may be simplified as two simple eutectic diagrams joined back to back: one for Mg-Mg$_2$Pb system and the other is Mg$_2$Pb-Pb.

9.13 Eutectoid and Peritectic Reactions

- In addition to the eutectic point, other invariant point may involve 3 different phases. An example of this reaction found in the copper-zinc system at 560°C and 74 wt% Zn – 26 wt% Cu (page 15); region around this point is enlarged as shown.
- Upon cooling a solid phase transforms into two other solid phases \(\rightarrow\) eutectoid (eutectic-like) reaction:
  \[
  \delta \xrightarrow{\text{Cooling}} \gamma + \epsilon \quad (9.14)
  \]
  The invariant point E (V shape) is termed eutectoid, and the horizontal tie line at 560°C is termed eutectoid isotherm. A eutectoid reaction is found in the iron-carbon system that is very important in the heat treatment of steels.
- Upon heating one solid phase transforms into a liquid phase and another solid phase \(\rightarrow\) peritectic reaction.
  \[
  \delta + L \xrightarrow{\text{Cooling}} \epsilon \quad (9.15)
  \]
  The invariant point, point P, is at 598°C and 78.6 wt% Zn – 21.4 wt% Cu. Five peritectic reactions may be found in the original phase diagram on page 15.
9.14 Congruent Phase Transformations (classification)

- Phase transformations for which there are no compositional alterations are called **congruent** transformations. **Examples:** allotropic transformations (e.g., $\alpha$-Fe to $\gamma$-Fe) and melting of pure metals.
- Conversely, those transformations for which at least one of the phases will experience a change in composition → called **incongruent transformations.** **Examples:** eutectic and eutectoid reactions, and melting of an alloy that belongs to an isomorphous system.
- The intermetallic compound Mg$_2$Pb melts congruently at the point M on the Mg-Pb diagram (see page 16).

9.15 Ceramic and Ternary Phase Diagrams

- Phase diagrams exist not only for metal-metal systems, but they also exist for ceramic systems (section 12.7).
- Phase diagrams have also been determined for metallic (as well as ceramic) systems containing more than two components; however, their representation and interpretation may be exceedingly complex. For example, a ternary (or three component) system has a 3-D phase diagrams.

9.16 The Gibbs Phase Rule (not covered)

**THE IRON–CARBON SYSTEM**

- Possibly the **most important binary alloy system.** Steels and cast irons are essentially iron-carbon alloys.
9.17 The Iron-Iron Carbide (Fe-Fe₃C) Phase Diagram

Figure shown represents a portion of the iron-carbon phase diagram with the following features:

- Pure iron (100 %wt Fe – 0 wt% C) upon heating along the left vertical axis:
  - At room temperature the stable form, called ferrite (or α iron), has a BCC crystal structure,
  - Ferrite experiences a polymorphic transformation to FCC austenite (or γ iron) at 912° C,
  - Austenite persists to 1394° C at which it reverts back to a BCC phase known as δ ferrite which finally melts at 1538° C.
- Composition axis extends only to 6.7 wt% C at which cementite (or iron carbide, Fe₃C) is formed along the right vertical axis.
- Carbon-iron system may extends from 6.7 wt% C to 100 wt% C (pure graphite). However, in practice all steels and cast irons have carbon contents < 6.7 wt% C. Thus we will consider only the iron-iron carbide system (Fe-Fe₃C) → 6.7 wt% C corresponds to 100 wt% Fe₃C.
- Carbon is an interstitial impurity in iron and form a single-phase solid solution with each of α ferrite, δ ferrite, and γ austenite.
- The maximum solubility in BCC α ferrite is 0.022 wt% C at 727° C. This limited solubility is explained by the shape and the size of the BCC interstitial positions, which make it difficult to accommodate the carbon atoms. Despite of this low concentration, carbon significantly influences the mechanical properties of ferrite. It is relatively soft and may be made magnetic at temperatures below 768° C with density 7.88 g/cm³. Next photomicrograph shows an α ferrite (90X).
- **Austenite** is *not stable* when alloyed by carbon alone below 727° C. The maximum solubility in FCC austenite is **2.14 wt% C at 1147° C** (100 times greater than that of \( \alpha \) ferrite), since the FCC interstitial positions are larger, and, therefore, the strains imposed on the surrounding iron atoms are much lower than for BCC ferrite (important for heat treatment of steels). Austenite is *nonmagnetic*. Next photomicrograph shows austenite (325X).

- The \( \delta \) ferrite is almost the same as \( \alpha \) ferrite except for the range of temperatures. The \( \delta \) ferrite is stable only at relatively high temperatures, and thus, it is **of no technological importance** and not discussed any further.

- **Cementite** (Fe\(_3\)C) forms when the solubility limit of carbon in \( \alpha \) ferrite is exceeded below 727° C, i.e.; compositions within \( \alpha + \text{Fe}_3\text{C} \) phase region. Cementite also coexists in \( \gamma + \text{Fe}_3\text{C} \) as solubility is exceeded between 727° C and 1147° C. **Cementite is hard and brittle** and the strength of some steels is greatly enhanced by its presence.

- Cementite is only **metastable**; it will remain as a compound indefinitely at room temperature. However, if heated to between 650 and 700 for several years, it will gradually change or transform into \( \alpha \) iron and carbon (graphite), which will remain upon subsequent cooling to room temperature. Thus, the phase diagram above is *not a true equilibrium* one because cementite is not an equilibrium compound. However, because as the decomposition rate of cementite is extremely sluggish, virtually all carbon in steel will be as \( \text{Fe}_3\text{C} \) instead of graphite, and the iron-iron carbide phase diagram is valid for all practical purposes (see section 11.2).

- Two-phase regions (4 of them) are labeled in the figure above; from which we notice
  - One **eutectic** invariant point at 4.3 wt% C and 1147° C; at which liquid solidifies to form austenite and cementite; for this *eutectic reaction*:
    \[
    \text{L} \xrightarrow{\text{Cooling}} \gamma + \text{Fe}_3\text{C} \quad (9.16)
    \]
  - One **eutectoid** invariant point at 0.76 wt% C and 727° C; at which \( \gamma \) solid phase transforms into \( \alpha \) iron and cementite; for this *eutectoid reaction* (important for heat treatment of steels):
    \[
    \gamma(0.76 \text{ wt% C}) \xrightarrow{\text{Cooling}} \alpha(0.022 \text{ wt% C}) + \text{Fe}_3\text{C}(6.7 \text{ wt% C}) \quad (9.17)
    \]

- **Ferrous alloys** are those in which iron is the primary component, but carbon and other alloying elements may present. There are three types of ferrous alloys: **iron, steel, and cast iron**.
  - Pure iron contains **< 0.008 wt% C**; composed of almost ferrite phase at room temperature.
  - Steel is iron-carbon alloy that contains between 0.008 – 2.14 wt% C, microstructure consists of both \( \alpha \) and \( \text{Fe}_3\text{C} \) phases. Upon cooling to room temperature, an alloy within this composition range must pass through at least a portion of \( \gamma \)-phase region; and thus changes in microstructure. In practice steel alloys rarely exceed **1.0 wt% C**.
  - Cast irons are ferrous alloys that contain 2.14 – 6.70 wt% C. However, commercial cast irons normally contain **< 4.5 wt% C** (section 11.2).
9.18 Development of Microstructure in Iron-Carbon Alloys

- The following discussion is confined to very slow cooling of steel alloys, in which equilibrium is continuously maintained.

9.18.a Eutectoid Alloys

- Consider an alloy of eutectoid composition 0.76 wt % C as it is cooled from point ‘a’ in the γ phase region at about 800° C, moving down along xx’, see figure.
- Initially, the alloy is entirely composed of the austenite phase with 0.76 wt % C and corresponds to a microstructure as shown.
- Continue cooling there will be no changes until the eutectoid temperature 727° C is reached. Upon crossing to point ‘b’, the austenite transforms according to Eq. (9.17). This eutectoid steel consists of alternating layers or lamellae of α and Fe₃C phases that form simultaneously during the transformation.
- This microstructure is called pearlite (it has the appearance of mother of pearl), see a photomicrograph of a eutectoid steel showing the pearlite which consists of grains (called colonies). Each colony has its own direction. The thick light layers are the ferrite phase and the cementite phase appears as thin lamellae most of which appear dark.
- Properties of pearlite are intermediate between soft, ductile ferrite and the hard, brittle cementite.
The microstructural change that accompanies this eutectoid transformation is represented schematically in the figure. Carbon atoms diffuse away from the 0.022 wt % ferrite regions and to the 6.7 wt % cementite layers, as the pearlite extends from the grain boundary into the unreacted austenite grain. The layered pearlite forms because carbon atoms need diffuse only minimal distances with the formation of this structure.

Subsequent cooling of pearlite from point ‘b’ will produce relatively insignificant microstructural changes.

9.18b Hypoeutectoid Alloys

(Similar to case 4 for the lead-tin alloy).

- Consider the composition $C_o$ to the left of the eutectoid between 0.022 – 0.76 wt % C; this is termed hypoeutectoid (less than eutectoid) alloy. Cooling down along line $yy'$.

- At point ‘c’ – about 875º C; the microstructure entirely consists of grains of the $\gamma$ phase.

- Cooling to point ‘d’ – about 775º C within $\alpha + \gamma$ phase region. Small $\alpha$ particles will form along the original $\gamma$ grain boundaries. Such composition may be determined using the approximate tie line (about 0.02 and 0.40 wt % C).

- Cooling further in the $\alpha + \gamma$ region from point ‘d’ to ‘e’ just above the eutectoid line will produce an increased fraction of the $\alpha$ phase as shown; $\alpha$ particles grow larger. Using a tie line at $T_e$ yield: the $\alpha$ phase will contain 0.022 wt % C, while the $\gamma$ phase will be of the eutectoid composition 0.76 wt % C.

- Lowering temperature below the eutectoid line to point ‘f’; all the $\gamma$ phase (existed at $T_e$) will transform to pearlite according to Eq. 9.17. There will be almost no change in the $\alpha$ phase that existed at point ‘e’, it will present as a continuous matrix phase surrounding the isolated pearlite colonies.

- From the inset at point ‘f’, the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the $\alpha + \gamma$ region. The ferrite that present in pearlite is called eutectoid ferrite, while that formed above $T_e$ is termed proeutectoid (pre- or before eutectoid) ferrite.
A photomicrograph of a 0.38 wt% C steel is shown next; large white regions correspond to proeutectoid ferrite. For pearlite, spacing between the \( \alpha \) and Fe\(_3\)C layers varies from grain to grain, some of the pearlite appears dark because the many close-spaced layers are vague at the magnification of the photomicrograph (635X).

The relative amounts of the proeutectoid and pearlite may be determined by using the lever rule in conjunction with a tie line. Consider an alloy composition \( C'_{\alpha} \) as shown. The fraction of the pearlite (\( \gamma \) in \( \alpha + \gamma \))

\[
W_p = \frac{T}{T + U} = \frac{C'_\alpha - 0.022}{0.76 - 0.022} = \frac{C'_\alpha - 0.022}{0.74}
\]

And the fraction of proeutectoid \( \alpha \) (\( \alpha \) in \( \alpha + \gamma \)) is computed as:

\[
W_{\alpha'} = \frac{U}{T + U} = \frac{0.76 - C'_\alpha}{0.76 - 0.022} = \frac{0.76 - C'_\alpha}{0.74}
\]

Of course, fractions of both total \( \alpha \) (eutectoid + proeutectoid) and cementite are determined using the lever rule and a tie line that extends across the total \( \alpha + \text{Fe}_3\text{C} \) phase region; from 0.022 to 6.7 wt % C.
9.18c Hypereutectoid Alloys

- Consider the composition $C_1$ to the right of the eutectoid between 0.76 – 2.14 wt % C; this is termed hypereutectoid alloy. Cooling down along line zz’.
- At point ‘g’, the microstructure entirely consists of grains of the $\gamma$ phase.
- Cooling to point ‘h’ within $\gamma$+Fe3C phase region, the cementite begins to form small Fe3C particles along the original $\gamma$ grain boundaries. This cementite is called proeutectoid cementite which forms before the eutectoid reaction. The cementite composition remain constant (6.7 wt% C) but the composition of the austenite phase will move along the line PO toward the eutectoid.
- Lowering temperature below the eutectoid line to point ‘i’; all the remaining austenite of eutectoid composition is converted into pearlite, thus, the resulting composition microstructure consists of pearlite and proeutectoid cementite as shown.
- A photomicrograph of a 1.4 wt% C steel is shown next; white proeutectoid cementite network surrounding the pearlite colonies (1000X). There is some difficulty in distinguishing between hypoeutectoid and hypereutectoid steels on the basis of microstructure.

- The relative amounts of both pearlite and proeutectoid Fe3C microconsituents may be computed for hypereutectoid steel alloys by using the lever rule in conjunction with a tie line. Consider an alloy composition $C'_1$ as shown (Page 22). The fraction of the pearlite:

$$ W_p = \frac{X}{V + X} \quad \text{(9.20)} $$

$$ = \frac{6.7 - C'_1}{6.7 - 0.76} = \frac{6.7 - C'_1}{5.94} $$

And the fraction of proeutectoid cementite is computed as

$$ W_{Fe3C'} = \frac{V}{V + X} \quad \text{(9.21)} $$

$$ = \frac{C'_1 - 0.76}{6.7 - 0.76} = \frac{C'_1 - 0.76}{5.94} $$

See Example 9.4
9.18.d Nonequilibrium Cooling

- So far, upon cooling, we have assumed conditions of metastable equilibrium have been continuously maintained; that is sufficient time has been allowed at each new temperature for any necessary in phase compositions and relative amounts.
- In most situations these cooling rates are impractically slow and really unnecessary, in fact, on many occasions nonequilibrium conditions are desirable.
- Two nonequilibrium effects of practical importance are (1) the occurrence of phase changes (transformations) at temperatures other than those predicted by phase boundary lines on the phase diagram, and (2) the existence at room temperature of nonequilibrium phases that do no appear on the phase diagram.

9.19 The Influence of Other Alloying Elements

- Adding alloying elements (Cr, Ni, Ti, ….) yields dramatic changes in the binary iron-iron carbide phase diagram. Alterations of the positions of the phase boundaries and the shapes of the phase regions depend on the alloying element and its concentration.
- One of these important changes is the shift in position of the eutectoid with respect to temperature and to carbon concentration.
- Figure shown illustrates the dependence of eutectoid temperature on alloy concentration for several alloying elements in steel.
- Figure shown illustrates the dependence of eutectoid composition on alloy concentration for several alloying elements in steel.
- Steels may also be alloyed to improve their corrosion resistance or to render them amenable to heat treatment.