

The Text books by Callister and Raghavan and others have been referred.

Module 2 Physical Metallurgy

Subject: Material Science and Engineering

Subject Code: BME303

Syllabus

Alloy Systems: Classification of Solid solutions, Hume- Rothery

Rules Diffusion: Diffusion Mechanisms: Vacancy Diffusion and Interstitial Diffusion, Fick's laws of diffusion, Factors affecting diffusion.

Phase Diagrams: Gibbs Phase Rule, Solubility limit, phase equilibrium and Phase Diagrams: Isomorphous systems, Invariant Binary Reactions: Eutectic reaction, Eutectoid reaction and Peritectic reaction, Lever Rule, Iron-Carbon Diagram. Effect of common alloying elements in steel. Numerical on Lever rule.

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Alloy Systems

The addition of impurity atoms to a metal result in the formation of a solid solution depending on the kinds of impurity, their concentrations, and the temperature of the alloy. The mixing of the elements in the solid is on the atomic scale. With regard to alloys, **Solvent** is the element or compound that is present in the greatest amount; on occasion, solvent atoms are also called **host atoms**. **Solute** is used to denote an element or compound present in a minor concentration.

A solution formed in the solid state when, as the solute atoms are added to the host material under the condition that the crystal structure is maintained and no new structures are formed is called a solid solution.

A solid solution is compositionally homogeneous; the impurity atoms are randomly and uniformly dispersed within the solid

Classification of Solid solutions

- 1. Interstitial and**
- 2. Substitutional**

Interstitial solid solution: For interstitial solid solutions, impurity atoms fill the *tetrahedral* and *octahedral*; voids or interstices among the host atoms. Typically, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%). For example, carbon is an interstitial solute in FCC iron and occupies the octahedral voids in the FCC structure.

Substitutional solid solution: When the solute and the solvent atoms are of comparable sizes, the solute substitutes for the solvent atom on a regular atomic site. For example, a 70% Cu-30% Zn alloy (alpha brass) has an FCC structure, with copper and zinc atoms occupying randomly the atomic sites of the FCC crystal.

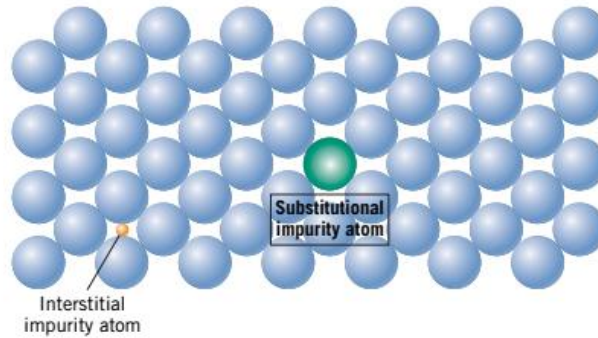


Figure: schematic representations of substitutional and interstitial impurity atoms

Hume- Rothery Rules

Rules for the formation of substitutional solid solution:

1. Atomic size factor. Appreciable quantities of a solute may be accommodated in this type of solid solution only when the difference in atomic radii between the two atom types is less than about $\pm 15\%$. Otherwise the solute atoms create substantial lattice distortions and a new phase forms.
2. Crystal structure. For appreciable solid solubility, the crystal structures for metals of both atom types must be the same.
3. Electronegativity factor. The more electropositive one element and the more electronegative the other, the greater the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.
4. Valences. Other factors being equal, a metal has more of a tendency to dissolve another metal of higher valency than to dissolve one of a lower valency

An example of a substitutional solid solution is found for copper and nickel. These two elements are completely soluble in one another at all proportions. With regard to the aforementioned rules that govern degree of solubility, the atomic radii for copper and nickel are 0.128 and 0.125 nm, respectively; both have the FCC crystal structure; and their electronegativities are 1.9 and 1.8. Finally, the most common valences are +1 for copper (although it sometimes can be +2) and +2 for nickel

Diffusion

DIFFUSION

The migration of atoms from their original lattice sites in a crystal structure to other sites is known as Diffusion.

Diffusion involves the movement of atoms, ions or molecules from one position to another position & occurs mainly due to another position & occurs mainly due to thermal agitation or the presence of concentration gradients.

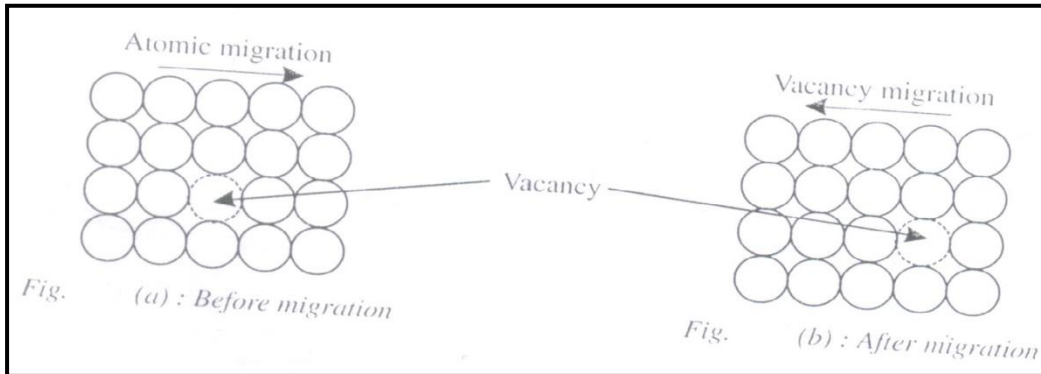
Diffusion in gaseous state is more than the liquid & solids.

DIFFUSION MECHANISMS

There 3 types of diffusion mechanisms can be explained in solids:

- I] Atomic diffusion by vacancy migration
- II] Atomic diffusion by Interstitialcy migration
- III] Diffusion by interchange of atoms

I] Atomic diffusion by vacancy migration:



When an atom moves into a vacancy, a new vacancy or a hole is created. In turn, this vacancy may receive an atom from any of the neighbouring sites. As a result the vacancy takes a *random walk* through the crystal.

II] Atomic diffusion by Interstitialcy migration:

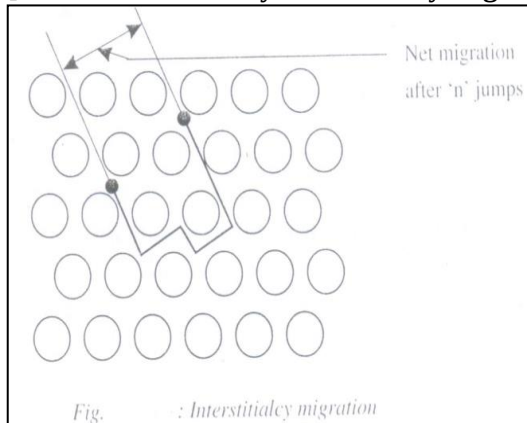


Fig: Atomic diffusion by Interstitialcy migration

FICKS I LAW OF DIFFUSIION:

It states that, the flux of atoms **J** moving across a unit surface area in unit time is proportional to the concentration gradient $\frac{dc}{dx}$.

Under steady state flow, $\mathbf{J} = -D \frac{dc}{dx}$

Where, J = No of atoms/unit area of diffusion per unit time (atoms/m².sec)

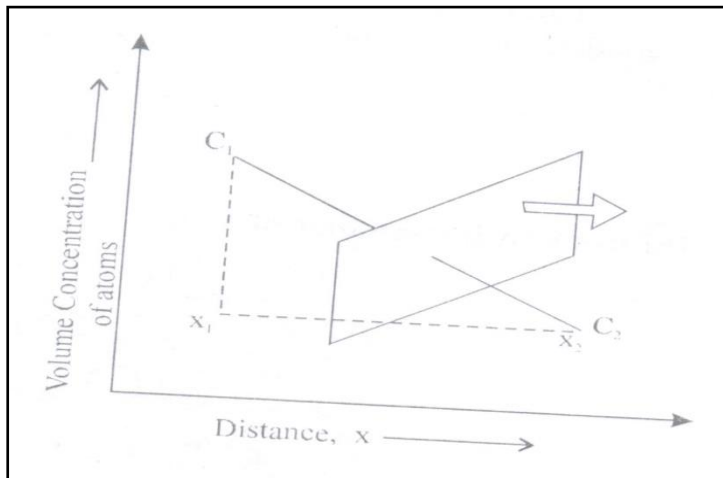
C = Volume concentration of atoms (atom/m³)

X = Distance between the planes in the direction of flow of atoms (m)

D = diffusion co-efficient or diffusivity (m²/sec)

-ve sign indicates that flux moves from higher to lower concentration.

The geometry of Fick's Ist law is illustrated below.



J = flux of atoms across plane
with unit area

$$J = -D \frac{dc}{dx} = -D [C_2 - C_1 / x_2 - x_1]$$

$\frac{dc}{dx}$ = Concentration gradient

FICKS II LAW OF DIFFUSION

This law relates to the rate of change in concentration with time. This non-steady state condition is represented by a second order differential equation.

It states that, $dc/dt = D [d^2c/dx^2]$

Where $\frac{dc}{dx}$ = Concentration gradient

D = diffusion coefficient

$$\frac{dc}{dt}$$

= the rate of accumulation of diffusing atoms at a point where the concentration gradient is dc/dx .
i.e., rate of compositional change

Fick's IInd law is also stated as, "the rate of compositional change is equal to the diffusivity times the rate of change of the concentration gradient".

In general, steady state diffusion in which conditions do not change with time is not commonly encountered in engineering materials. In most cases non-steady state diffusion in which the concentration of solute atoms at any point in the material changes with time takes place. Ex: If carbon is being diffused into the surface of a steel camshaft to harden its surface, the concentration of the carbon under the surface at any point will change with time as the diffusion process progresses. It is for these cases of non-steady state diffusion in which diffusivity is independent of time. Fick's IInd law of diffusion is applied.

Diffusivity

Diffusivity or the coefficient of diffusion (D) is defined as the amount of substance diffusing in unit time across unit area through a unit concentration gradient & its unit is m^2/sec .

The coefficient of diffusion of various materials varies with crystal structure & temperature.

ACTIVATION ENERGY

- In any diffusion mechanism, work must be done if the atoms are to move from one location to another.
- To do this work, an energy barrier must be overcome for the atoms to begin a jump from one site to another site.
 - ✓ *The minimum energy required by the atoms to overcome this energy barrier is called the Activation energy of diffusion.*
- In a vacancy mechanism, energy is required to pull the atoms from their positions to vacant atomic sites
- In the Interstitialcy mechanism energy is required to force the atoms between other atoms to different interstitial positions.

Activation energy depends on a number of factors. They are:

 - A small atom has lower activation energy than a large atom or molecule.
 - Interstitial movements require more energy than vacancy movements.
 - High activation energies are required for atomic diffusion for those materials which are strongly bonded & have higher melting points.

Ex: Tungsten, boron-carbide, silicon carbide.

Arrhenius equation

An Arrhenius type equation for atomic diffusion is given by,

$$D = D_0 e^{(-Q/RT)}$$

Where D = Diffusion coefficient (m²/sec)

D₀ = Constant (m²/sec)

Q = Activation energy for diffusion (J/mol)

R = Universal gas constant (8.314 J/mol-K)

T = Absolute temperature (K)

The values of D₀ & Q are determined from a plot of $\ln D$ along y-axis & $1/T$ along x-axis. This plot yields a straight line, the slope of which is $-Q/R$. The intercept on the y-axis is $\ln D_0$.

FACTORS AFFECTING ATOMIC DIFFUSION

- 1] TEMPERATURE: High temperature provides the necessary activation energy to the atoms to begin diffusion. So a higher temperature initiates diffusion faster.
- 2] CRYSTAL STRUCTURE: If a crystal structure is distorted, i.e., if there are more imperfections the rate of diffusion is increased.
- 3] ATOMIC PACKING FACTOR: If APF is high; the rate of diffusion will be decreased. Diffusion is much slower in FCC-iron than in BCC-iron.

4] GRAIN BONDARIES: The diffusion process proceeds more rapidly along the grain boundaries since it is a zone of crystal imperfections.

5] GRAIN SIZE: Since diffusion through grain boundaries is faster than through the grains themselves, a material with finer grains will have a faster rate of diffusion.

6] ATOMIC SIZE: Diffusion occurs more readily when the size of the diffusing atom is less.
Ex : Carbon in iron.

7] CONCENTRATION GRADIENT: Higher the concentration gradient higher will be the rate of diffusion.

Phase Diagrams/ equilibrium diagrams:

Phase diagrams are maps that give the relationships between phases *in equilibrium* in a system as a function of temperature, pressure and composition

Component

Components are pure metals and/or compounds of which an alloy is composed.

System

System, which has two meanings. System may refer to a specific body of material under consideration (e.g., a ladle of molten steel), or it may relate to the series of possible alloys consisting of the same components but without regard to alloy composition (e.g., the iron-carbon system).

Phase

A phase can be defined as a physically distinct and chemically homogeneous and mechanically separable region of a system that has a particular chemical composition and structure.

Ex: Water in liquid or vapour state is single phase.

Gibbs Phase Rule

Gibbs phase rule is a thermodynamic law that represents a criterion for the number of phases that coexist within a system at equilibrium. It is expressed by the simple equation:

$$P + F = C + N \quad \text{Eq (1)}$$

Where,

P is the number of phases present

F is termed the *number of degrees of freedom*, or the number of externally controlled variables (e.g., temperature, pressure, composition) that must be specified to define the state of the system completely or

F is the number of these variables that can be changed independently without altering the number of phases that coexist at equilibrium.

C , the number of components in the system

N is the number of noncompositional variables (e.g., temperature and pressure)

As most phase diagrams are constructed at is constant (1 atm), the parameter N is 1—temperature is the only noncompositional variable. Therefore, Eq (1) becomes:

$$P + F = C + 1 \quad \text{Eq (2)}$$

In the case the number of components, $C=2$, then Eq (2) takes the form:

$$P + F = 2 + 1 = 3 \text{ or } F = 3 - P \quad \text{Eq (3)}$$

One can completely describe the characteristics of any alloy that exists within a phase fields or at the phase boundaries by knowing the number of phases that exist under equilibrium .

For a Single phase region, $F=2$ as $P=1$; This means that to completely describe the characteristics of any alloy that exists within the single phase region, we must specify two parameters—composition and temperature, which locate, respectively, the horizontal and vertical positions of the alloy on the phase diagram.

For a Two phase region, $F=1$ as $P=2$; Thus, it is necessary to specify either temperature or the composition of one of the phases to completely define the system. One may choose temperature or the composition.

Note: that only the nature of the phases is important in this treatment and not the relative phase amounts

For a Three phase region, $F=0$ as $P=3$; This means that the compositions of all three phases—as well as the temperature—are fixed

Solubility limit

For many alloy systems and at some specific temperature, there is a maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution; this is called a solubility limit. The addition of solute in excess of this solubility limit results in the formation of another solid solution or compound that has a distinctly different composition.

Phase Equilibria

Equilibrium is a state in which opposing forces or influences are balanced. A system is at equilibrium if its free energy is at a minimum under some specified combination of temperature, pressure, and composition. In a macroscopic sense, this means that the

characteristics of the system do not change with time but persist indefinitely—that is, the system is stable. A change in temperature, pressure, and/or composition for a system in equilibrium results in an increase in the free energy and in a possible spontaneous change to another state by which the free energy is lowered.

Metastable: in solid systems, that 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 changes as time progresses

Binary isomorphous systems

The simplest binary phase diagram is obtained for a system exhibiting complete liquid solubility as well as solid solubility. The two components dissolve in each other in all proportions both in the liquid and the solid states. Clearly, the two components must have the same crystal structure besides satisfying the other Hume Rothery's conditions for extensive solid solubility. Ex: Cu–Ni, Ag–Au, Ge–Si and Al_2O_3 – Cr_2O_3

Figure shows the phase diagram of Al_2O_3 – Cr_2O_3 . Pure Al_2O_3 and pure Cr_2O_3 form the left and the right end of the composition axis. They are arranged in alphabetical order from left to right. The composition is read as per cent of Cr_2O_3 starting from 0% at left and going to 100% at the right end. Alternatively, the composition can be read as per cent of Al_2O_3 from right to left. Temperature is shown along the y-axis. There are only two phases on the phase diagram, the liquid and the solid phases. The single-phase regions are separated by a two-phase region ($L + S$), where both liquid and solid co-exist. In all binary phase diagrams, a two-phase region separates single-phase regions, as given by the “1-2-1” rule. As we move from a single-phase region (1), we cross into a two-phase region (2), and then again into a single-phase region (1). The phase boundary between the liquid and the two-phase region is called the *liquidus*. The boundary between the solid and the two-phase region is called the *solidus*.

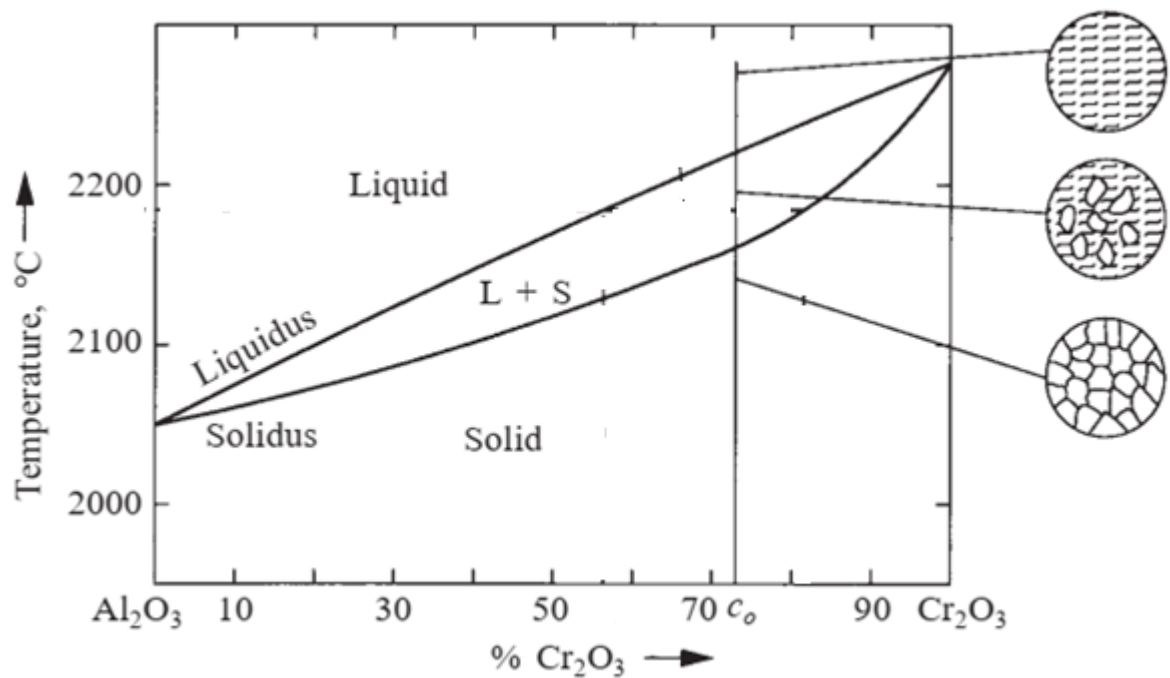


Figure: The Al_2O_3 - Cr_2O_3 phase diagram. Microstructural changes in an overall composition c_0 are sketched on the right

Invariant binary reactions

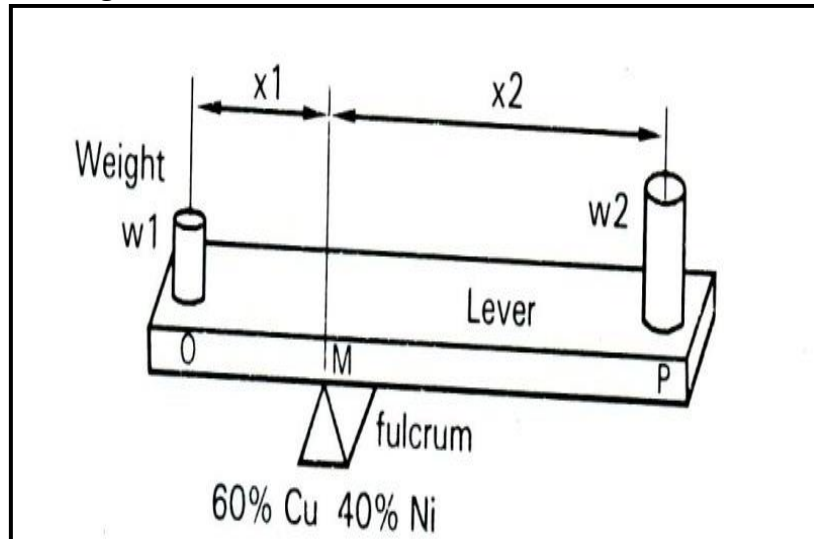
An invariant reaction for a binary alloy is one occurring when three phases are in equilibrium. Application of the Gibbs phase rule to this system under constant pressure conditions indicates that it has no degrees of freedom and, therefore, the composition of the phases and the temperature of the reaction are all fixed.

Table-1: Summary of invariant reactions in binary systems.

Reaction	Symbolic equation	Schematic presentation	Example
Eutectic	$L \leftrightarrow \alpha + \beta$		Fe-C, 4.27% C, 1147 $^{\circ}\text{C}$
Eutectoid	$\alpha \leftrightarrow \beta + \gamma$		Fe-C, 0.80% C, 723 $^{\circ}\text{C}$
Peritectic	$L + \alpha \leftrightarrow \beta$		Fe-C, 0.16% C, 1495 $^{\circ}\text{C}$
Peritectoid	$\alpha + \beta \leftrightarrow \gamma$		
Monotectic	$L_1 \leftrightarrow L_2 + \alpha$		Fe-C, 0.51% C, 1495 $^{\circ}\text{C}$

Lever Rule

It is possible to determine the amount or quantity of each phase at a given temperature using the lever rule or inverse lever rule. The lever rule can be explained by considering a simple balance as shown in figure.



Simple balance to demonstrate lever rule

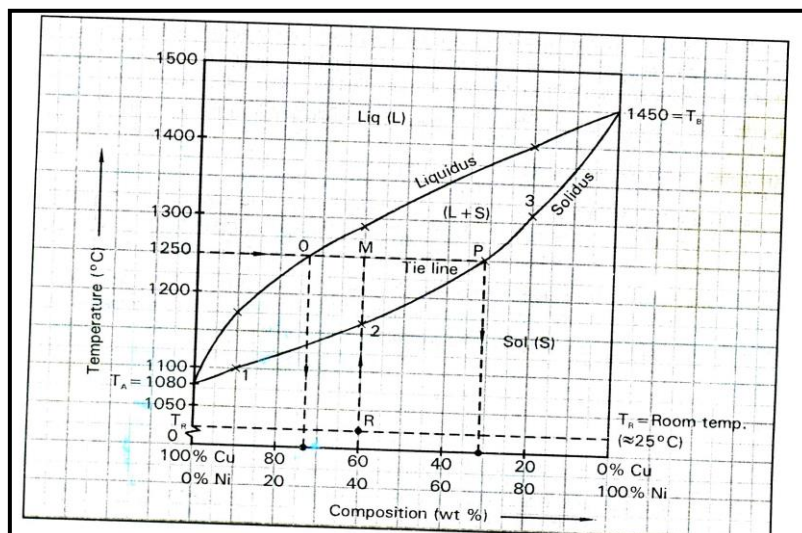
Comparing the simple balance with the phase diagram in figure 5.9, the horizontal constant temperature tie line (OMP) represents the lever, the total composition of the alloy (60% Cu and 40% Ni) represents the fulcrum, and the compositions of the two phases represents the weights (w_1 & w_2) at the ends of the lever. If the lever is to be balanced, or be in equilibrium without moving up or down on either side.

$$\text{Weight (w1)} \times \text{distance (x1)} = \text{weight (w2)} \times \text{distance (x2)}$$

(1)

In metallurgy, the relative amounts of the two phases present are determined in a similar way to that of the weights needed to balance the lever, i.e., the amount of a given phase multiplied by its lever arm is = to the amount of the other phase multiplied by its (i.e., other) lever arm.

Applying lever rule to the copper - nickel alloy system shown in figure



we have

$$\begin{aligned} \text{(i) amount of solid phase at } M &= \frac{OM}{OP} \times 100 \\ &= \frac{73-60}{73-31} \times 100 = 30.95 \% \end{aligned}$$

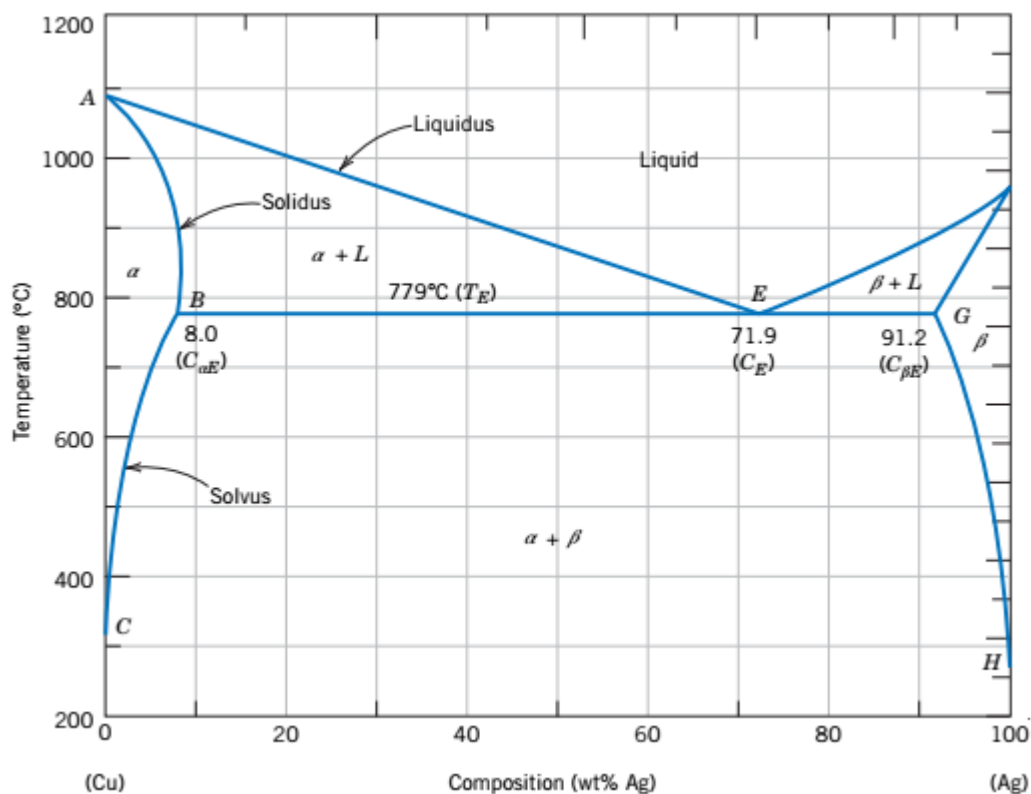
$\therefore$ Amount of solid phase at $M = 30.95 \%$

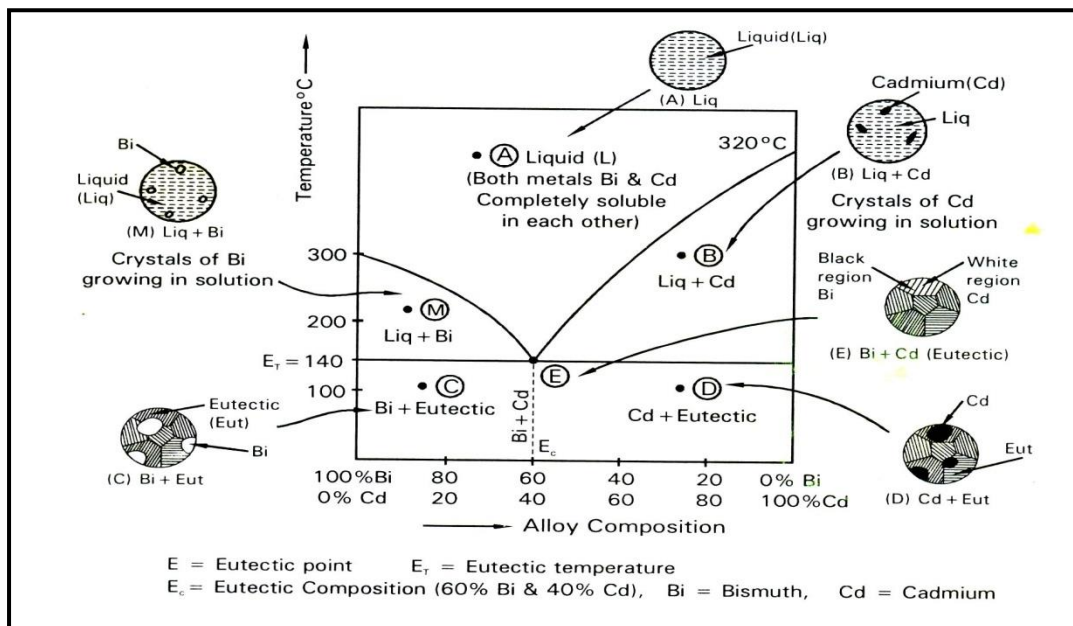
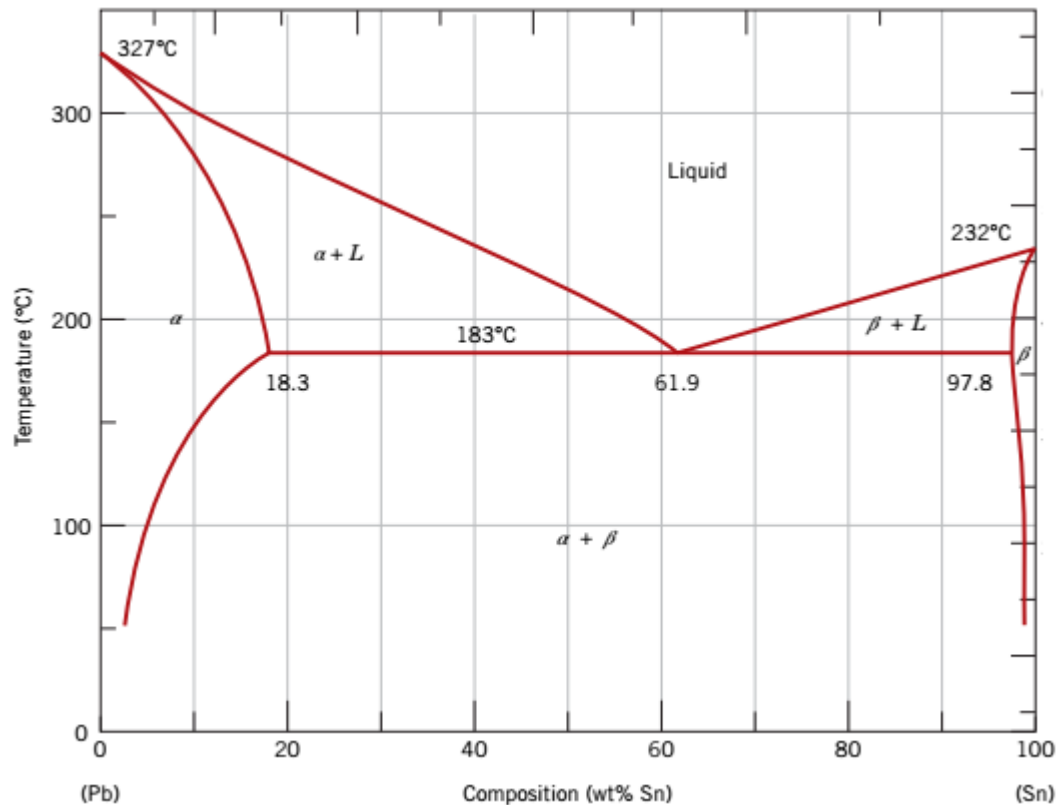
$$\begin{aligned} \text{(ii) amount of liquid phase at } M &= \frac{MP}{OP} \times 100 \\ &= \frac{60-31}{73-31} \times 100 = 69.04 \% \end{aligned}$$

Amount of liquid phase at $M = 69.04 \%$

Note that, in the above equations the right side of the tie line gives the proportion of the phase on the left i.e., liquid phase, and left side of the tie line gives the proportion of the phase to the right i.e., solid phase.

Important phase- diagrams



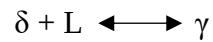


Iron-Carbon Diagram:

Fe and Fe_3C (iron carbide) are the components in the Fe- Fe_3C phase diagram. It is also possible to have a phase diagram with Fe and C (graphite) as the components. Graphite is more stable than Fe_3C . So, the Fe- Fe_3C diagram can be considered to be a metastable phase diagram. Most steels contain only iron carbide and not graphite.

The composition is plotted on the x-axis as weight per cent of carbon. Pure iron melts at 1535°C. A peritectic invariant reaction occurs at 1493°C with the peritectic composition at 0.18% carbon:

cool $\longrightarrow$



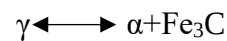
The product phase γ is called *austenite*. A eutectic reaction occurs at 1150°C with the eutectic composition at 4.3% carbon:

cool $\longrightarrow$



A eutectoid reaction occurs at 725°C with the eutectoid composition at 0.8% carbon:

cool $\longrightarrow$



Here, austenite (γ) decomposes into two phases—ferrite (α) and cementite (Fe_3C).

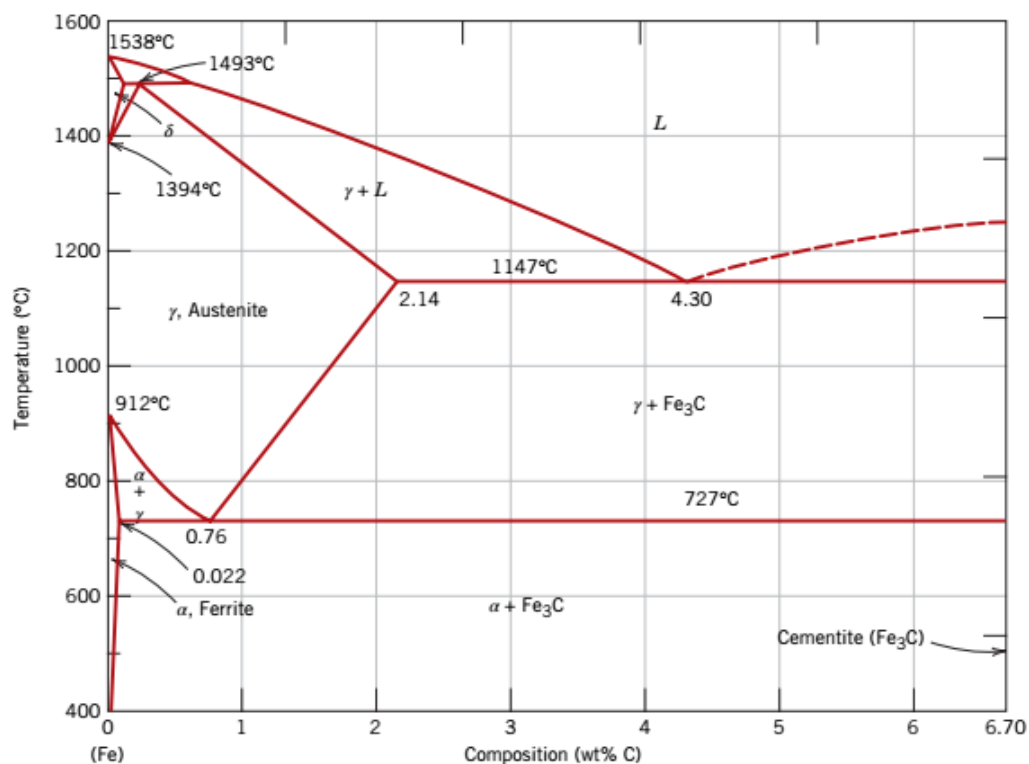
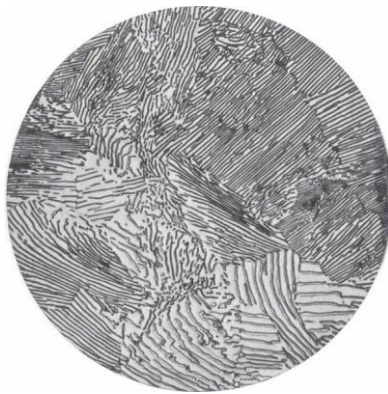


Figure: The iron–iron carbide phase diagram

Fe–C alloys containing 0–1.4% carbon are called *steels*. Consider the microstructures of slowly cooled steels of different carbon content. When the carbon content is negligible, the structure of steel is essentially polycrystalline α (ferrite), which is the interstitial solid solution of carbon in BCC iron.

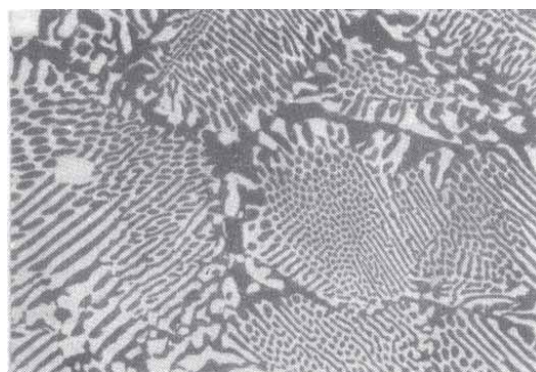
When the steel has the eutectoid composition of 0.8% carbon, the microstructure consists of alternate layers of thin, parallel plates of (ferrite) and Fe_3C (cementite). This eutectoidal mixture is called *pearlite*. Pearlite is a microconstituent, and not a single phase. It is so named as it has an iridescent appearance under the microscope, resembling the mother of pearl as shown in Figure below.



Microstructure of eutectoid steel showing pearlite, magnified 1000 times.

Beyond 0.8%, high carbon steels contain proeutectoid cementite in addition to pearlite.

Fe–C alloys with more than 2% carbon are called *cast irons*. Consider, for example, the cooling of a cast iron with 3% carbon.. On crossing the liquidus into the (L + γ) region, proeutectic (austenite) crystallizes first. On passing through the eutectic temperature, liquid of eutectic composition decomposes to a mixture of austenite and cementite. On further cooling through the eutectoid temperature, the austenite decomposes to pearlite, yielding white cast iron. The microstructure of white cast iron consists of cementite and pearlite, see Fig. below. Due to the presence of the large fraction of cementite, white cast iron is very hard and brittle.



Microstructure of white cast iron, magnified 650 times. White regions are cementite and dark regions are unresolved pearlite

Effect of common alloying elements in steel

Additions of other alloying elements (Cr, Ni, Ti, etc.) bring about rather dramatic changes in the binary iron–iron carbide phase diagram, Figure 9.24. The extent of these alterations of the positions of phase boundaries and the shapes of the phase fields depends on the particular alloying element and its concentration. One of the important changes is the shift in position of the eutectoid with respect to temperature and to carbon concentration. These effects are illustrated in Figures 9.34 and 9.35, which plot the eutectoid temperature and eutectoid composition (in wt% C) as a function of concentration for several other alloying elements. Thus, other alloy additions alter not only the temperature of the eutectoid reaction but also the relative fractions of pearlite and the proeutectoid phase that form. Steels are normally alloyed for other reasons, however usually either to improve their corrosion resistance or to render them amenable to heat treatment

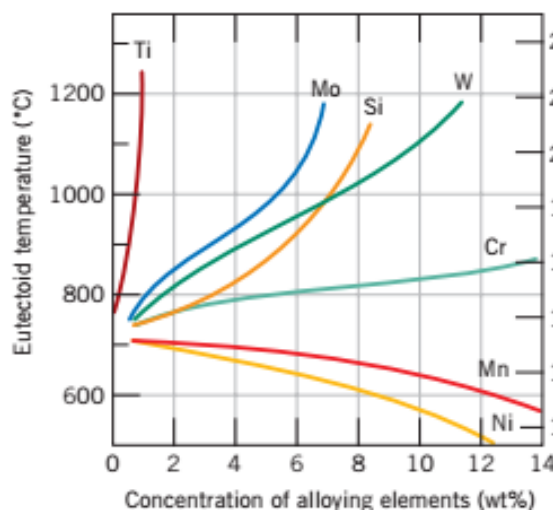


Figure 9.34 The dependence of eutectoid temperature on alloy concentration for several alloying elements in steel. (From Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)

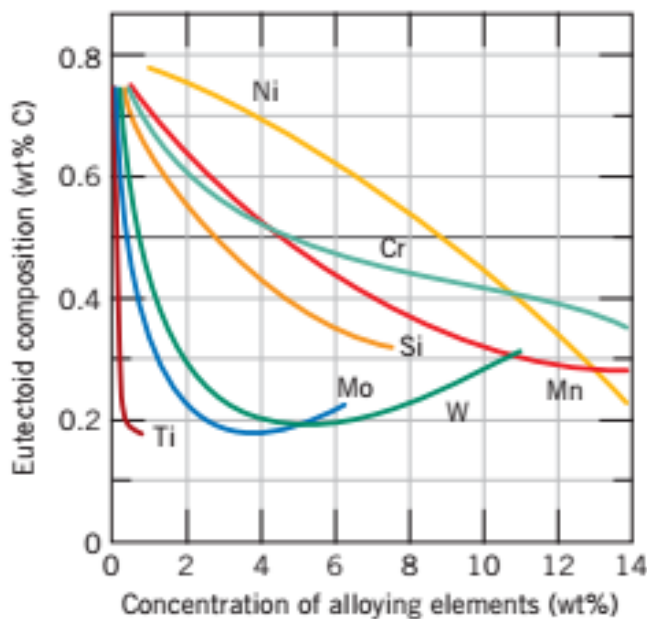


Figure 9.35 The dependence of eutectoid composition (wt% C) on alloy concentration for several alloying elements in steel. (From Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 127.)