

ME 3392 -ENGINEERING MATERIALS AND METALLURGY

UNIT- I

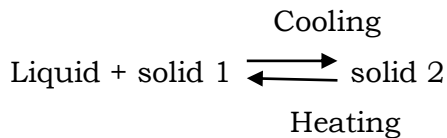
Alloys and Phase Diagrams

Constitution of alloys – Solid solutions, substitutional and interstitial – phase diagrams, Isomorphous, eutectic, eutectoid, peritectic, and peritectoid reactions, Iron – carbon equilibrium diagram, Classification of steel and cast Iron microstructure, properties and application

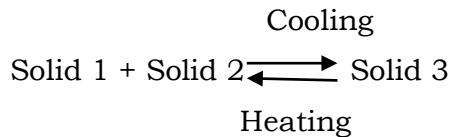
TWO MARKS:

1. State peritectic and peritectoid reactions. (APR/May 2010)

The Peritectic reaction can be written as



The peritectoid reaction can be written as



2. Distinguish between steel and cast iron. Also classify steel with respect to carbon percentage. (APR/May 2010)

The alloys of iron-carbon system containing 0.06% to 2.0% carbon are known as **steel**. Those alloys having carbon from 2.0% to 6.7% are called **cast-iron**.

Steels that contain 0.8% C are called eutectoid steels. Steels having less than 0.8% C are known as **hypoeutectoid steels**. Steels having more than 0.8% C are known as **hypereutectoid steels**.

3. What are interstitial solid solutions and interstitial compounds? (APR/May 2010)

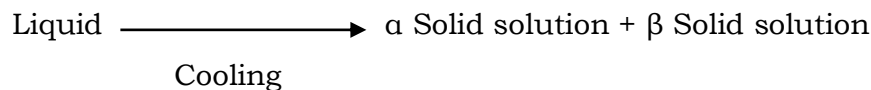
In interstitial solid solution, the solute atoms fit into the space between the solvent or parent atoms.

The compound formed by two or more metals in an apparently stoichiometric proportion is called intermetallic compounds.

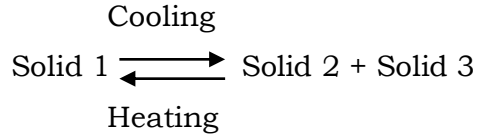
4. Differentiate between eutectic and eutectoid phase reactions. (APR/May 2010)

The eutectic reaction can be written as

Eutectic temperature



The eutectoid reaction can be written as



5. Define Solid Solution. (NOV/DEC 2009)

A solid solution may be defined as a solid that consists of two or more elements atomically dispersed in a single-phase structure.

6. How are steels classified? (NOV/DEC 2009)

Steels can be classified as follows:

1. Plain carbon (Or non-alloy) steels.
 - (i) Low carbon steels,
 - (ii) Medium carbon steels,
 - (iii) High carbon steels.
2. Alloys steels
 - (i) Low alloy steels,
 - (ii) High alloy steels.

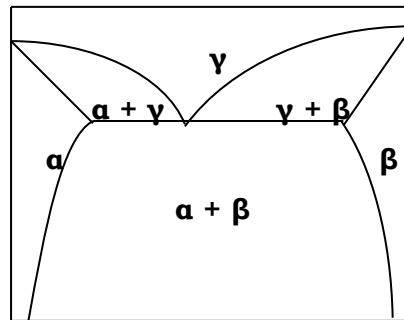
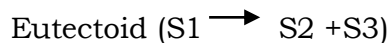
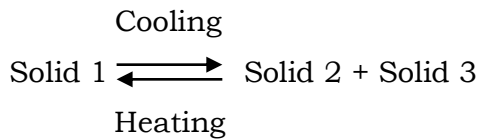
7. What do you mean by substitutional solid solution? Briefly explain the rules governing the formation of substitutional solid solution. (May/June 2009)

- ✓ When the solute atoms (impurities) substitute for parent solvent atoms in a crystal lattice, they are called substitutional atoms and the mixture of the two elements is called a substitutional solid solution.
- ✓ Hume Rothery's rules govern the formation of substitutional solid solution.

1. Size factor
2. Crystal structure
3. Valence
4. Electro negativity

8. Name and explain any one type of binary solid to solid state transformation reaction with ideal phase diagram? (May/June 2009)

The eutectoid reaction can be written as



9. Why carbon solubility is more in an austenite? APR/May 2008)

Austenite is a primary solid solution based on γ iron having FCC structure. Carbon solubility is more in austenite because austenite is an interstitial solid structure of carbon in iron.

10. List the advantages of alloy steels as compared to plain carbon steels. (APR/May 2008)

Better harden ability.
Less distortion and cracking.
Improved strength, toughness and resistance to abrasion and wear.
Higher elastic ration and endurance strength.

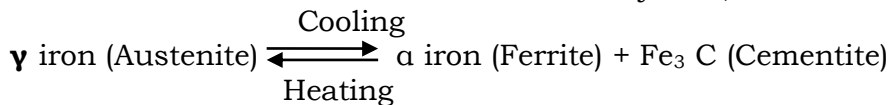
11. What is substitutional solid solution? Give two examples. (Nov/Dec 2007)

When the solute atoms (impurities) Substitute for parent solvent atoms in a crystal lattice, they are called substitutional atoms, and the mixture of the two elements is called substitutional solid solution.

Example : Cu-Ni system, Cu-Zn system, and Au-Cu system

12. Give and example of eutectoid reaction. (Nov/Dec 2007)

The eutectoid reaction is observed in Fe-C system, as shown below.

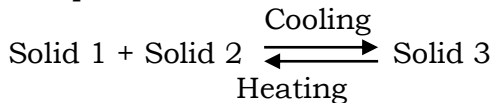


13. Distinguish between hypo-eutectoid steels and hyper-eutectoid steels. (May/June 2007)

Hypoeutectoid steels having less than 0.8% C are known as hypoeutectoid steels.

14. Define peritectoid reaction. (May/June 2007)

- ✓ Peritectoid reaction is an isothermal reversible reaction in which two solid phases transform into a third solid phase upon cooling.
- ✓ The peritectoid reaction can be written as



15. State the conditions under which two metallic elements will exhibit unlimited solid Solubility. (Nov/Dec 2006)

- ✓ To exhibit unlimited solid solubility, the solute and solvent elements should obey the following general rules of Hume Rothery.

16. Define the terms “ferrite” and “austenite” in iron-carbon alloy systems. (Nov/Dec 2006)

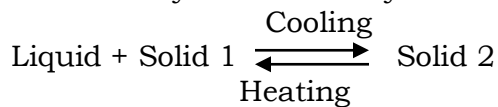
- ✓ Ferrite is a primary solid solution based on α iron having BCC structure. Austenite is a primary solid solution based on γ iron having FCC structure. Both are interstitial solid solution of carbon in iron.

17. What are the effects of crystal structure and atomic radii on formation of solid solution between two metallic elements Hume Rothery's Rules? (May/ June 2006)

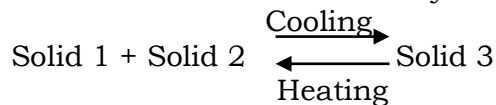
- ✓ Crystal structure : The two metallic elements that form solid solution must have the same crystal structure. Otherwise there is some point at which a transition occurs from one phase to a second phase with a different structure.
- ✓ Atomic radii : The solute and solvent elements atoms must be of similar size, with less than a 15% difference in atomic radius.

18. Define Peritectic and Eutectoid reactions. (Nov/Dec 2006)

- ✓ In peritectic reaction, upon cooling, a solid and a liquid phase transform isothermally and reversibly to a solid phase having a different composition.



- ✓ Eutectoid reaction is an isothermal reversible reaction in which one solid phase transforms into two intimately mixed new solid phases, upon cooling.



19. What is an alloy?

A metal alloy, or simply an alloy, is a mixture of two or more metals or a metal (metals) and a non-metal (non-metals)

20. What is meant by base metal?

In an alloy, the element which is present in the largest proportion is called the base metal.

21. What are alloying elements?

In an alloy, all elements other than the base metal are called the alloying elements

22. Differentiate between substitutional and interstitial solid solution.

In a substitutional solid solution, the solute atoms (impurities) substitute for parent solvent atoms in a crystal lattice.

In interstitial solid solution, the solute atoms fit in to the space between the solvent or parent atoms

23. State Hume Rothery's rules for formation of substitutional solid solutions. (May/June 2005)

Size factor: The atoms must be of similar size, with less than a 15% difference in atomic radius (in order to minimize the lattice strain).

Crystal structure: The materials must have the same crystal structure.

Valence: The atoms must have the same valence.

Electro negativity: The atoms must have approximately the same electro negativity.

24. What are intermediate phases? (Apr/May 2011)

If an alloying element is added in excess of the limit of solid solubility, a second phase appears along with the primary solution. If the second phase differs in both crystal structure and properties from primary solid solution, then it is known as an 'intermediate' phase.

25. How many components are found in an alloy?

Two or more components are found in an alloy.

26. Define 'phase. What different kinds of phases are possible?

A phase is defined as any physically distinct, homogeneous, and mechanically separable portion of substance. Three different kinds of phases are solid, liquid and vapour.

27. What are intermetallic compounds?

The compounds formed by two or more metals in apparently stoichiometric proportion is called intermetallic compounds.

28. What is an equilibrium phase diagram?

A phase diagram can be defined as a plot of the composition of phases as a function of temperature in any alloy system under equilibrium conditions.

29. State Gibb's phase rule?

Gibb's phase rule is given by

$$F = C - P + 2$$

F = Degrees of freedom of system or the number of variables that may be changed independently without altering the equilibrium.

C = Number of components forming the system

P = Number of phases present in the system.

30. What is liquidus line? A solidus line? A solvus line?

In a phase diagram, liquidus line is the line or boundary that separates liquid and liquid + solid phase regions. Solidus line is the line or boundary that separates solid a solid + liquid phase regions. Solvus lines separate single phase solid regions from two phase solid regions.

31. What is tie-line?

A tie line is simply an isothermal line drawn through the point of consideration, extending across the two phase region and terminating at the phase boundary lines on either side.

32. Define Cementite and Pearlite. (Nov/Dec 2008)

Cementite is the name given to the carbide of iron (Fe_3C). It is the hard, brittle, intermetallic compound of iron with 6.69% of carbon.

Pearlite is the eutectoid mixture of ferrite (87.5%) and cementite (12.5%). It is formed when austenite decomposes during cooling. It contains 0.8% of carbon.

33. Define Martensite and Bainite.

Martensite is the super saturated solid solution of carbon in a iron. It is formed when a steel is very rapidly cooled from the austenitic state.

Bainite is a decomposition product of austenite consisting of an aggregate of ferrite and carbide. Bainite has hardness in between the hardness of pearlite and martensite.

34. Why is the iron-carbon equilibrium diagram usually not shown beyond 6.67% carbon?

This is because in practice, all steels and cast iron have carbon contents less than 6.67 wt % C.

35. How does cast iron differ from steels in terms of carbon content? (Nov'08)

Composition from 0.008% to 2% carbon represent steel, and those above 2% carbon represent cast iron.

36. Define polymorphism. (Nov/Dec 2009)

Pure iron is an allotropic metal. Allotropy refers to the possibility of existence of two or more different crystal structures for a substance depending upon temperature. This phenomenon is also known as polymorphism.

37. What are cooling curves?(May/June 2005)

Cooling curves are obtained by plotting the measured temperatures at equal intervals during the cooling period of a melt to a solid.

38. Write the constitution of austenite and its crystal structure. (May/June 2013)

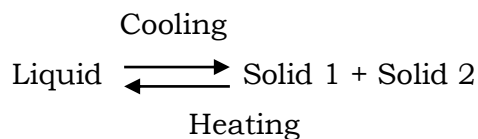
Austenite is a primary solid solution based on γ iron having FCC structure. Carbon solubility is more in austenite because austenite is an interstitial solid structure of carbon in iron.

39. Classify plain carbon steel. (May/June 2013) .(NOV 2013)

- (i) Low carbon steels,
- (ii) Medium carbon steels,
- (iii) High carbon steels.

40. Define Eutectic reactions.(NOV 2013)

Fe-C, Al-Mn, Pb-Sn form an eutectic system.



16 MARKS:

**1. How are solid solution classified? Give two examples for each?
(Apr'08,May'13)**

Solid Solution Type:

When the two components of a binary alloy remain completely mixed in each other both in liquid and solid state, the two components are said to be soluble in each other and a different type of solution may be formed. It is called a solid solution.

SOLID SOLUTIONS

A solid solution forms when, as the solute atoms are added to the host material, the crystal structure is maintained, and no new structures are formed. In other words, when elements completely dissolve in each other in liquid and or solid state the resulting phase is called *solid solution*. Solid solutions form readily when solvent and solute atoms have similar sizes and electron structures, so that it is compositionally or chemically homogeneous and the component atoms of the elements cannot be distinguished physically or separated mechanically. There is a homogeneous distribution of the constituents in the solid state so as to form a single phase or solid solution. Basically, solid solutions are of two types:

(a) Substitutional Solid Solution

When the two metals in solid solution form a single face centred cubic lattice, i.e., in general solute or impurity atoms replace or substitute for the host atoms, is called as substitutional solid solution. One may also define solid solutions as crystalline phases of a variable composition. Atoms of a solute *B* can be arranged in the crystal lattice of a solvent *A* either by substituting for some atoms of the latter in the crystal lattice or by occupying the interatomic spaces between atoms, or interstices.

We may note that the atoms of the two metals be of almost same size, i.e., the difference in atomic radii between the two atom types be less than about $\pm 15\%$. Otherwise the solute atoms will create substantial lattice distortion and a new phase will form. For appreciable solid solubility the crystal structures or metals of both atoms must be same.

If one element has more electropositivity and the other more electronegativity, then there is greater likelihood that they will form an intermetallic compound instead of a substitutional solid solution. It is also observed that other factors being equal, i.e. atomic size, crystal structure and electronegativity, a metal will have more of a tendency to dissolve another metal of higher valency than one of a lower valency. A familiar example of substitutional solid solution is found for copper and nickel to form monel.

These two elements are completely soluble in another at all proportions. Brass, an alloy of copper and zinc, is another example, which forms solid solutions most readily as the atoms of these two elements have similar sizes and electronic structure unlimited solubility in the solid state can be observed in copper-gold, and germanium-silicon alloys. Polymorphous metals may possess unlimited solubility within a single modification of the space lattice.

For example, Fe_α can form a continuous series of solid solutions with Cr (BCC lattices) and Fe_γ , a continuous series of solid solutions with Ni (FCC lattices). The formation of solid solutions is always associated with an increase of electric resistance and decrease of the temperature coefficient of electric resistance. Solid solutions are usually less plastic (except for copper-based solid solutions) and always harder and stronger than pure metals. Substitutional solid solutions are of two types:

- (i) Random substitutional solid solutions and
- (ii) Ordered substitutional solid solutions.

When there is no order in the substitution of the two metal elements (Fig. 9.1(a)), the chance of one metal element occupying any particular atomic site in the crystal is equal to the atomic percent of the element in the alloy. Obviously, in such a situation the concentration of solute atoms can vary considerably throughout the lattice structure. Such type of the resulting solid solution is called a *random* or *disordered* substitutional solid solution.

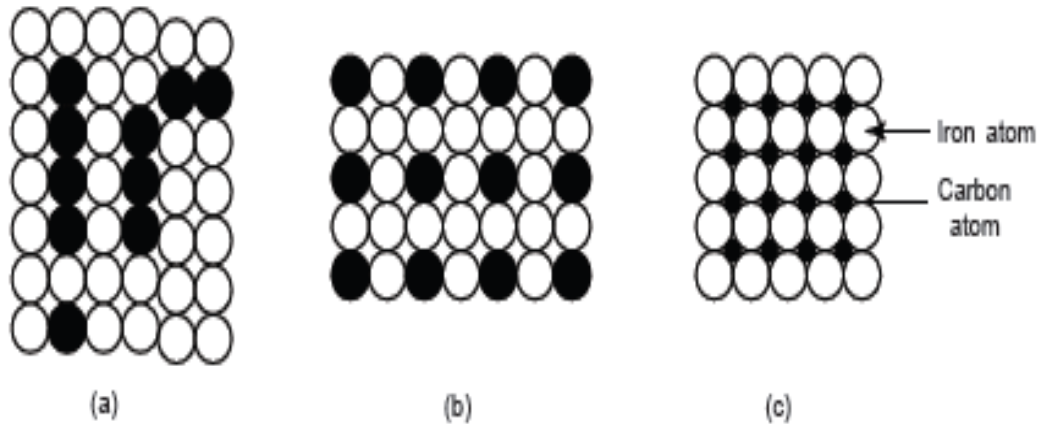


Fig. 9.1 (a) Solid solutions (b) substitutional solid solutions and (c) interstitial solid solution

Many substitutional solid solutions can be in an ordered state at relatively low temperatures, i.e. unlike atoms of two elements are distributed between the sites of the space lattice not statistically, but in a perfectly definite order. Such solid solutions are called *ordered*; the term '*superstructure*' is also in use. Such ordering is common at low temperatures because greater thermal agitation tends to destroy the orderly arrangement. [Fig. (b)]. The change from a disordered to ordered state takes place at a definite temperature or in a definite temperature range. The temperature at which a solid solution becomes completely disordered is called the *Kurnakov point* (θ_K). Ordering usually takes place under the conditions when a solid solution is cooled slowly from the temperature region above θ_K .

Ordered solid solutions can be found in systems with either substantial or unlimited solubility in the solid state; in that case complete ordering can occur with concentrations of the solid solution elements corresponding to simple atomic ratios of the components of the type, say AB or AB_3 . Partial ordering may be observed in systems with concentration ratios close to the indicated ones. The arrangement of atoms in ordered solid solutions of two Cu and Au alloys of the corresponding to $AuCu_3$ and $AuCu$ are shown in Fig.9.2. The appearance and disappearance of an order in the arrangement of atoms in solid solutions is associated with changes in the properties of an alloy.

Ordering increases the electrical conductivity, temperature coefficient of electric resistance, hardness, and strength, but decreases the ductility of an alloy. In ferromagnetic alloys, it changes magnetic properties; for instance, the magnetic

permeability of perm alloys (magnetic iron-nickel alloys) can drop on ordering to a small fraction of the original value. Some alloys are paramagnetic in disordered state, but become ferromagnetic after ordering, such as Heusler (Mn-Cu-Al) alloys.

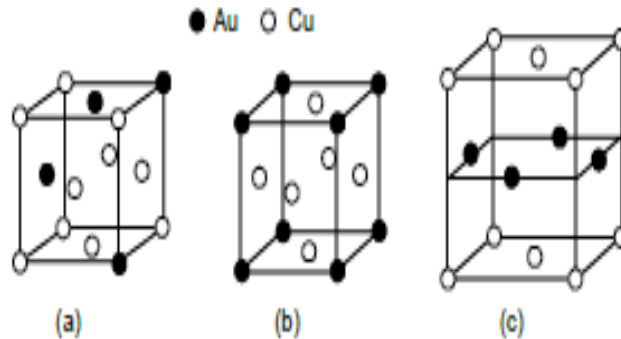


Fig. 9.2 Crystal lattice of Cu-Au alloys: (a) disordered solid solution; (b) ordered solid solution (AuCu_3 alloy); (c) ordered solid solution (AuCu alloy)

Usually, substitutional solid solutions have a *random arrangement* of the constituent atoms on the atomic sites, especially at elevated temperatures. This is so, as configurationally entropy makes a greater contribution in lowering the free energy with increasing temperature, as we have $G = H - TS$. This random arrangement of the constituent atoms in a solid solution may change over to an ordered arrangement on cooling to lower temperatures, if ordering lowers the enthalpy of the crystal sufficiently.

(b) Interstitial Solid Solutions

These can form, for instance, on melting together transition metals and non-metals with a small atomic radius (H , N , C or B).

The possibility of obtaining an interstitial solution is mainly determined by the size factor; i.e., the size of a solute atom must be equal to or slightly smaller than the size of an interstitial void.

Interstitial solid solutions always have a limited solubility and form preferably in solvents having an HCP or FCC lattice with interstices of a radius of $0.41 R$, where R is the radius of a solvent atom. In BCC lattices, the solubility is low, since the size of interstices does not exceed $0.29 R$.

Examples of interstitial solid solutions of commercial application are solid solution of carbon in Fe_γ , and Fe_α , Fe_r , which has an FCC lattice, can dissolve upto 2.14% (by mass) of carbon; Fe_α (BCC lattice) does not practically dissolve carbon, the maximum solubility being around 0.02 (by mass). *Other elements like:* nitrogen for maintaining stainless steel in austenitic condition for nitriding condition and hydrogen when introduced into steels during welding operations, acid cleaning and plating results in hydrogen embrittlement and causes a sharp decrease in ductility.

Lattice distortions appearing on the formation of interstitial solid solutions are stronger than those in the substitutional solid solutions, because of which the properties of alloys can be changed more drastically. As the concentration of a solute in a solid solution increases, this increases noticeably the electric resistance, coercive force, hardness and strength, but decreases the ductility and toughness. Interstitial solid solutions usually have very limited solubility and are normally considered of secondary importance. Alloys containing more than two elements can form either substitutional or interstitial solution. For example, when iron is melted together with manganese and carbon, manganese and iron form substitutional solid solution while carbon and iron, interstitial solid solution.

In conclusion we can say that solid solutions are crystals whose properties are close to those of the solvent, since they retain the same crystal lattice and type of bond. In particular, solid solutions of metals are distinguished by high plasticity: they are readily deformable in the hot state and many of them, in the cold state.

Solid solutions are the bases of most commercial structural and special alloys.

2. Draw iron –carbon equilibrium diagram and label all the phases. Also enumerate the properties of the following phase. (May/June 2012, 2010, 2008, 2009)

THE IRON-IRON CARBIDE (Fe-Fe₃C) PHASE DIAGRAM

Iron and carbon are polymorphous elements.

Iron-carbon alloys exist in different phases in steels and cast irons. In steels, the iron and carbon exists as two separate phases, ferrite and cementite. There are two following phase diagrams of iron-carbon system:

(i) Iron-iron carbide (Fe-Fe₃C) phase diagram

(ii) Iron-carbon (Fe-C) phase diagram

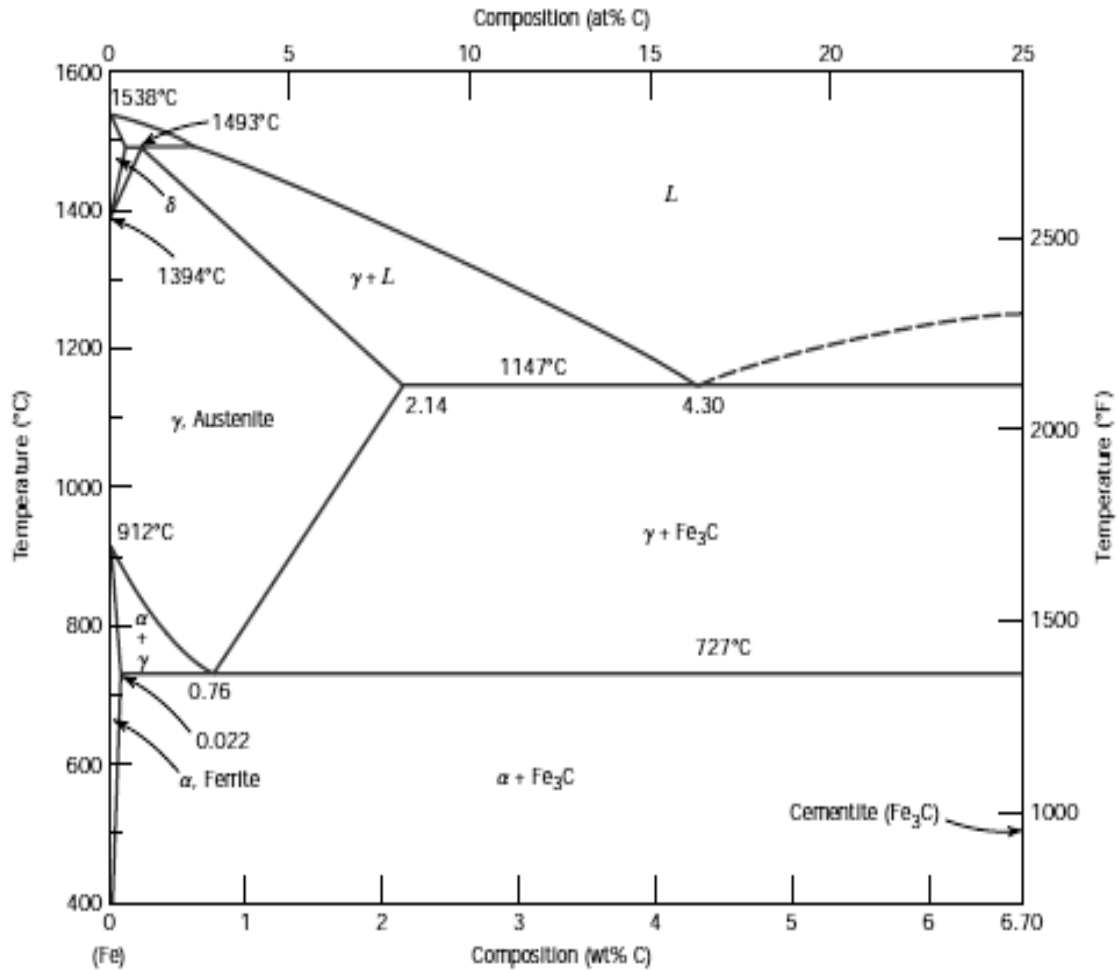


FIGURE 10.26 The iron-iron carbide phase diagram. (Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski, Editor-in-Chief, 1990. Reprinted by permission of ASM International, Materials Park, OH.)

A portion of the iron-carbon phase diagram is presented in Figure. Pure iron, upon heating, experiences two changes in crystal structure before it melts. 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 (1674°F). This austenite persists to 1394°C (2541°F), at which temperature the FCC austenite reverts back to a BCC phase known as δ ferrite, which finally melts at

1538°C (2800°F). All these changes are apparent along the left vertical axis of the phase diagram.

The composition axis in Figure 10.26 extends only to 6.70 wt% C; at this concentration the intermediate compound iron carbide, or **cementite** (Fe_3C), is formed, which is represented by a vertical line on the phase diagram. Thus, the iron-carbon system may be divided into two parts: an iron-rich portion, as in Figure and the other (not shown) for compositions between 6.70 and 100 wt% C (pure graphite). In practice, all steels and cast irons have carbon contents less than 6.70 wt% C; therefore, we consider only the iron-iron carbide system.

Figure would be more appropriately labeled the Fe- Fe_3C phase diagram, since Fe_3C is now considered to be a component. Convention and convenience dictate that composition still be expressed in “wt% C” rather than “wt% Fe_3C ”; 6.70 wt% C corresponds to 100 wt% Fe_3C . Carbon is an interstitial impurity in iron and forms a solid solution with each of α and δ ferrites, and also with austenite, as indicated by the α , δ , and γ single-phase fields in Figure 10.26. In the BCC α ferrite, only small concentrations of carbon are soluble; the maximum solubility is 0.022 wt% at 727°C (1341°F).

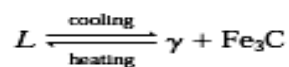
The limited solubility is explained by the shape and size of the BCC interstitial positions, which make it difficult to accommodate the carbon atoms. Even though present in relatively low concentrations, carbon significantly influences the mechanical properties of ferrite. This particular iron-carbon phase is relatively soft, may be made magnetic at temperatures below 768°C (1414°F), and has a density of 7.88g/cm³. Fig. is a photomicrograph of α ferrite. The austenite, or γ phase of iron, when alloyed with just carbon, is not stable below 727°C (1341°F), as indicated in Fig.

The maximum solubility of carbon in austenite, 2.14 wt%, occurs at 1147°C (2097°F). This solubility is approximately 100 times greater than the maximum for BCC ferrite, since the FCC interstitial positions are larger, and, therefore, the strains imposed on the surrounding iron atoms are much lower. As the discussions that follow demonstrate, phase transformations involving austenite are very important in the heat treating of steels. In passing, it should be mentioned that austenite is nonmagnetic. Fig. shows a photomicrograph of this austenite phase.

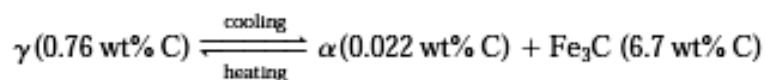
The δ ferrite is virtually the same as α ferrite, except for the range of temperatures over which each exists. Since the δ ferrite is stable only at relatively high temperatures, it is of no technological importance and is not discussed further. Cementite (Fe_3C) forms when the solubility limit of carbon in α ferrite is exceeded below 727°C (1341°F) (for compositions within the $\alpha + \text{Fe}_3\text{C}$ phase region). As indicated in Fig., Fe_3C will also coexist with the γ phase between 727 and 1147°C (1341 and 2097°F).

Mechanically, cementite is very hard and brittle; the strength of some steels is greatly enhanced by its presence. Strictly speaking, cementite is only metastable; that is, it will remain as a compound indefinitely at room temperature. But if heated to between 650 and 700°C (1200 and 1300°F) for several years, it will gradually change or transform into α iron and carbon, in the form of graphite, which will remain upon subsequent cooling to room temperature. Thus, the phase diagram in Fig. is not a true equilibrium one because cementite is not an equilibrium compound. However,

In as much as the decomposition rate of cementite is extremely sluggish, virtually all the carbon in steel will be as Fe_3C instead of graphite, and the iron-iron carbide phase diagram is, for all practical purposes, valid. As will be seen in Section 13.2, addition of silicon to cast irons greatly accelerates this cementite decomposition reaction to form graphite. The two-phase regions are labeled in Fig. It may be noted that one eutectic exists for the iron-iron carbide system, at 4.30 wt% C and 1147°C (2097°F); for this eutectic reaction,



the liquid solidifies to form austenite and cementite phases. Of course, subsequent cooling to room temperature will promote additional phase changes. It may be noted that a eutectoid invariant point exists at a composition of 0.76 wt% C and a temperature of 727°C (1341°F). This eutectoid reaction may be represented by



or, upon cooling, the solid γ phase is transformed into α iron and cementite. (Eutectoid phase transformations) The eutectoid phase changes described by Equation 10.19 are very important, being fundamental to the heat treatment of steels, as explained in subsequent discussions. Ferrous alloys are those in which iron is the prime component, but carbon as well as other alloying elements may be present. In the classification scheme of ferrous alloys based on carbon content, there are three types: iron, steel, and cast iron. Commercially pure iron contains less than 0.008 wt% C and, from the phase diagram, is composed almost exclusively of the ferrite phase at room temperature. The iron-carbon alloys that contain between 0.008 and 2.14 wt% C are classified as steels. In most steels the microstructure consists of both α and Fe₃C phases. Upon cooling to room temperature, an alloy within this composition range must pass through at least a portion of the γ phase field; distinctive microstructures are subsequently produced, as discussed below. Although a steel alloy may contain as much as 2.14 wt% C, in practice, carbon concentrations rarely exceed 1.0 wt%. The properties and various classifications of steels are treated in Section 13.2. Cast irons are classified as ferrous alloys that contain between 2.14 and 6.70 wt% C. However, commercial cast irons normally contain less than 4.5 wt% C.

3. Draw a typical isomorphism phase diagram and explain the structural change of an alloy.

[May-2009]

BINARY ISOMORPHOUS SYSTEMS

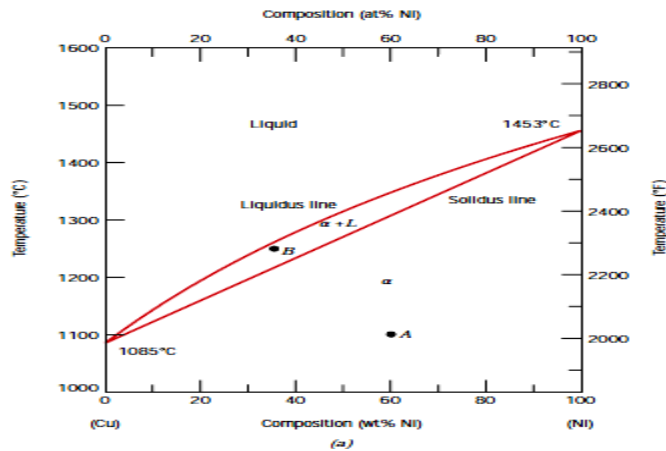
Possibly the easiest type of binary phase diagram to understand and interpret is that which is characterized by the copper-nickel system (Figure *a*). Temperature is plotted along the ordinate, and the abscissa represents the composition of the alloy, in weight percent (bottom) and atom percent (top) of nickel. The composition ranges from 0 wt% Ni (100 wt% Cu) on the left horizontal extremity to 100 wt% Ni (0 wt% Cu) on the right. Three different phase regions, or fields, appear on the diagram, an alpha (α) field, a liquid (*L*) field, and a two-phase $\alpha + L$ field. Each region is defined by the phase or phases that exist over the range of temperatures and compositions delimited by the phase boundary lines.

The liquid L is a homogeneous liquid solution composed of both copper and nickel. The α phase is a substitutional solid solution consisting of both Cu and Ni atoms, and having an FCC crystal structure. At temperatures below about 1080°C, copper and nickel are mutually soluble in each other in the solid state for all compositions. This complete solubility is explained by the fact that both Cu and Ni have the same crystal structure (FCC), nearly identical atomic radii and electro negativities, and similar valences, as discussed in Section 5.4. The copper–nickel system is termed **isomorphous** because of this complete liquid and solid solubility of the two components. A couple of comments are in order regarding nomenclature. First, for metallic alloys, solid solutions are commonly designated by lowercase Greek letters (α , γ , β , etc.). Furthermore, with regard to phase boundaries, the line separating the L and $\alpha+L$ phase fields is termed the *liquidus line*, as indicated in Figure a ; the liquid phase is present at all temperatures and compositions above this line. The *solidus line* is located between the α and $\alpha+L$ regions, below which only the solid α phase exists.

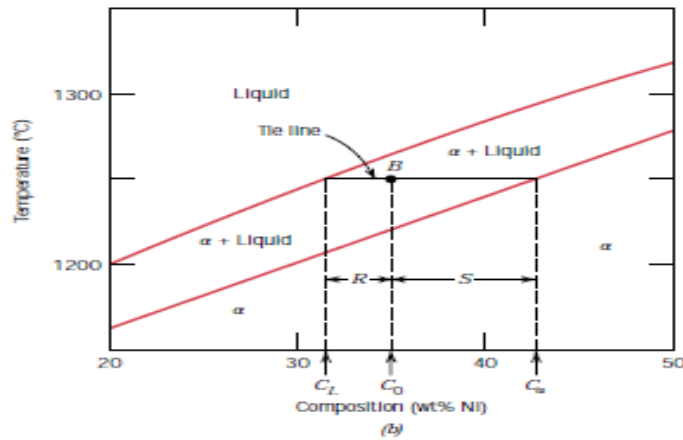
A couple of comments are in order regarding nomenclature. First, for metallic alloys, solid solutions are commonly designated by lowercase Greek letters (α , γ , β , etc.). Furthermore, with regard to phase boundaries, the line separating the L and $\alpha+L$ phase fields is termed the *liquidus line*, as indicated in Fig. the liquid phase is present at all temperatures and compositions above this line. The *solidus line* is located between the α and $\alpha+L$ regions, below which only the solid α phase exists. For Fig. the solidus and liquidus lines intersect at the two composition extremities; these correspond to the melting temperatures of the pure components. For example, the melting temperatures of pure copper and nickel are 1085°C and 1453°C, respectively. Heating pure copper corresponds to moving vertically up the left-hand temperature axis. Copper remains solid until its melting temperature is reached. The solid-to-liquid transformation takes place at the melting temperature, and no further heating is possible until this transformation has been completed.

For any composition other than pure components, this melting phenomenon will occur over the range of temperatures between the solidus and liquidus lines; both solid α and liquid phases will be in equilibrium within this temperature range. For example, upon heating an alloy of composition 50 wt% Ni–50 wt% Cu (Fig. a), melting

begins at approximately 1280°C (2340°F); the amount of liquid phase continuously increases with temperature until about 1320°C (2410°F), at which the alloy is completely liquid.



(a) The copper–nickel phase diagram.

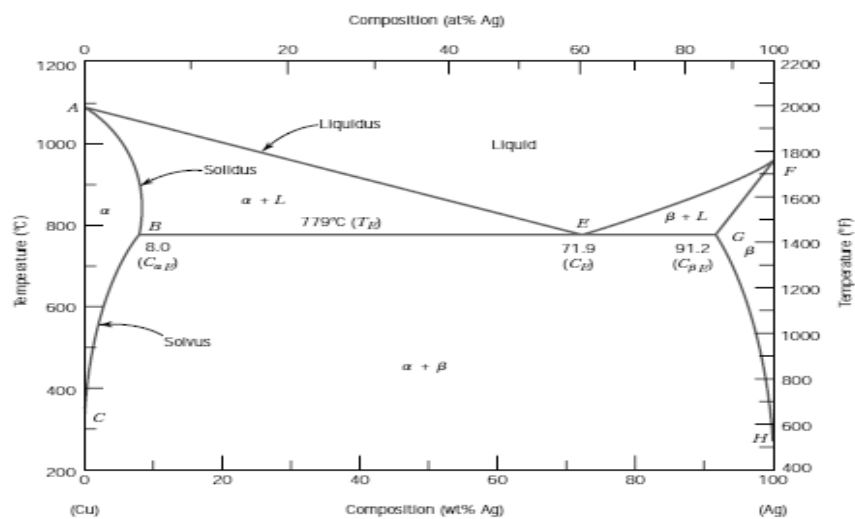
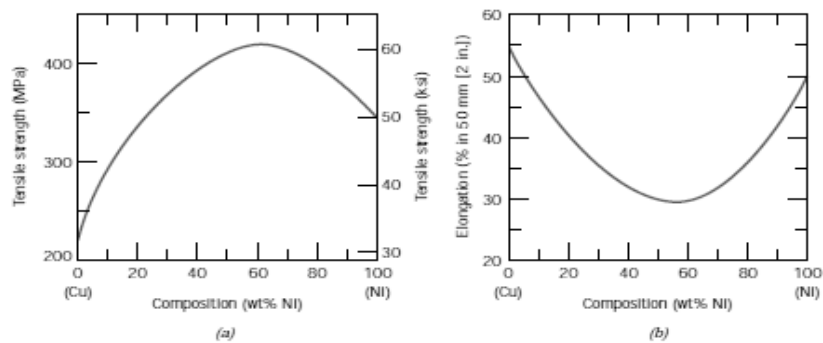


(b) A portion of the copper–nickel phase diagram for which compositions and phase amounts are determined at point B.

BINARY EUTECTIC SYSTEMS

Another type of common and relatively simple phase diagram found for binary alloys is shown in Figure 10.6 for the copper–silver system; this is known as a binary eutectic phase diagram. A number of features of this phase diagram are important and worth noting. First of all, three single-phase regions are found on the diagram: α , β , and liquid. The α phase is a solid solution rich in copper; it has silver as the solute component and an FCC crystal structure. The β phase solid solution also has an FCC structure, but copper is the solute. The α and β phases are considered to include pure copper and pure silver, respectively.

For the copper–nickel system, (a) tensile strength versus composition, and (b) ductility (%EL) versus composition at room temperature. A solid solution exists over all compositions for this system.



The copper–silver phase diagram. (Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski, Editor-in-Chief, 1990. Reprinted by permission of ASM International, Materials Park, OH.)

(PHASE DIAGRAM OF PARTIAL SOLID SOLUBILITY)

Thus, the solubility in each of these solid phases is limited, in that at any temperature below line *BEG* only a limited concentration of silver will dissolve in copper (for the α phase), and similarly for copper in silver (for the β phase). The solubility limit for the α phase corresponds to the boundary line, labeled *CBA*, between the $\alpha/(\alpha+\beta)$ and $\alpha/(\alpha+L)$ phase regions; it increases with temperature to a maximum [8.0 wt% Ag at 779°C (1434°F)] at point *B*, and decreases back to zero at the melting temperature of pure copper, point *A* [1085°C (1985°F)].

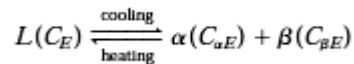
At temperatures below 779°C (1434°F), the solid solubility limit line separating the α and $\alpha+\beta$ phase regions is termed a **solvus line**; the boundary *AB* between the α and $\alpha+L$ fields is the **solidus line**, as indicated in Fig. For the β phase, both solvus and solidus lines also exist, *HG* and *GF*, respectively, as shown. The maximum solubility of copper in the β phase, point *G* (8.8 wt% Cu), also occurs at 779°C (1434°F). This horizontal line *BEG*, which is parallel to the composition axis and extends between these maximum solubility positions, may also be considered to be a solidus line; it represents the lowest temperature at which a liquid phase may exist for any copper–silver alloy that is at equilibrium.

There are also three two-phase regions found for the copper–silver system (Figure 10.6): $\alpha+L$, $\beta+L$, and $\alpha+\beta$. The α and β phase solid solutions coexist for all compositions and temperatures within the $\alpha+\beta$ phase field; the $\alpha+L$ liquid and $\beta+L$ liquid phases also coexist in their respective phase regions. Furthermore, compositions and relative amounts for the phases may be determined using tie lines and the lever rule as outlined previously.

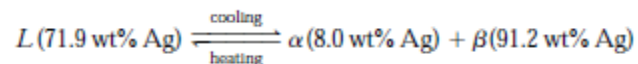
As silver is added to copper, the temperature at which the alloys become totally liquid decreases along the liquidus line, line *AE*; thus, the melting temperature of copper is lowered by silver additions. The same may be said for silver: the introduction of copper reduces the temperature of complete melting along the other liquidus line, *FE*. These liquidus lines meet at the point *E* on the phase diagram, through which also passes the horizontal isotherm line *BEG*. Point *E* is called an **invariant point**, which is designated by the composition *CE* and temperature *TE*; for

the copper–silver system, the values of CE and TE are 71.9 wt% Ag and 779°C (1434°F), respectively.

An important reaction occurs for an alloy of composition CE as it changes temperature in passing through TE ; this reaction may be written as follows:



Or, upon cooling, a liquid phase is transformed into the two solid α and β phases at the temperature TE ; the opposite reaction occurs upon heating. This is called a **eutectic reaction** (eutectic means easily melted), and CE and TE represent the eutectic composition and temperature, respectively; $C_{\alpha E}$ and $C_{\beta E}$ are the respective compositions of the α and β phases at TE . Thus, for the copper–silver system, the eutectic reaction, Equation 10.8, may be written as follows:

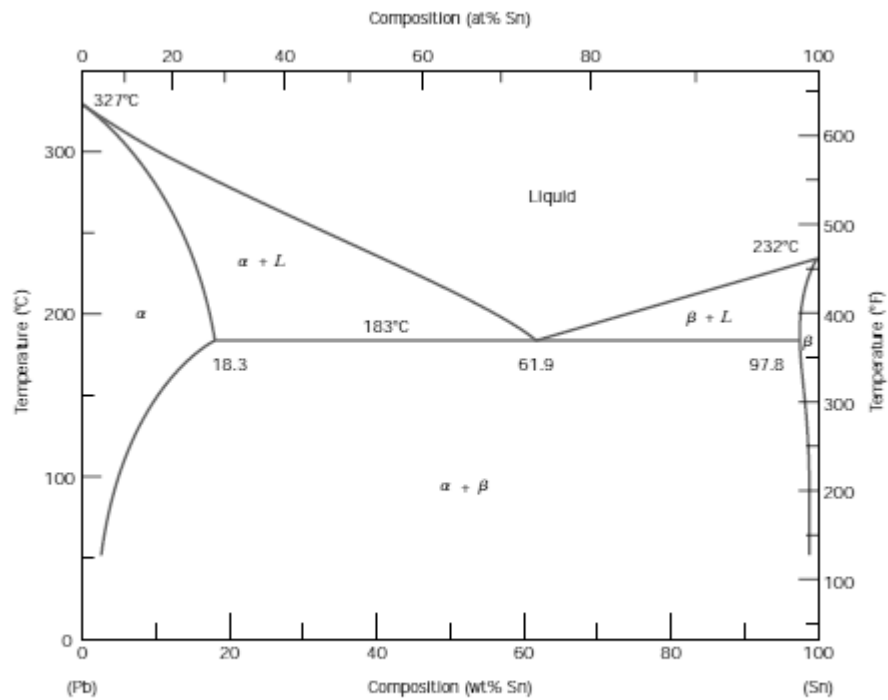


Often, the horizontal solidus line at TE is called the *eutectic isotherm*.

The eutectic reaction, upon cooling, is similar to solidification for pure components in that the reaction proceeds to completion at a constant temperature, or isothermally, at TE . However, the solid product of eutectic solidification is always two solid phases, whereas for a pure component only a single phase forms. Because of this eutectic reaction, phase diagrams similar to that in Figure 10.6 are termed eutectic phase diagrams; components exhibiting this behavior comprise a eutectic system.

In the construction of binary phase diagrams, it is important to understand that one or at most two phases may be in equilibrium within a phase field. This holds true for the phase diagrams in Figures 10.2a and 10.6. For a eutectic system, three phases (α , β , and L) may be in equilibrium, but only at points along the eutectic isotherm. Another general rule is that single-phase regions are always separated from each other by a two-phase region that consists of the two single phases that it separates. For example, the $\alpha+\beta$ field is situated between the α and β single-phase regions in Figure.

Another common eutectic system is that for lead and tin; the phase diagram (Figure 10.7) has a general shape similar to that for copper–silver. For the lead–tin system the solid solution phases are also designated by α and β ; in this case, α represents a solid solution of tin in lead, and for β , tin is the solvent and lead is the solute. The eutectic invariant point is located at 61.9 wt% Sn and 183°C (361°F). Of course, maximum solid solubility compositions as well as component melting temperatures will be different for the copper–silver and lead–tin systems, as maybe observed by comparing their phase diagrams.



The lead–tin phase diagram. (Adapted from *Binary Alloy Phase Diagrams*.)

On occasion, low-melting-temperature alloys are prepared having near-eutectic compositions. A familiar example is the 60–40 solder, containing 60 wt% Sn and 40 wt% Pb. Figure 10.7 indicates that an alloy of this composition is completely molten at about 185°C (365°F), which makes this material especially attractive as a low-temperature solder, since it is easily melted.

4. Explain the Hume-Rothery rules of solid solubility.(May/June 2012)

While developing an alloy, it is frequently desirable to increase the strength of the alloy by adding a metal that will form a solid solution. Hume-Rothery has framed *empirical rules* that govern the choice of alloying elements in the formation of substitutional solutions. We may note that if an alloying element is chosen at random, it is likely to form an objectionable intermediate phase instead of a solid solution. Extensive solid solubility by substitution occurs, when

(i) the solute and solvent atoms do not differ by more than 15% in size, i.e. diameter. Within this limit of size factor, each of the metals will be able to dissolve appreciably (to the order of 10%) in the other metal. However, if the atomic size factor is greater than 15%, solid solution formation tends to be severely limited and is usually only a fraction of one percent.

(ii) the electronegativity difference between the elements is small. If the chemical affinity of two metals is greater, then the solid solubility will be more restricted. When the chemical affinity of two metals is great, they tend to form an intermediate phase rather than a solid solution.

(iii) the valency and the crystal structures of the elements are the same. If the alloying element has a different valence from that of the base metal, the number of valence electrons per atom (called the electron ratio), will be changed by alloying. We may note that the crystal structures are more sensitive to a decrease in the electron ratio than to an increase. Obviously, a metal of high valence can dissolve only a small amount of lower valence metal; whereas the lower valence metal may have good solubility for a higher valence metal. Moreover, only metals that have the same type of lattice (for example FCC) can form a complete series of solid solutions. For complete solubility, it is found that the size factor must usually be less than 8%. Examples of binary and ternary systems exhibiting complete solid solubility are Cu-Ni and Ag-Au-Pt respectively.

5. What is cooling curve? How does the time temperature cooling curve of an alloy of eutectic composition different from that of a pure metal?

COOLING CURVE (TIME TEMPERATURE CURVE)

It is interesting to study the manner in which temperature changes with time as the liquid metal solidifies.

Figure 9.4 shows a cooling curve which are distinctly divided into two portions while exhibiting the fall of temperature of time, the cooling curve exhibit that the temperature remains practically constant over a period of time.

This constant temperature is called as the point of arrest. The solidification occurs during temperature arrest. During this period, heat is still lost from the mass of metal but release of kinetic energy compensates the heat loss whereby temperature remains constant. The released heat at constant temperature is called the latent heat.

Due to this, at certain stages the fall in temperature of the metal or alloy is totally arrested for a specific time. Such points are termed critical points. One can determine the critical points by the abrupt inflection of curves due to thermal effects in transformations. Following three types of cooling curves are commonly used in plotting the phase diagrams.

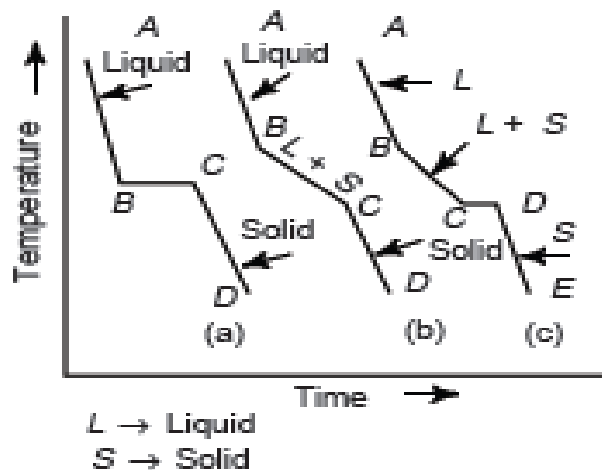


Fig. 9.4

(i) Curve (a): Applying Eq. 1 under constant pressure, for region AB when $P = 1$, $C = 1$, $F = 1$, i.e. system has single degree of freedom (called univariant). Obviously, only variant that changes in temperature. Between B and C both liquid and solid phases are present, $P = 2$, $C = 1$ so that $F = 0$, i.e. system has no degree of freedom (called as non-variant). Obviously, temperature remains constant (pressure is already constant) and the mass between B and C is marshy (partly liquid and partly solid). On further cooling from C to D the system reaches room temperature. The slopes of lines AB and CD indicate specific heat of liquid and solid metals, respectively (Fig. 9.4a). There is also another way to plot the cooling curve. One can plot the temperature against time taken to cool through a specific temperature interval (say 5°C) as shown in Fig. 9.5. Such cooling curves are called derived or inverse rate curve.

We may note that the single temperature arrest during latent heat loss in cooling curve (Fig. 9.4) is the property of the pure metal. The temperature of solidification is the characteristic of that metal.

When two or more metals are mixed in liquid state to form an alloy and allowed to cool, the solidification occurs over a range of temperature. Figure 9.4(b) shows a cooling curve for an alloy of metals A and B. We can see that curve AB is the same as for pure metals. The freezing line BC drops until the whole mass is solid at point C. Applying Eq. (1) to the system between B and C (Fig. 9.4b) with $P = 2$, $C = 2$, $F = 1$, i.e. there is one degree of freedom. The temperature will change (the pressure is constant). Obviously BC portion of the curve is due to the fall in temperature recorded during freezing in a binary alloy. From point C, the solid further cools along the line CD to reach room temperature.

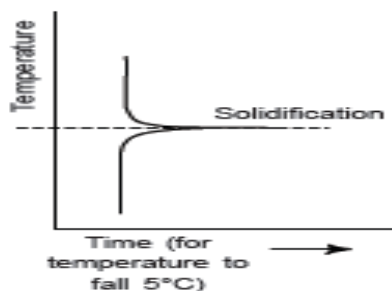


Fig. 9.5 Inverse rate or derived cooling curve.

Figure 9.4(c) is the freezing curve for another binary system whose two components are completely soluble in liquid state but not at all soluble in solid state. They are liquid along AB upto point B of the cooling curve. At point B the component with larger content starts solidifying and temperature falls along BC. At point C the components solidify simultaneously at constant temperature, the lowest for a given alloy system, and are termed as eutectic alloys. At D the only phase that is present is solid and cools along DE as usual. Point D on the curve is called as eutectic point.

We may now consider the cooling curve for pure metal for evaluating the effect of slow and fast cooling. Figure. 9.6 shows two cooling curves for the same pure metal. We may note that constant temperature of crystallization is available only if cooling maintains equilibrium with surrounding. From Fig. 9.6, we can see that if cooling is rapid enough than temperature does not remain constant during solidification. Obviously, the more rapid the cooling lower is the temperature at which crystal formation begins to occur. This is due to rearrangement of molecules or atoms during freezing will need some time and rapid cooling may not be very conducive for such rearrangement. From Fig. 9.3 it is evident that the solidified portion of the metal will release heat, which is latent heat of fusion and will thus increase the temperature of surrounding molten metal. The phenomenon of temperature rise of molten metal is called recalescence which may sometimes may even cause the growing of molten metal.

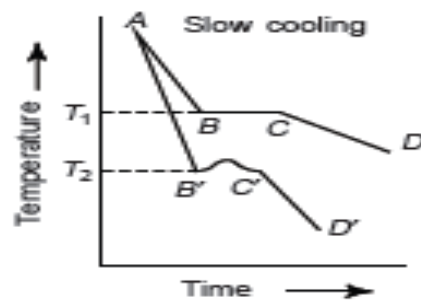


Fig. 9.6 Slow and rapid cooling curves for a pure metal

6. Explain the following invariant reactions with reference to a phase diagram.

(a) Eutectic reaction

(b) Eutectoid reaction

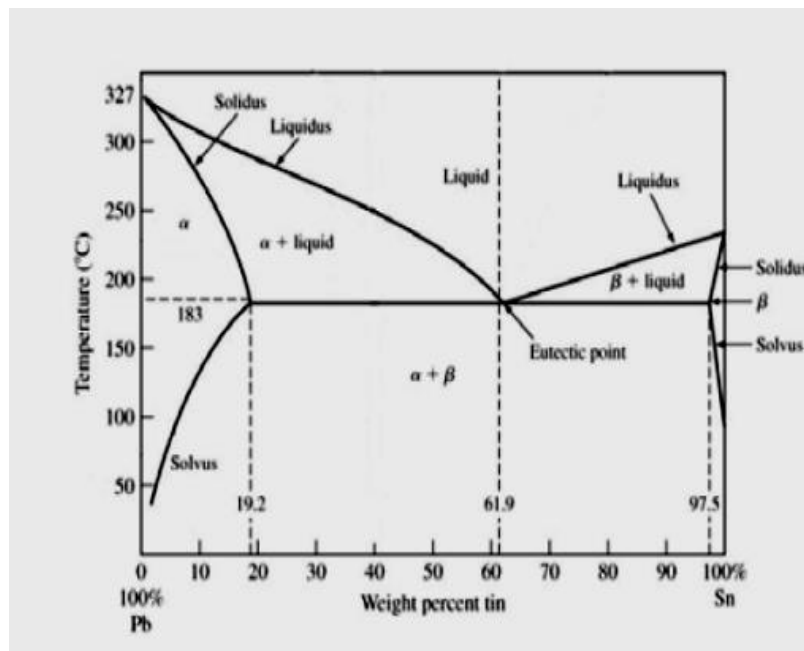
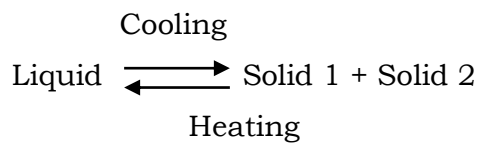
(c) Peritectic reaction

(d) Peritectoid reaction [Nov'09,Nov'12] (NOV 2013)

Eutectic Type:

When two metals are completely soluble in the liquid state but partly or completely insoluble in the solid state, are termed as eutectic type.

Fe-C, Al-Mn, Pb-Sn form an eutectic system.



Peritectic Type:

In this case liquid and solid combine to form a new solid. The melting points of two metals differ considerably. Ag and Pt form such a system.

In the eutectic system, the crystals of β solid solution precipitated at the beginning of solidification react with the liquid alloy having definite composition to

form new crystals of a solid solution. In the peritectic reaction, two phases are used to produce one different phase with reaction just the opposite of eutectic reaction.

The peritectic reaction similar to other systems of solidification of different metals, but is comparatively less common. This reaction also occurs at constant temperature. One can write this reaction as

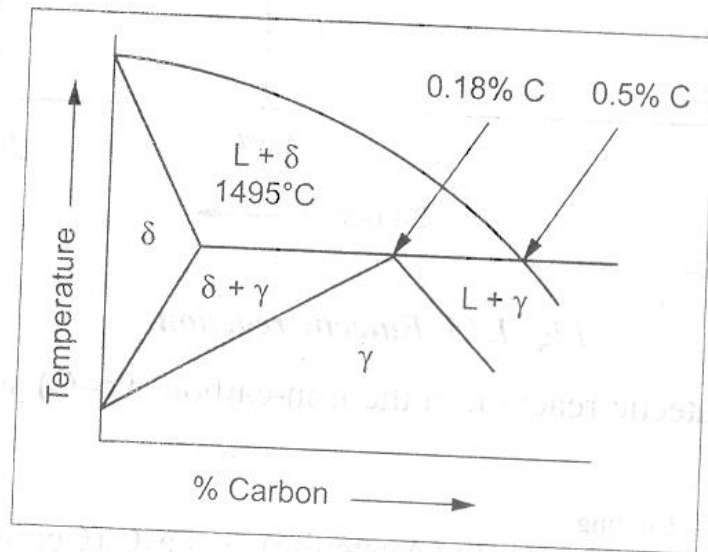


i.e.,



The temperature at which peritectic reaction occurs is denoted by T_d . Below T_d , the liquid phase disappears upon completion of the transformation.

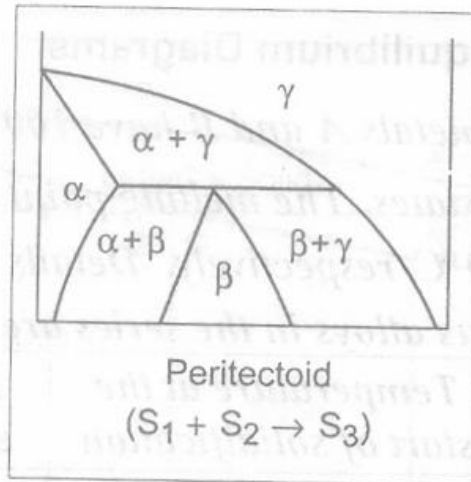
Pt-Ag is a good example of peritectic reaction.



Peritectoid reaction:

There is also peritectoid reaction. This is the reaction of two solids into a third solid. One can represent this reaction as





Eutectoid Type:

In this one solid decomposes into two different solids. Obviously, solid to solid transformation takes place. Fe-C, Cu-Zn, Al-Cu, Cu-Sn, etc form eutectoid system. Eutectoid transformation takes place at a constant temperature and the products of transformation are present as intimate mixture having appearance under the microscope. The eutectoid reaction is of the form:

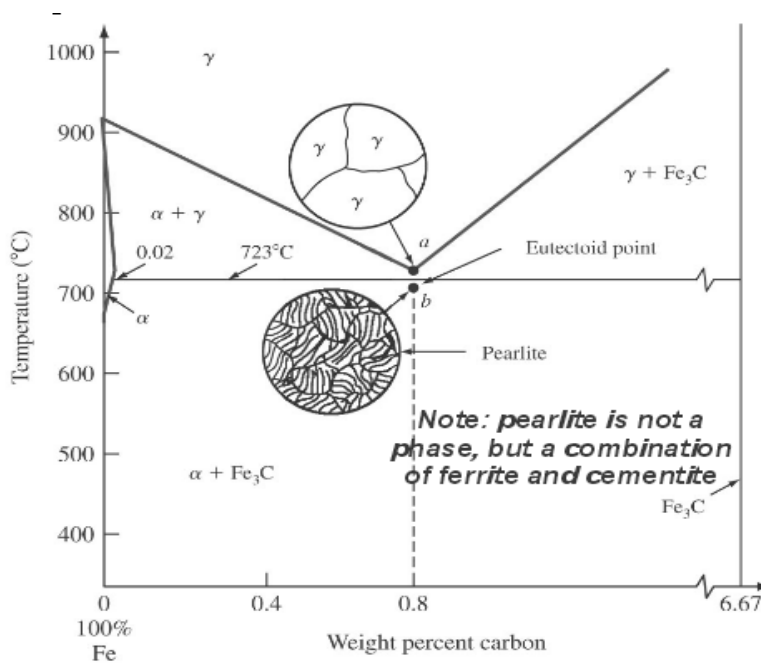
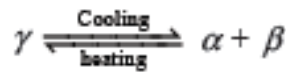


Table-1: Summary of invariant reactions in binary systems.

Reaction	Symbolic equation	Schematic presentation	Example
Eutectic	$L \leftrightarrow \alpha + \beta$		Fe-C, 4.27% C, 1147 °C
Eutectoid	$\alpha \leftrightarrow \beta + \gamma$		Fe-C, 0.80% C, 723 °C
Peritectic	$L + \alpha \leftrightarrow \beta$		Fe-C, 0.16% C, 1495 °C
Peritectoid	$\alpha + \beta \leftrightarrow \gamma$		

7. What are the micro-constituents of iron-carbon alloys? Explain the general characteristics of each. [Nov-'07, Apr'08, Nov'09] .(NOV 2013)

Micro-constituents of iron-carbon (Fe-C) alloys:

The Several terms used in iron-carbon (Fe-C) alloys are:

1. Ferrite (α -iron),
2. Austenite (γ -iron),
3. Cementite (iron carbide, Fe₃C),
4. Pearlite (88wt% ferrite, 12wt% cementite, or 99.2wt% iron, 0.8wt% carbon),
5. Bainite,
6. Martensite,
7. Ledeburite (ferrite-cementite eutectic, 4.3% carbon).

1. Ferrite:

the α -iron, is a materials science term for iron, or a solid solution with iron as the main constituent, with a body centred cubic (bcc) crystal structure. It is the component which gives steel and cast iron their magnetic properties, and is the classic example of a ferromagnetic material. Practically speaking, ferrite can be considered pure iron. Ferrite is stable below 910 °C (1,670 °F).

Above this temperature the face centered cubic (fcc) form of iron, austenite (γ -iron), is stable. Above 1,390 °C (2,530 °F), up to the melting point at 1,539 °C (2,802

°F), the body centered cubic (bcc) crystal structure is again the more stable form for delta-ferrite (δ -Fe).

Only a very small amount of carbon can be dissolved in ferrite; the maximum solubility is about 0.02 wt% at 723 °C (1,333 °F) and 0.005% carbon at 0 °C (32 °F). This is because carbon dissolves in iron interstitially, with the carbon atoms being about twice the diameter of the interstitial "holes", so that each carbon atom is surrounded by a strong local strain field. Hence the enthalpy of mixing is positive (unfavourable), but the contribution of entropy to the free energy of solution stabilizes the structure for low carbon content.

2. Pearlite:

Pearlite is a two-phased, lamellar (or layered) structure composed of alternating layers of ferrite (88 wt%) and cementite (12wt%) that occurs in some steels and cast irons. During slow cooling pearlite forms by a eutectoid reaction as austenite is cooled below 727°C (the eutectoid temperature).

See Figure 5.60 (below, cited from the same Book above) for the lamellar microstructure of Pearlite. Mild steel (carbon steel with up to about 0.2 wt% C) consist mostly of ferrite, where the amount of pearlite increases with increasing the carbon content is increased.

3. Austenite:

the γ -iron, is a metallic non-magnetic allotrope of iron or a solid solution of iron, with an alloying element (typically carbon). In plain-carbon steel, austenite exists above the critical eutectoid temperature of 727 °C); other alloys of steel have different eutectoid temperatures. It is named after Sir William Chandler Roberts-Austen (1843-1902)

4. Cementite:

iron carbide (Fe_3C), is a chemical compound of an orthorhombic crystal structure. It is a hard, brittle material, normally classified as a ceramic in its pure form, though it is more important in metallurgy. Cementite forms directly from the melt in the case of white cast iron. In carbon steel, it either forms from austenite during cooling or from martensite during tempering. An intimate mixture with ferrite,

the other product of austenite, forms a lamellar structure called pearlite. Much larger lamellae, visible to the naked eye, make up the structure of Damascus steel.

5. Martensite:

named after the German metallurgist Adolf Martens (1850–1914), most commonly refers to a very hard form of steel crystalline structure, but it can also refer to any crystal structure that is formed by displacive transformation. Martensite is not shown in the equilibrium phase diagram of the iron-carbon system because it is a metastable phase, the kinetic product of rapid cooling of steel containing sufficient carbon.

6. Bainite:

first described by E. S. Davenport and Edgar Bain, is a phase that exists in steel microstructures after certain heat treatments. Bainite is one of the decomposition products that may form when austenite is cooled past the eutectoid temperature of 727 °C. appearing as a fine non-lamellar structure, bainite commonly consists of ferrite, carbide, and retained austenite.

In these cases it is similar in constitution to pearlite, but with the ferrite forming by a displacive mechanism similar to martensite formation, usually followed by precipitation of carbides from the supersaturated ferrite or austenite. The temperature range for transformation to bainite is between those for pearlite and martensite. When formed during continuous cooling, the cooling rate to form bainite is higher than that required to form pearlite, but lower than that to form martensite, in steel of the same composition.

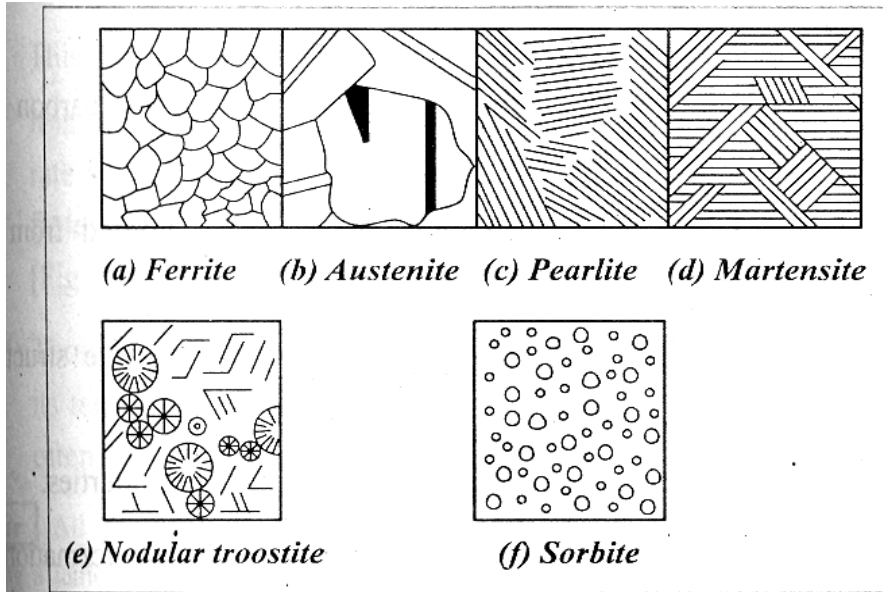


Fig. 1.24. Microstructures of some Fe–C alloy constituents

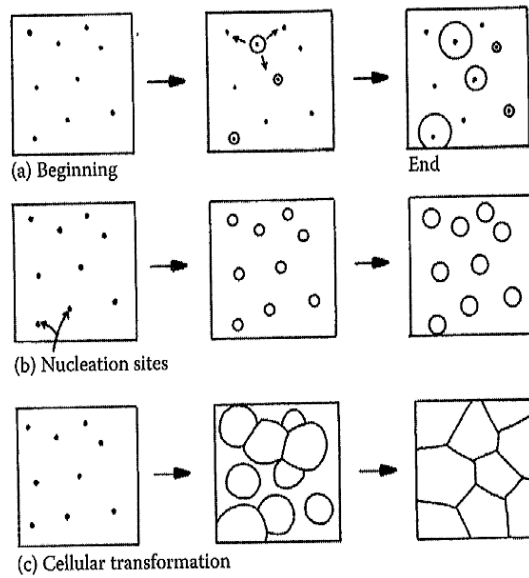


FIGURE 5.24
 (a) Nucleation at a constant rate during the whole transformation. (b) Site saturation—all nucleation occurs at the beginning of transformation. (c) Cellular transformation.

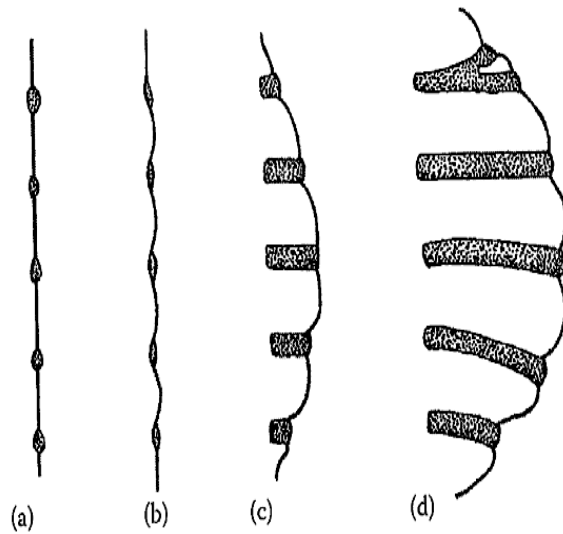


FIGURE 5.55
Schematic diagram showing a possible sequence of steps during the development of cellular precipitation.

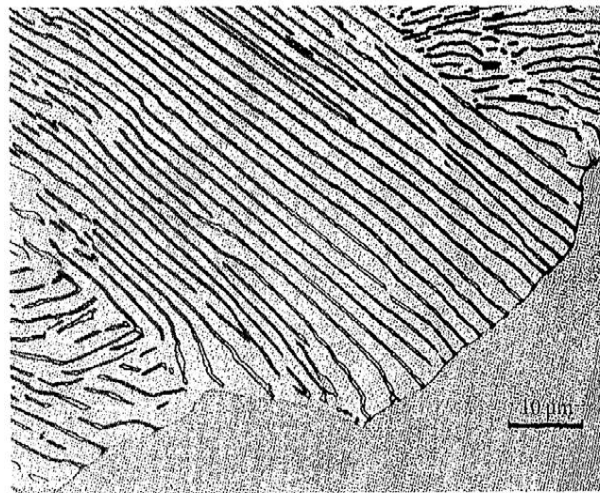


FIGURE 5.60
Pearlite colony advancing into an austenite grain. (After Darken, L.S. and Fisher, R.M., in *Decomposition of Austenite by Diffusional Processes*, Interscience, New York, 1962.)

8. (1) Elements A & B melt at 700° C and 1000° C respectively. Draw a typical isomorphous phase diagram between the elements A & B.

(2) Elements A & B melt at 700° C & 1000° C respectively. They form a eutectic at 35%A at temperature 500° C. Draw a typical phase diagram between A & B. [May/June-2006]

(1)

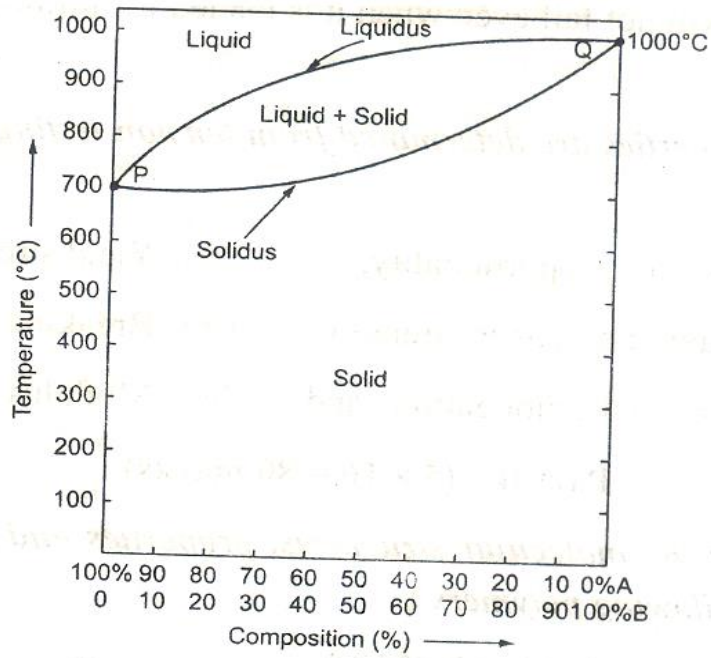


Fig. 1. Isomorphous phase diagram

(2)

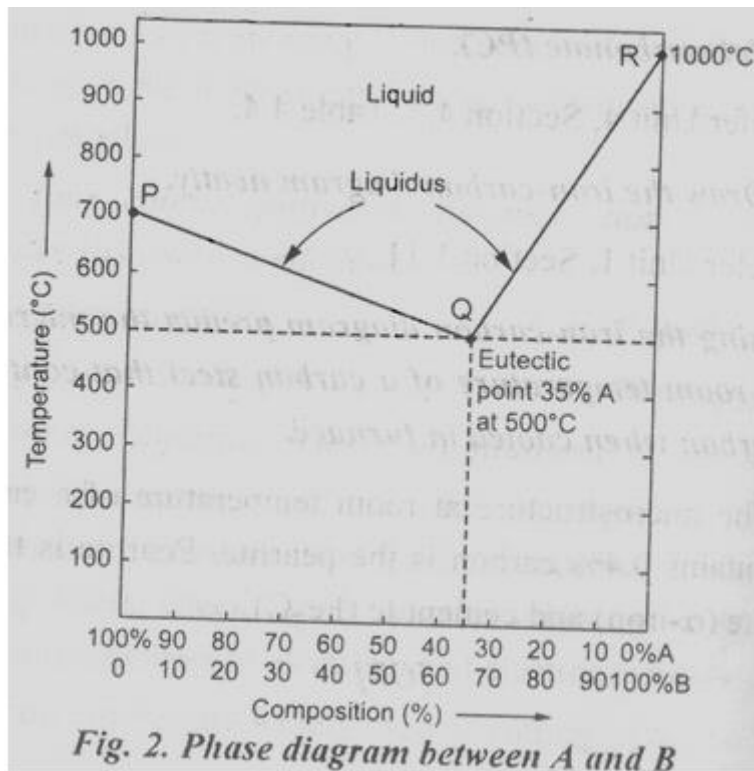


Fig. 2. Phase diagram between A and B

9. Metal A has melting point at 1000° C. Metal B has melting point of 500° C. Draw one phase diagram (between the elements A & B) for each of the following conditions.

(i) The two elements exhibit unlimited solid solubility.

(ii) The alloy systems show formation of two terminal solid solution and a eutectic point at 50%A and at 700° C. [Nov/Dec-2006]

(i)

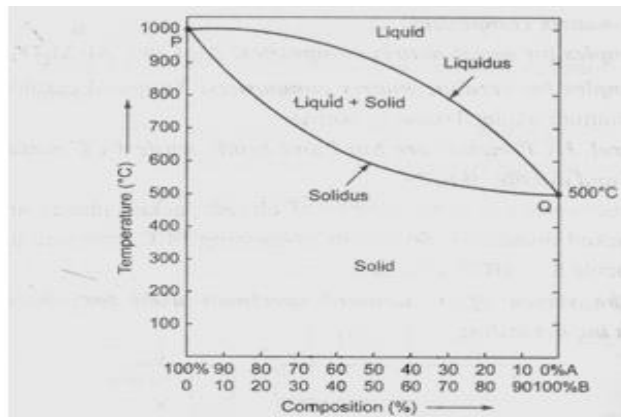


Fig. 1. Isomorphous phase diagram (in which two elements exhibit unlimited solid solubility)

(ii)

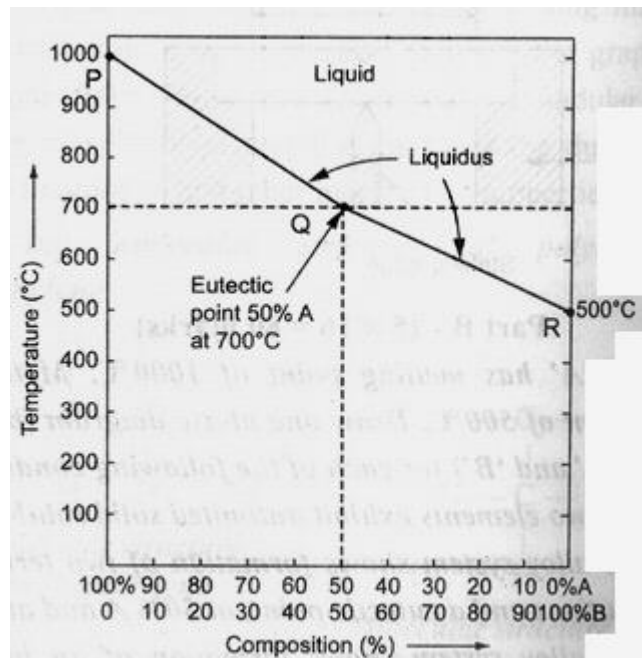


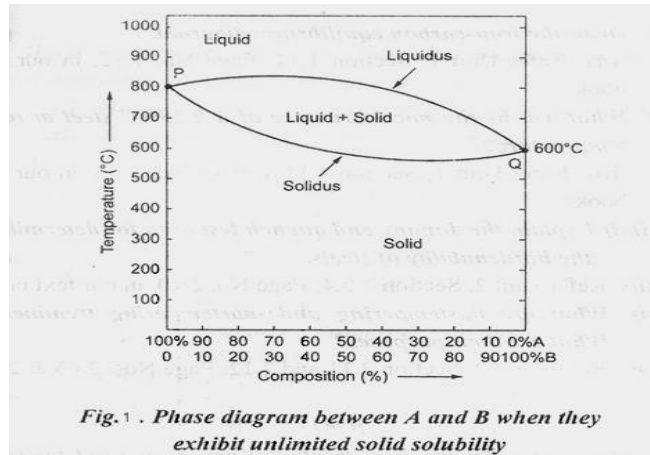
Fig. 2. Phase diagram between A & B

10. Two metal A and B have melting points 800°C and 600°C respectively.

(i) Draw a phase diagram between A and B if they exhibit unlimited solid solubility.

(ii) Draw a phase diagram between A and B if a eutectic reactions occurs at composition 40%B and at temperature 400°C . Assume that the maximum solid solubility in either case is 5% and the room temperature solubility in either case is 1%.[May/June-2007]

(i)



(i)

