Properties of Engineering Materials

Phase Diagrams

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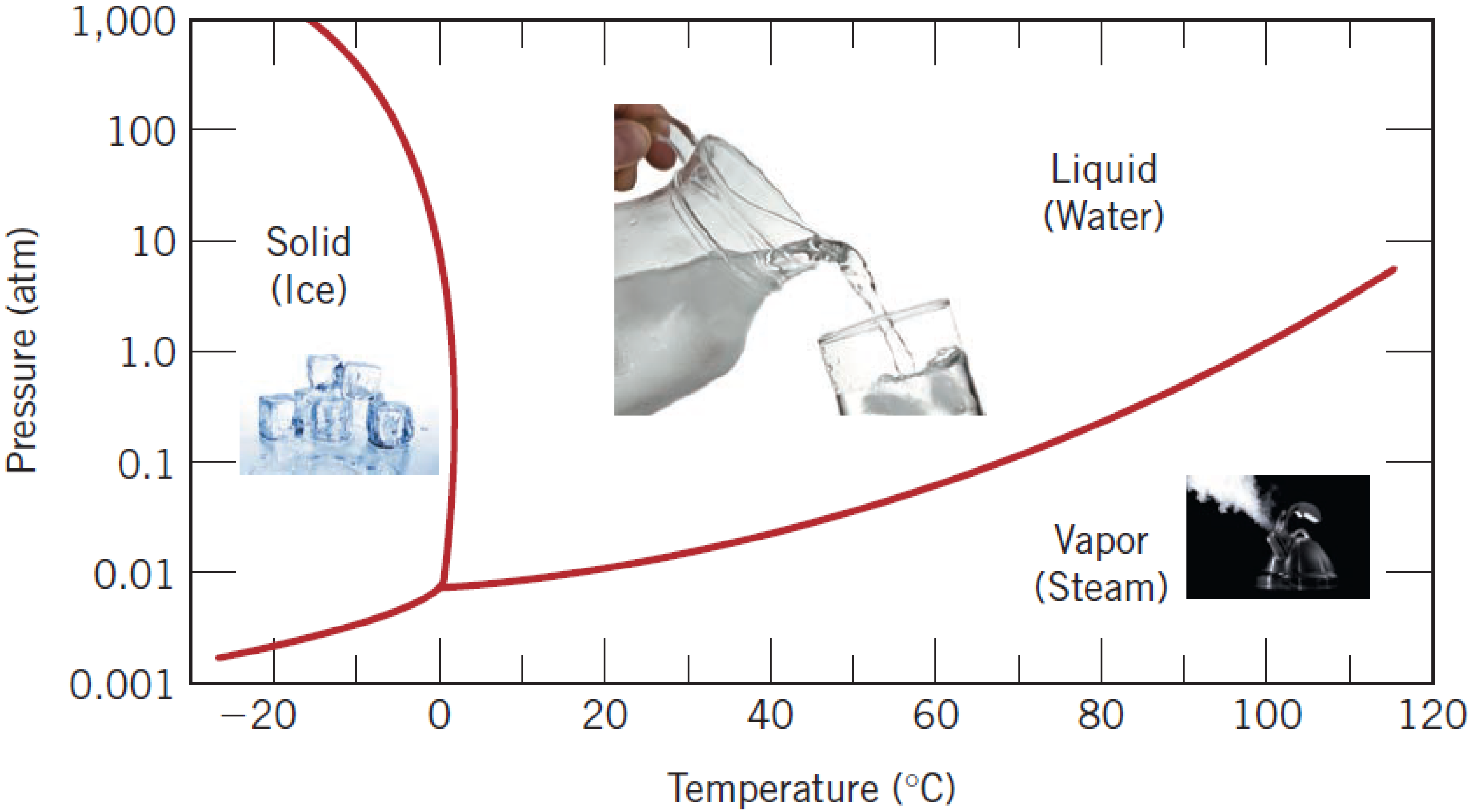
Introduction



Phase diagram for pure H_2O

Definitions & Basic Concepts

- ***Components***: are pure metals and/or compounds of which an alloy is composed.
  - E.g.; in a copper–zinc brass, the components are Cu and Zn.
- ***System***: the series of possible alloys consisting of the same components, but without regard to alloy composition (e.g., the iron–carbon system).

Solubility Limit

- ***Solubility Limit***: maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution.
  - 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.

Solubility Limit

For example, at 20° C the maximum solubility of sugar in water is 65 wt%.

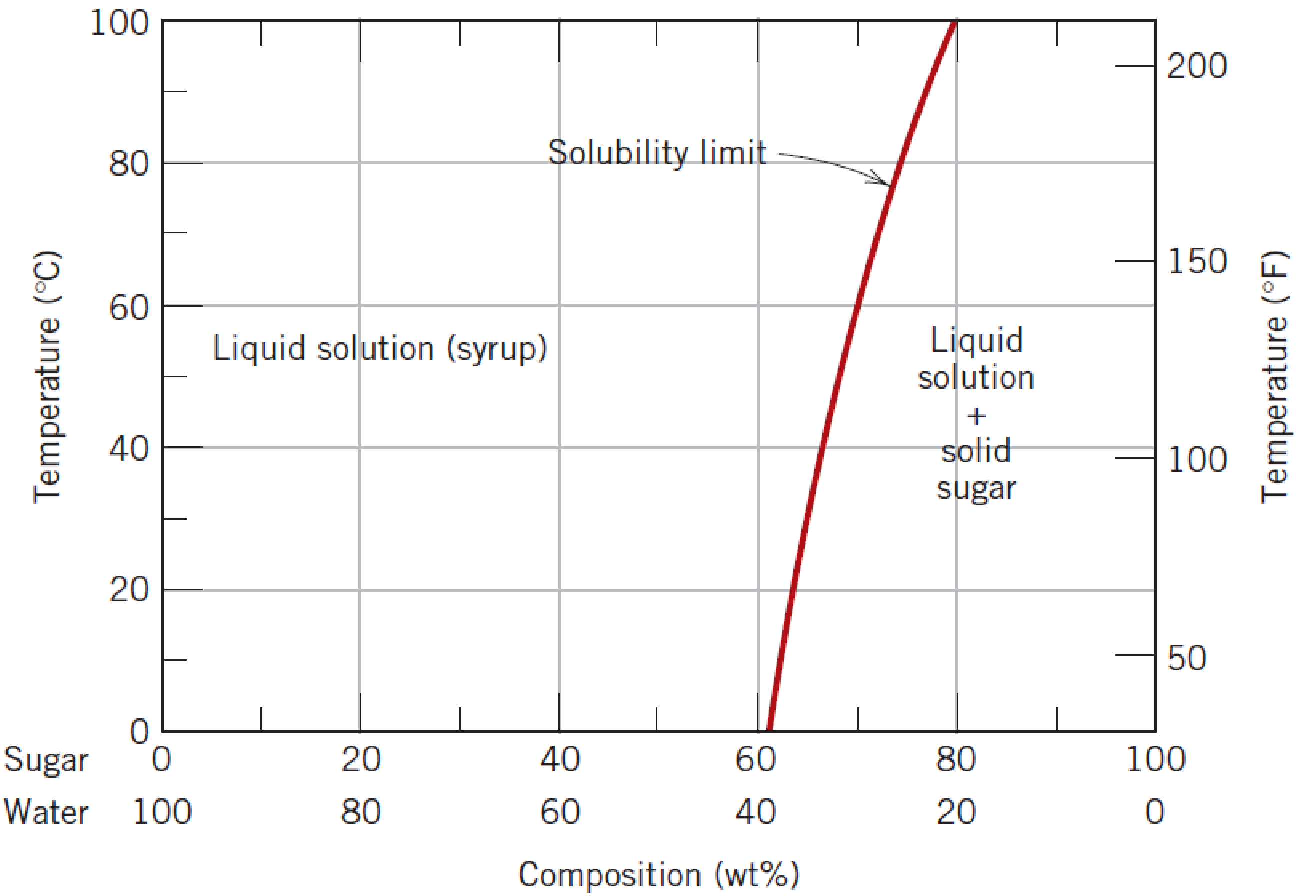


Figure 9.1 The solubility of sugar ($C_{12}H_{22}O_{11}$) in a sugar–water syrup.

Phases

- ***A Phase***: a homogeneous portion of a system that has uniform physical and chemical characteristics.
    - Every pure material is considered to be a phase; so also is every solid, liquid, and gaseous solution.
    - For example, the sugar–water syrup solution just discussed is one phase, and solid sugar is another.
- In phase diagrams, different phases are separated by boundaries; these boundaries are called Phase Boundaries.

Microstructure

- Many times, the physical properties and, in particular, the mechanical behavior of a material depend on the microstructure.
    - characterized by the *number of phases present*, *their proportions*, and *the manner in which they are distributed or arranged*.
    - depends on such variables as *the alloying elements present*, *their concentrations*, and *the heat treatment of the alloy*.

Phase Equilibria

- ***Equilibrium*** is described in terms of the ***free energy*.**
    - free energy is a function of the *internal energy of a system*, and also the *randomness or disorder* of the atoms or molecules (or entropy).
- 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.

Phase Equilibria

- ***Phase Equilibrium***: equilibrium as it applies to systems in which more than one phase may exist.
  - A change in temperature, pressure, and/or composition for a system in equilibrium will result in an increase in the free energy and in a possible spontaneous change to another state whereby the free energy is lowered.
- Sugar has 65% solubility in water at 20° C, but would increase up to 80% when temperature rises to 100° C.

Phase Equilibria

- In many metallurgical and materials systems of interest, phase equilibrium involves just solid phases.
- ***Metastable*** state: when a state of equilibrium is never completely achieved as the rate of approach to equilibrium is extremely slow.

One-Component (Unary) Phase Diagrams

- Three externally controllable parameters that will affect phase structure: temperature, pressure, and composition
  - Phase diagrams are constructed when various combinations of these parameters are plotted against one another.
- One component system: composition is held constant.

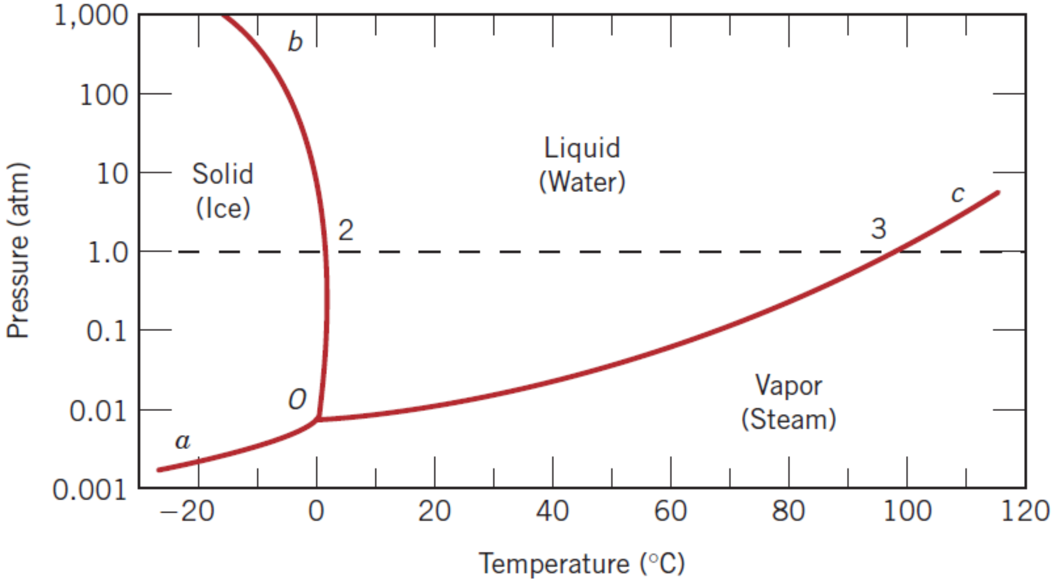


Figure 9.2 Pressure–temperature phase diagram for H_2O. Intersection of the dashed horizontal line at 1 atm pressure with the solid–liquid phase boundary (point 2) corresponds to the melting point at this pressure (*T* = 0° C). Similarly, point 3, the intersection with the liquid–vapor boundary, represents the boiling point (*T* = 100° C).

Binary Phase Diagrams (P = 101.3 kPa)

Binary Isomorphous Systems

The liquid *L* is a homogeneous liquid solution composed of both Cu and Ni.

The α phase is a substitutional solid solution consisting of both Cu and Ni atoms, and having an FCC crystal structure.

Below 1085 ° C, both Ni & Cu are totally soluble in each other for all compositions. Hence, Cu-Ni system is termed ***isomorphous***.

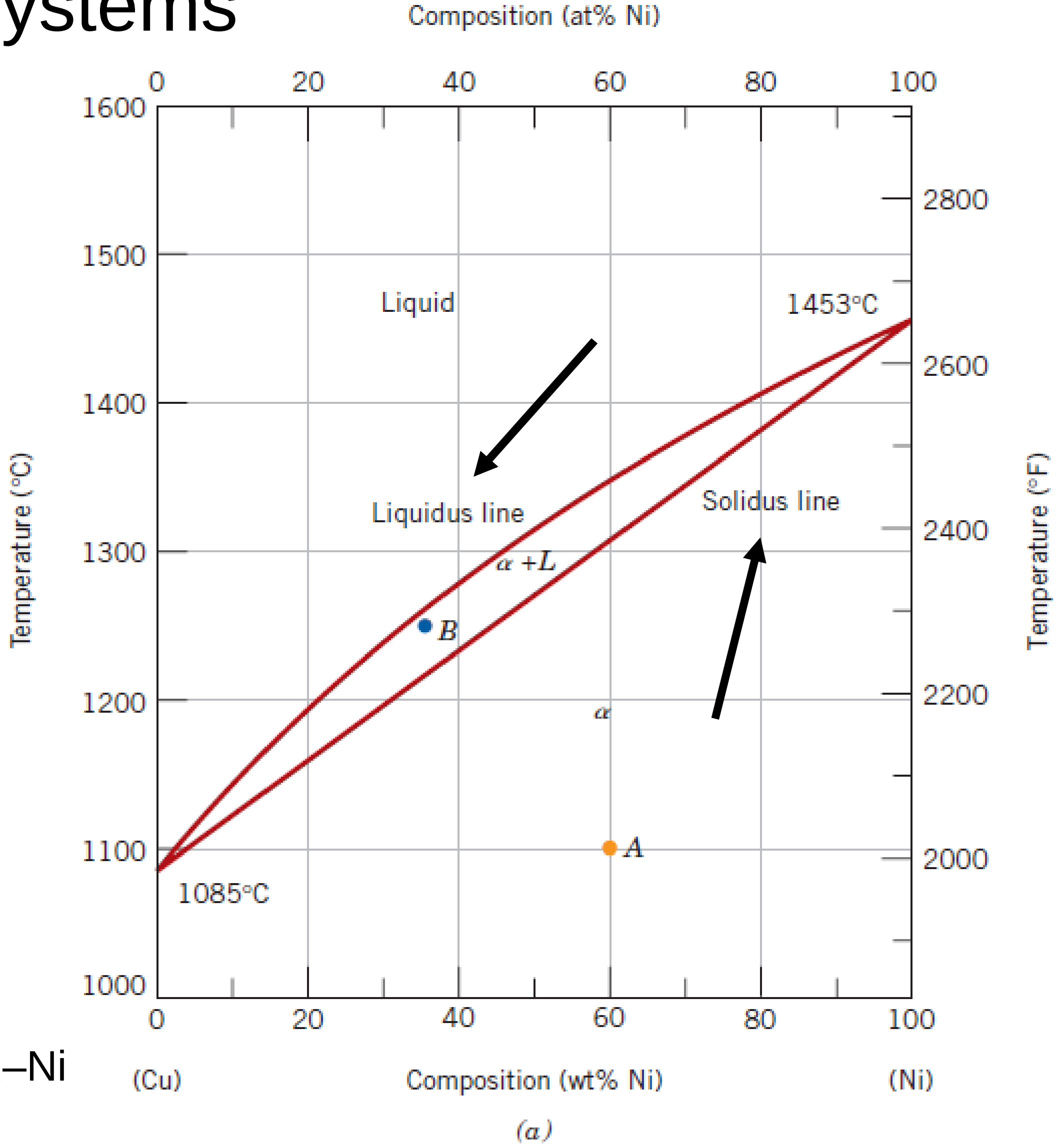


Figure 9.3 (*a*) The Cu–Ni phase diagram.

Interpretation of Phase Diagrams

Phases Present

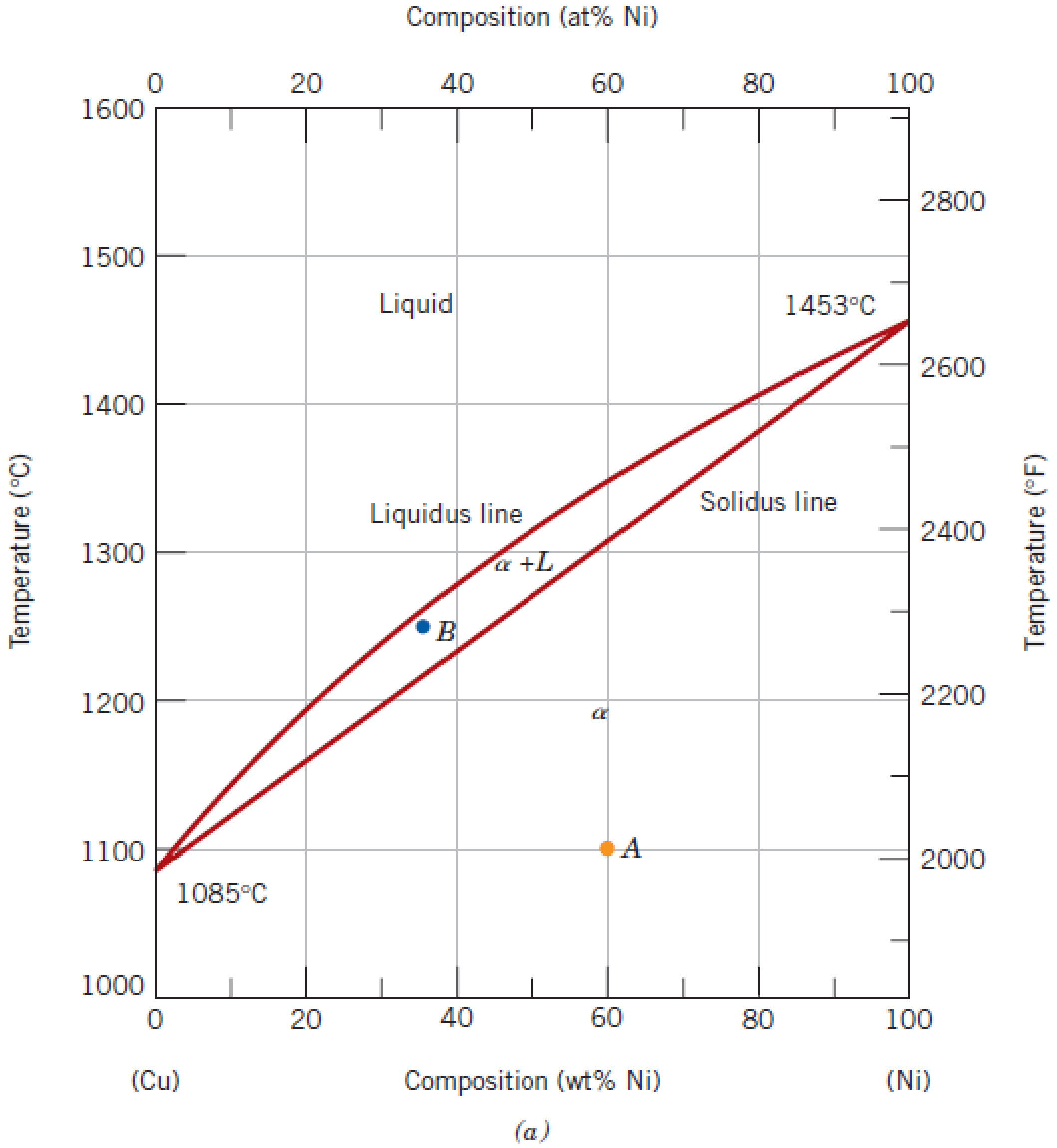
Locate the temperature–composition point on the diagram and notes the phase(s) with which the corresponding phase field is labeled.

Example 1.

Point A:

Example 2.

Point:



(a)

Interpretation of Phase Diagrams

Determination of Phase Compositions

(1) A tie line is constructed across the two-phase region at the temperature of the alloy.

(2) The intersections of the tie line and the phase boundaries on either side are noted.

(3) Perpendiculars are dropped from these intersections to the horizontal composition axis, from which the composition of each of the respective phases is read.

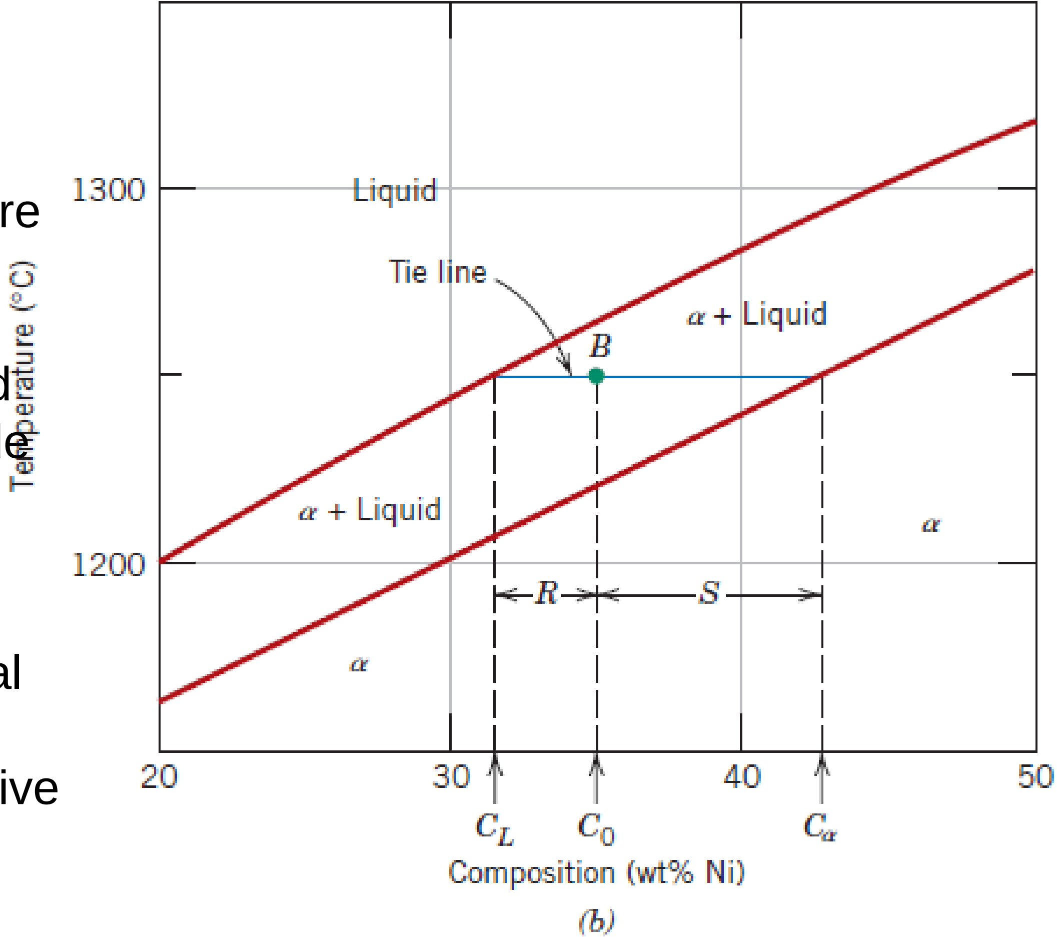


Figure 9.3 (*b*) A portion of the Cu– Ni phase diagram for which compositions and phase amounts are determined at point *B*.

Interpretation of Phase Diagrams
Determination of Phase Compositions

The perpendicular from the intersection of the tie line with the liquidus boundary meets the composition axis at 31.5 wt% Ni–68.5 wt% Cu, which is the composition of the liquid phase, C_L.

Likewise, for the solidus–tie line intersection, we find a composition for the α solid solution phase, C_α, of 42.5 wt% Ni–57.5 wt% Cu.

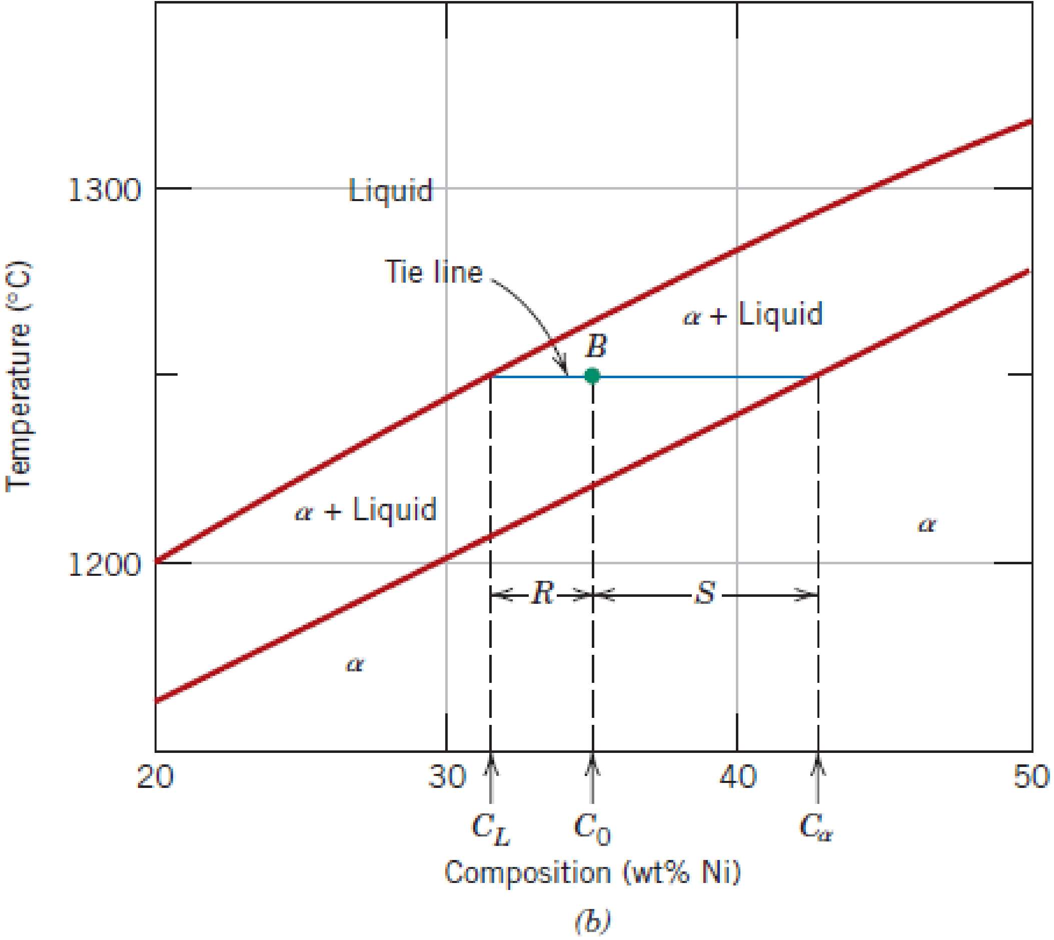


Figure 9.3 (*b*) A portion of the Cu– Ni phase diagram for which compositions and phase amounts are determined at point *B*.

Interpretation of Phase Diagrams

Determination of Phase Amounts / Inverse Lever Rule

(1) The tie line is constructed 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 tie line from the overall alloy composition to the phase boundary for the *other* phase, and dividing by the total tie line length.

(4) The fraction of the other phase is determined in the same manner.

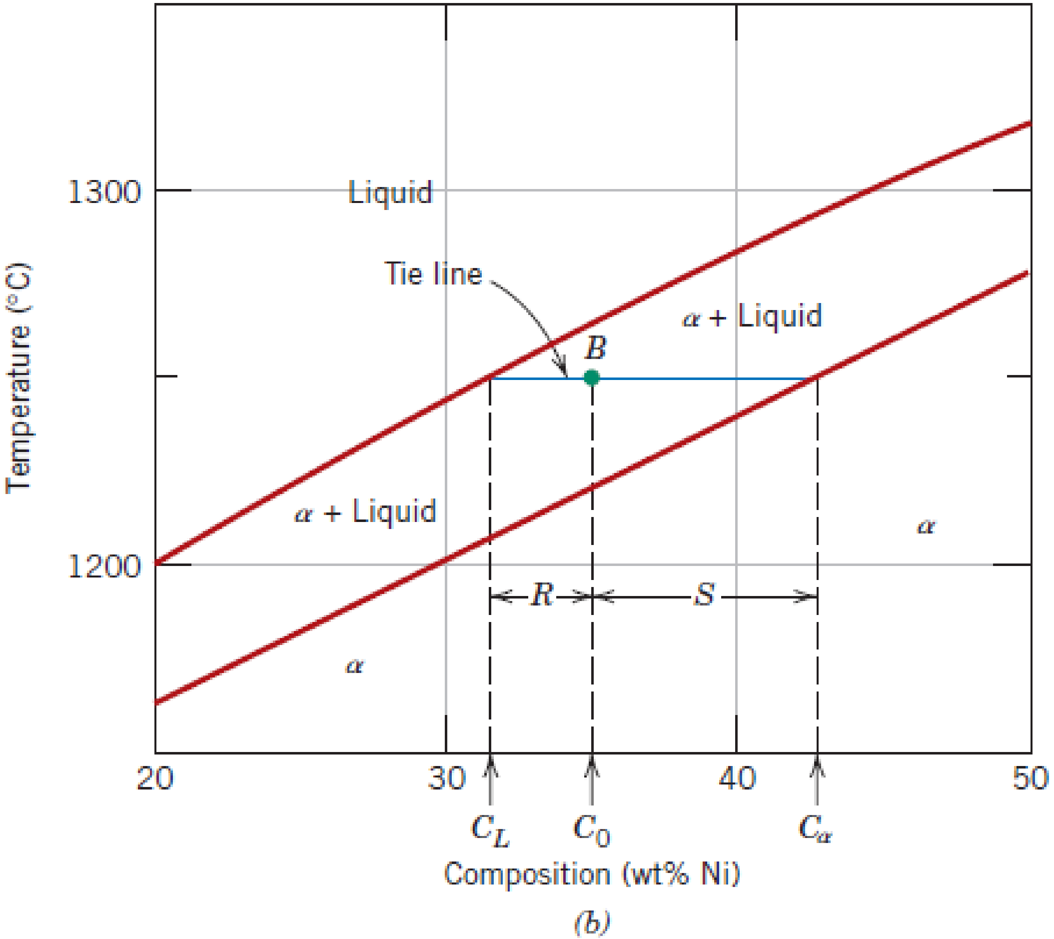


Figure 9.3 (*b*) A portion of the Cu– Ni phase diagram for which compositions and phase amounts are determined at point *B*.

Interpretation of Phase Diagrams

Determination of Phase Amounts / Inverse Lever Rule

Example: Let’s calculate the amounts of the liquid and α phases at point *B*.

(1) The overall composition at *B* is C_0 = 35 wt.% Ni.

(2) Fraction of liquid =

$$W_L = \frac{S}{R+S}$$

$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

$$W_L = \frac{42.5-35}{42.5-31.5} = 0.68$$

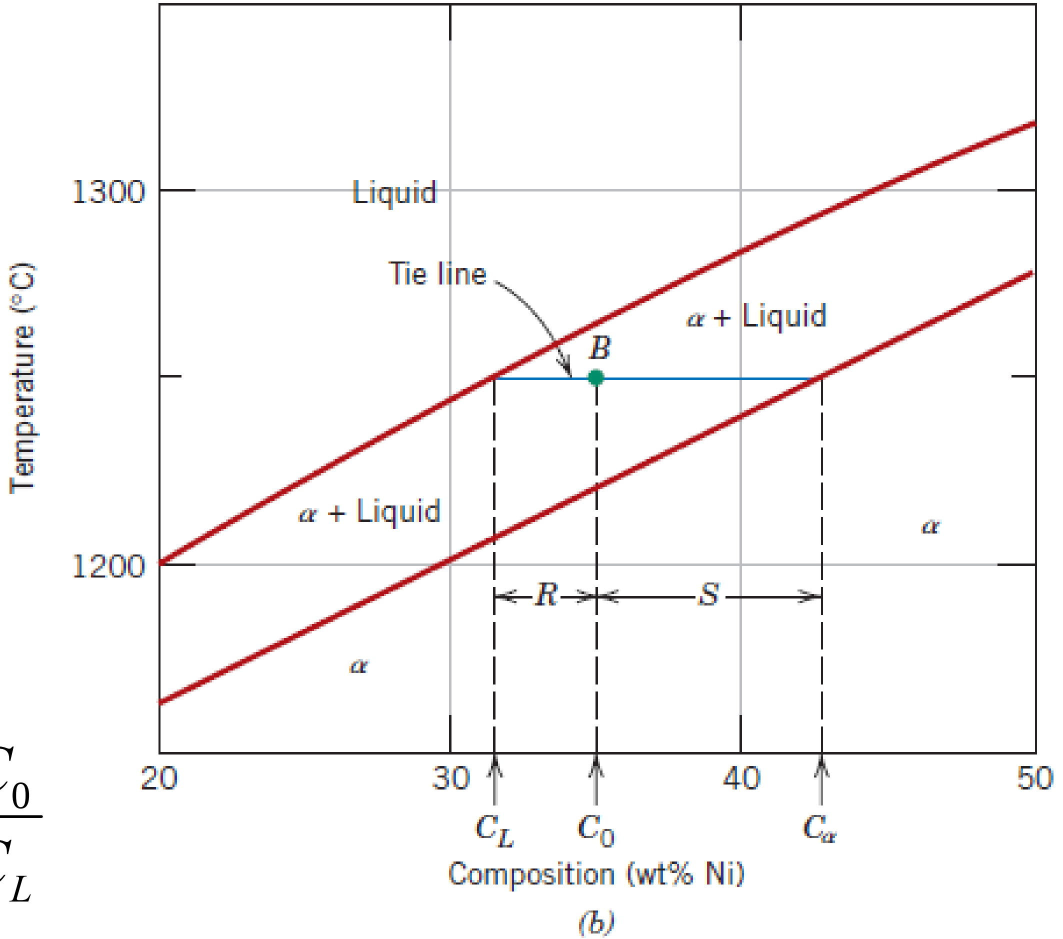


Figure 9.3 (*b*) A portion of the Cu– Ni phase diagram for which compositions and phase amounts are determined at point *B*.

Development of Microstructure in Isomorphous Alloys / Equilibrium Cooling

At 1300° C, point *a*, the alloy is completely liquid (of composition 35 wt% Ni–65 wt% Cu)

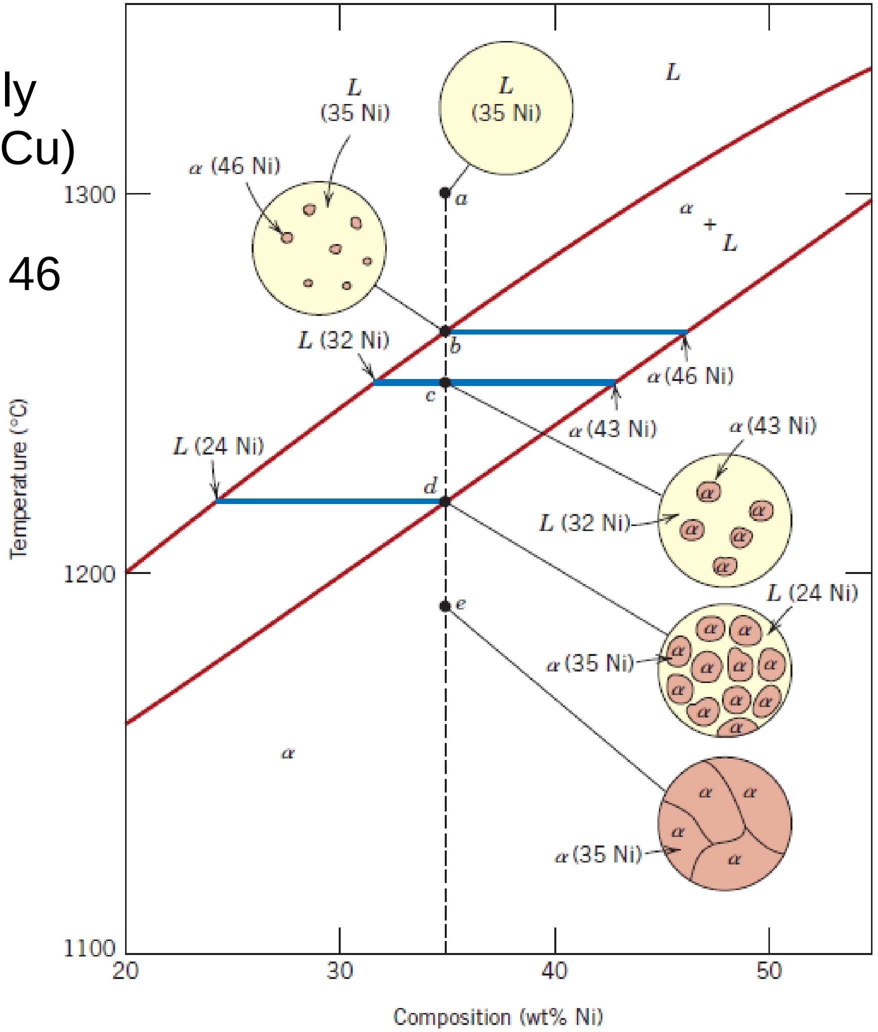
At point *b*, α begins to form. composition: 46 wt% Ni. *L* composition: 35 wt% Ni.

The fraction of the α phase will increase with continued cooling.

At 1250 ° C, point c. α = 43 wt% Ni, *L* = 32 wt%Ni.

At 1220 ° C, point d. α = 35 wt% Ni, *L* = 24 wt%Ni.

below 1220 ° C, point e. α = 35 wt% Ni, and no *L.*



Development of Microstructure in Isomorphous Alloys / Nonequilibrium Cooling

- Equilibrium cooling: a result of diffusion.
  - Readjustments in the compositions of the liquid and solid phases in accordance with the phase diagram
- Nonequilibrium cooling: cooling rate is rapid, no time for diffusion.
  - No time for (ideal) readjustments of phases.

Development of Microstructure in Isomorphous Alloys / Nonequilibrium Cooling

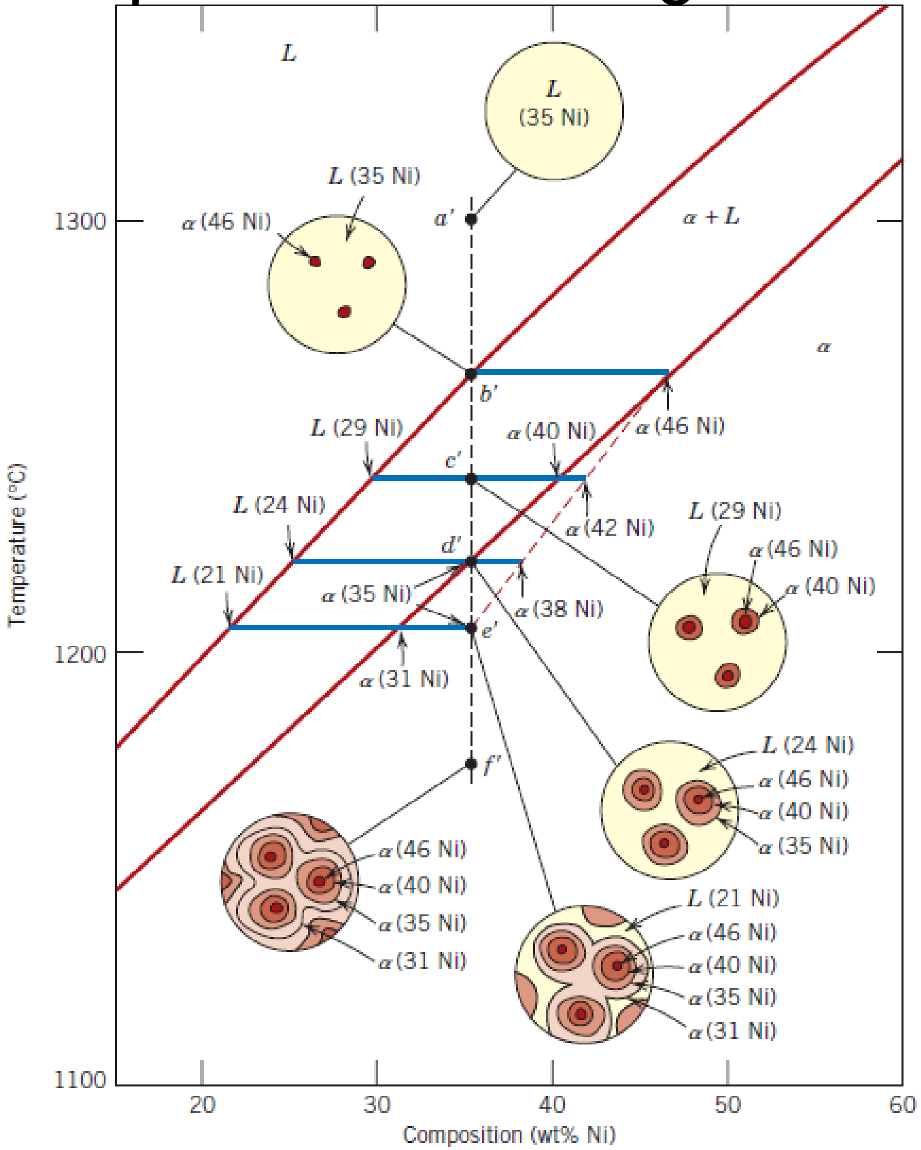
Nonequilibrium cooling:

-Shift of the solidus line to lower temperatures.

-An average composition results rather than a fixed one.

-Segregation results: concentration gradients are established across the grains.

- the center of each grain, which is the first part to freeze, is rich in the high melting element (Ni), whereas the concentration of the low-melting element increases with position from this region to the grain boundary (termed ***core structure***).



Development of Microstructure in Isomorphous Alloys / Nonequilibrium Cooling

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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, or an increase in strength and hardness by additions of the other component.

Mechanical Properties of Isomorphous Alloys

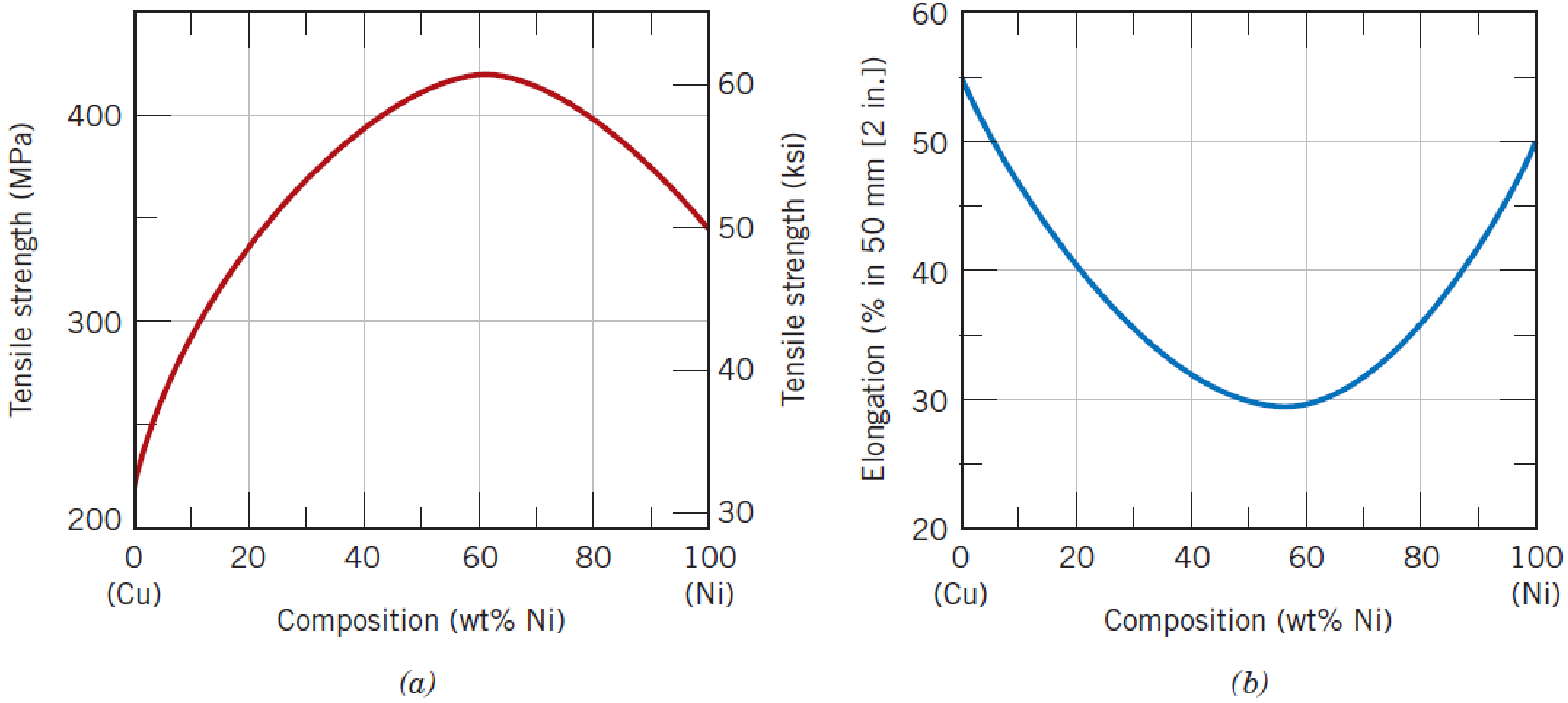


Figure 9.6 For the copper–nickel system, (*a*) tensile strength versus composition, and (*b*) ductility (%EL) versus composition at room temperature. A solid solution exists over all compositions for this system.

Binary Eutectic Systems

Eutectic: transformation of ***liquid*** into ***two solids***.

Limited solubility of one element into the other.

Solvus line: the solid solubility limit line separating the α and α+β phase regions

Maximum solubility of Ag in Cu = 8 wt% Ag at 779 ° C.

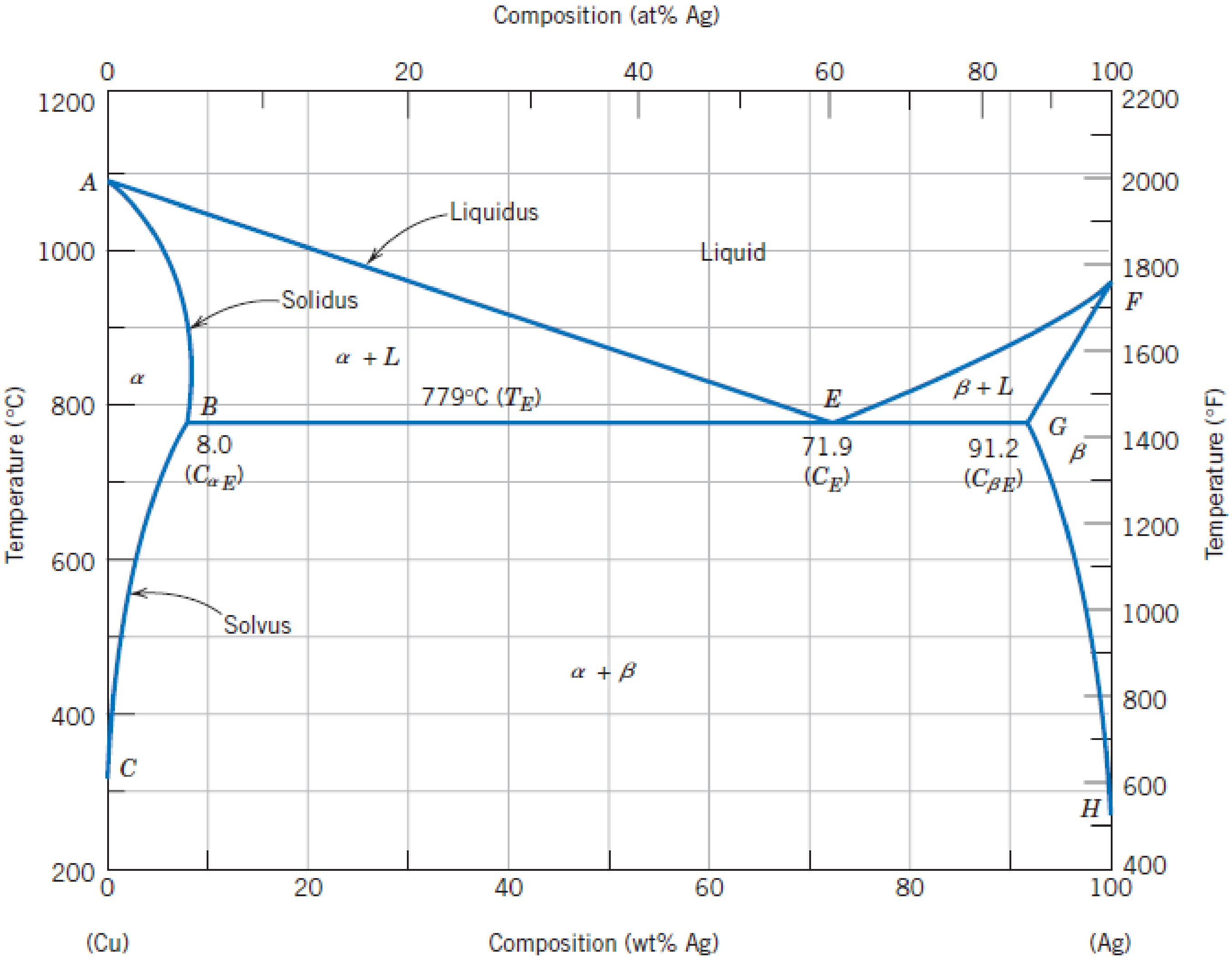


Figure 9.7 The copper–silver phase diagram.

Binary Eutectic Systems

Invariant point = eutectic point: point at which the two liquidus lines meet.

At T_E & C_E: $$L(C_E) \underset{\text{heating}}{\overset{\text{cooling}}{\Leftrightarrow}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

For Cu – Ag system: $$L(71.9\,\text{wt}\,\%\,\text{Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\Leftrightarrow}} \alpha(8.0\,\text{wt}\,\%\,\text{Ag}) + \beta(91.2\,\text{wt}\,\%\,\text{Ag})$$

The eutectic reaction, upon cooling, is similar to solidification for pure components in that the reaction proceeds to completion at a constant temperature.

Development of Microstructure in Eutectic alloys

- At *a* (350 °C): liquid with C_1 composition.
- At *b* (330 °C): α starts to form within the *L*.
- At *c* (275 °C): single α phase, no further transformation upon cooling.

Applicable for alloys containing between 0 and about 2 wt% Sn.

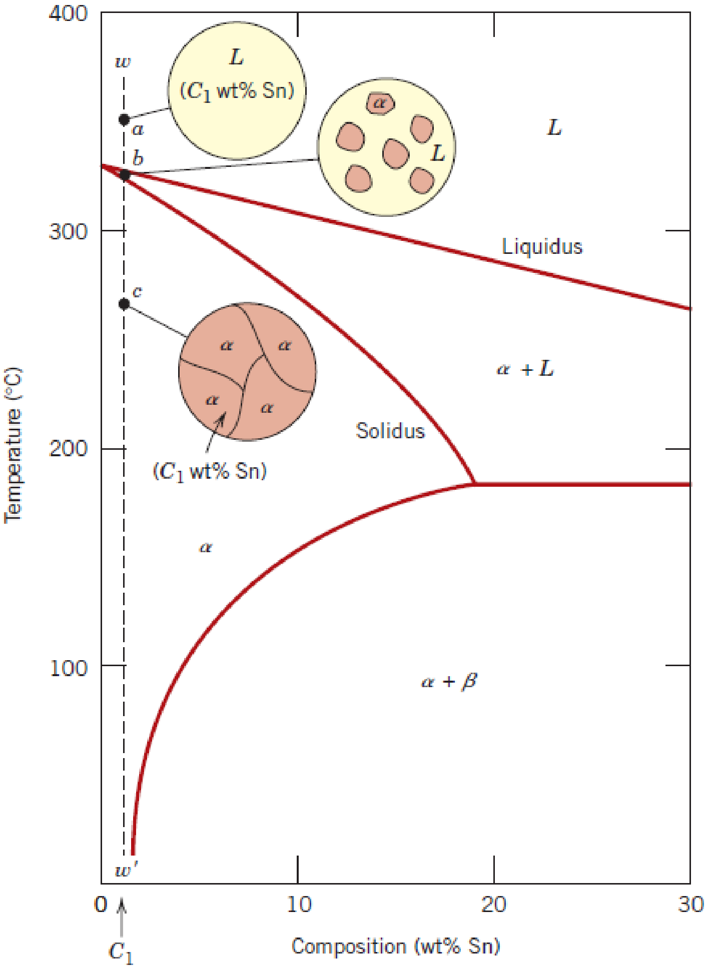


Figure 9.11 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_1 as it is cooled from the liquid-phase region.

Development of Microstructure in Eutectic alloys

- At *d* : liquid with C_2 composition.
- At *e:* α forms and *L* is present.
- At *f*: single α phase, no more *L*.
- At *g*: solubility limit of Sn in Pb is exceeded, β precipitates form.
- Crossing *g*: β particles will grow in size because the mass fraction of the phase increases slightly with decreasing temperature.

Applicable for alloys containing about 2 wt% Sn to 18.3 wt% Sn

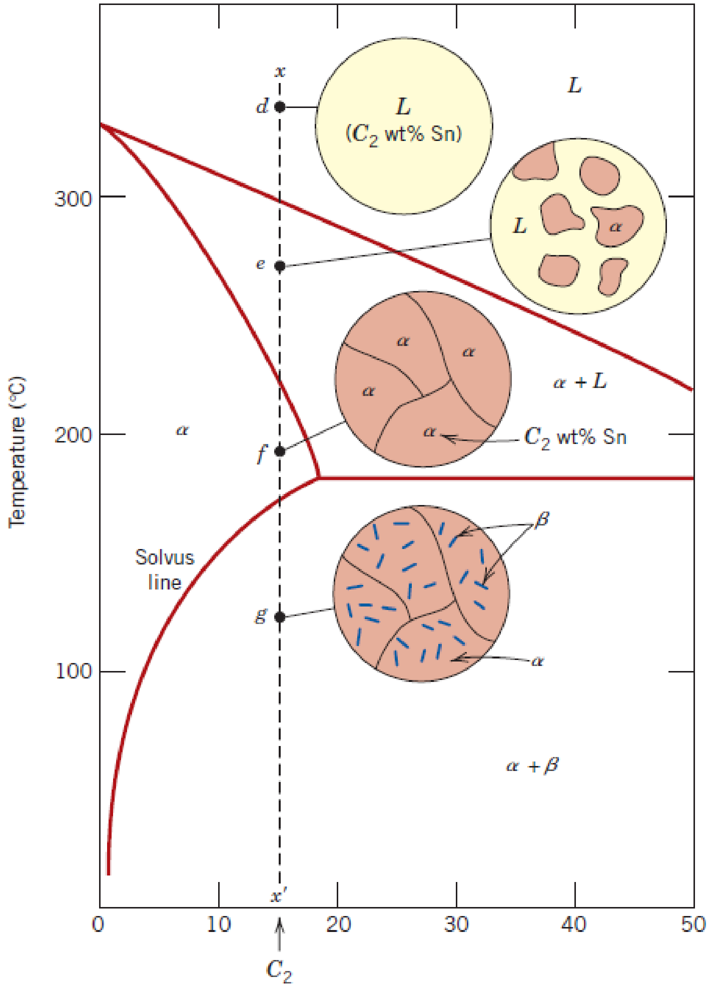


Figure 9.11 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_2 as it is cooled from the liquid-phase region.

Development of Microstructure in Eutectic alloys

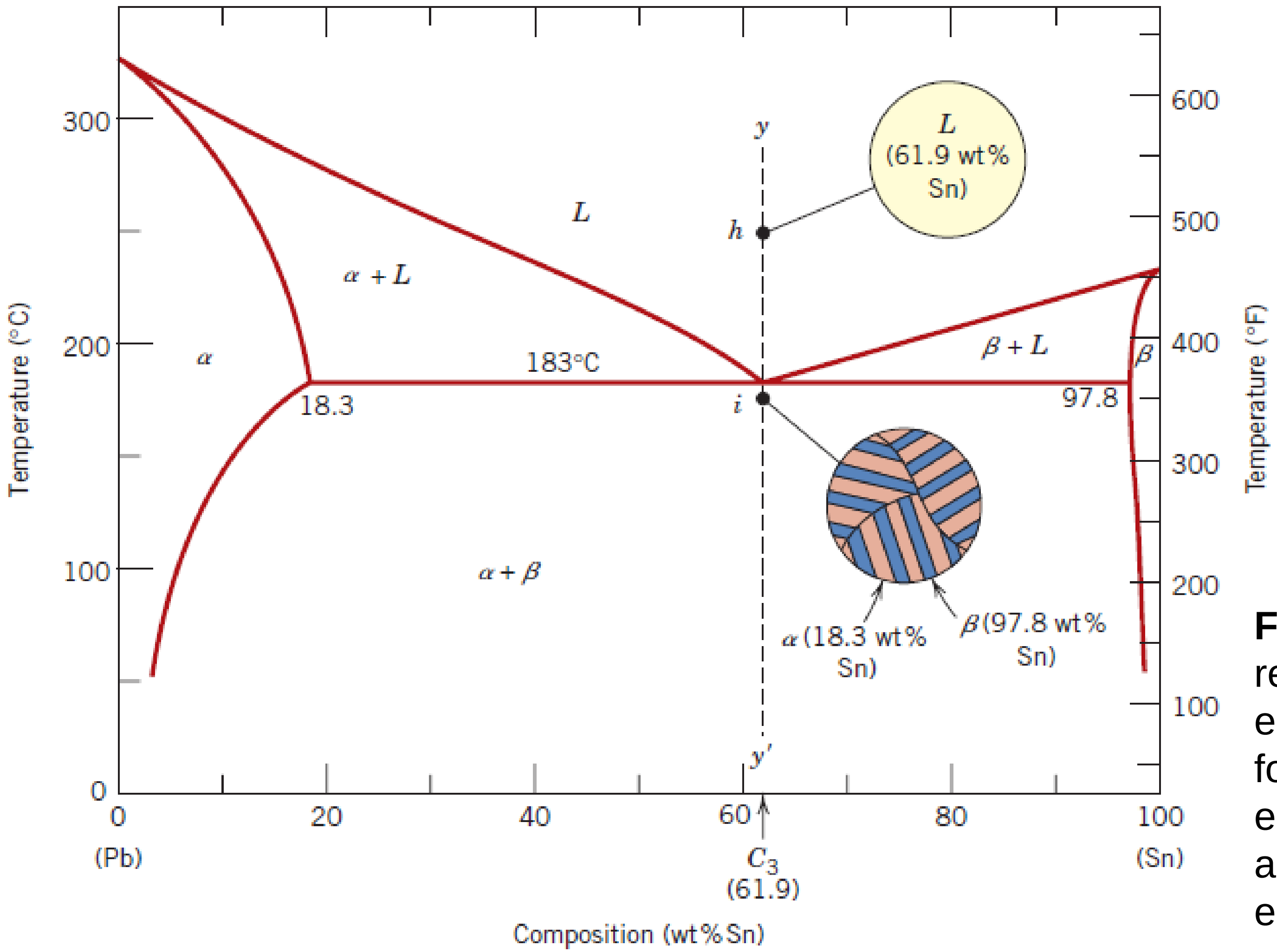


Figure 9.13 Schematic representations of the equilibrium microstructures for a lead– tin alloy of eutectic composition C_3 above and below the eutectic temperature.

Development of Microstructure in Eutectic alloys

- At *h* : liquid with C_3 composition.
- At *i* (crossing the eutectic temperature line)*: L* transforms to α and β.

$$L(61.9\,\text{wt}\,\%\,\text{Sn}) \underset{\text{heating}}{\overset{\text{cooling}}{\Leftrightarrow}} \alpha(18.3\,\text{wt}\,\%\,\text{Sn}) + \beta(97.8\,\text{wt}\,\%\,\text{Sn})$$

- The microstructure (eutectic structure) of the solid that results from this transformation consists of alternating layers (sometimes called lamellae) of the and phases that form simultaneously during the transformation.
- No pronounced microstructural changes upon cooling below point *i*.

Applicable for the alloy containing 61.9 wt% Sn only.

Development of Microstructure in Eutectic alloys

Figure 9.14 Photomicrograph showing the microstructure of a lead–tin alloy of eutectic composition. This microstructure consists of alternating layers of a lead-rich α-phase solid solution (dark layers), and a tin-rich β-phase solid solution (light layers). 375 ×.

Development of Microstructure in Eutectic alloys

- Lead atoms diffuse toward the α-phase layers because this α phase is lead-rich (18.3 wt% Sn–81.7 wt% Pb); conversely, the direction of diffusion of tin is in the direction of the β, tin-rich (97.8 wt% Sn–2.2 wt% Pb) layers.

- The eutectic structure forms in these alternating layers because, for this lamellar configuration, atomic diffusion of lead and tin need only occur over relatively short distances.

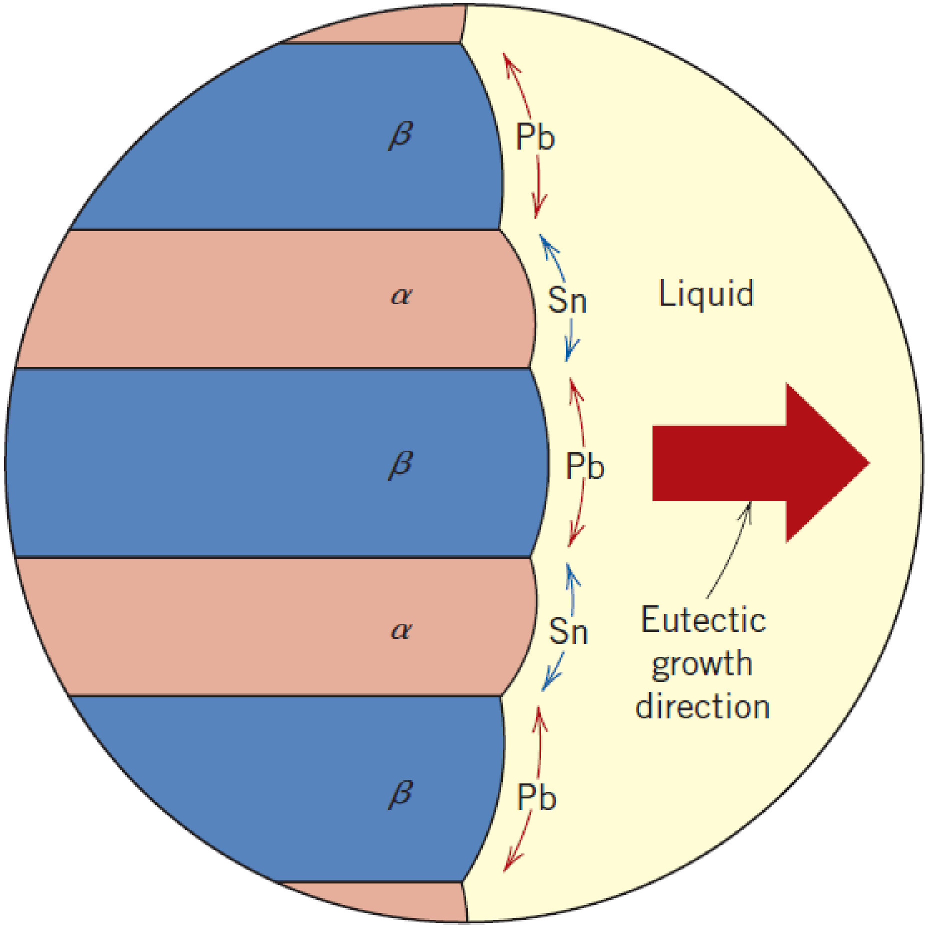


Figure 9.15 Schematic representation of the formation of the eutectic structure for the lead–tin system. Directions of diffusion of tin and lead atoms are indicated by blue and red arrows, respectively.

Development of Microstructure in Eutectic alloys

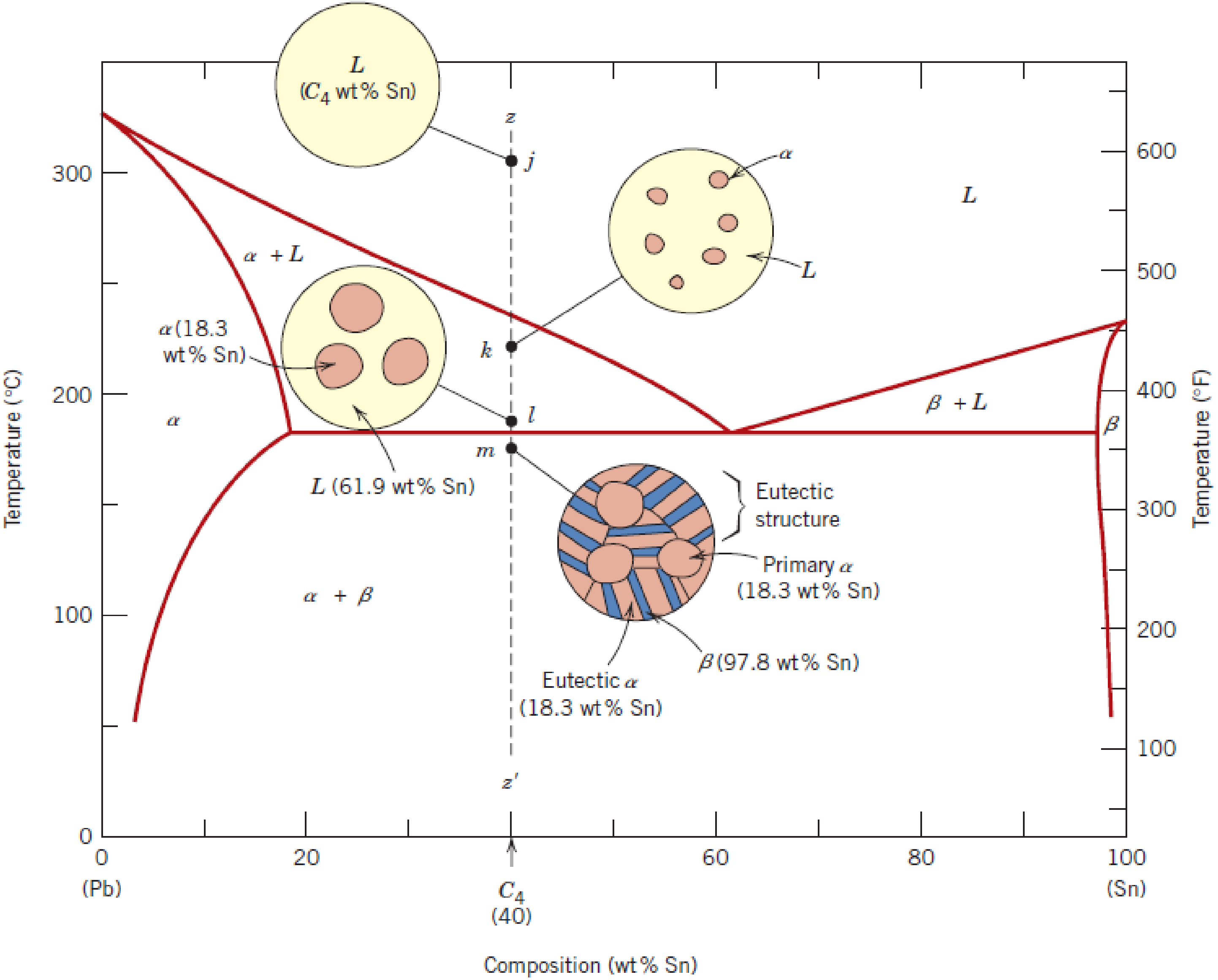


Figure 9.16 Schematic representations of the equilibrium microstructures for a lead–tin alloy of composition C_4 as it is cooled from the liquid-phase region.

Development of Microstructure in Eutectic alloys

- At *j* : liquid with C_4 composition.
- At *k:* α starts to form.
- At *l*: more α forms where it grows in size.
    - α that forms at temperatures higher than the eutectic temperature is called proeutectoid or ***primary*** α.
- At *m*: eutectic temperature is crossed. Here, the remaining liquid which had the eutectic composition at point l will experience a eutectic reaction; alternating layers of α (***eutectic*** α) and β phases.

Development of Microstructure in Eutectic alloys

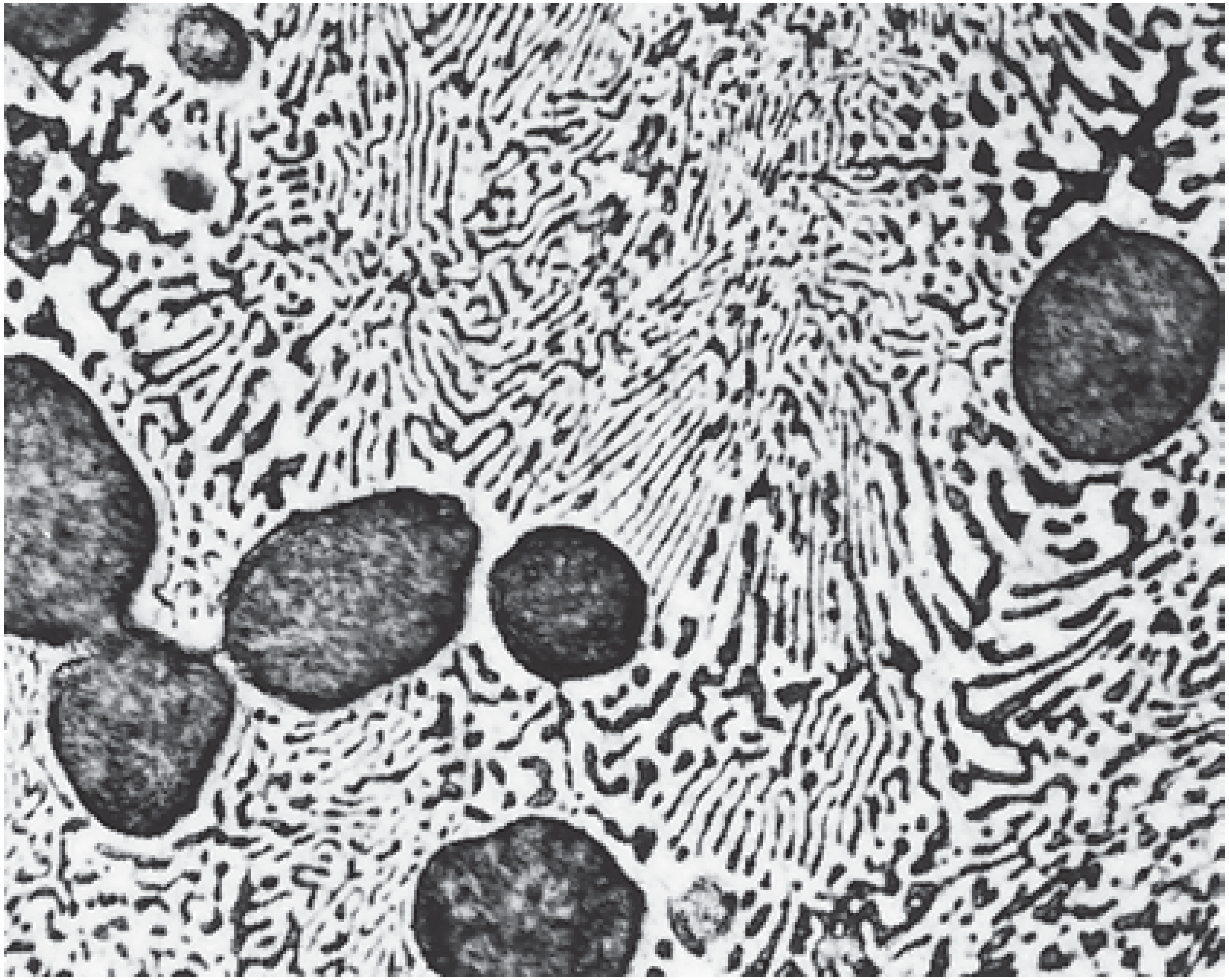


Figure 9.17 Photomicrograph showing the microstructure of a lead–tin alloy of composition 50 wt% Sn–50 wt% Pb. This microstructure is composed of a primary lead-rich α phase (large dark regions) within a lamellar eutectic structure consisting of a tin-rich β phase (light layers) and a lead-rich α phase (dark layers). 400×.

Development of Microstructure in Eutectic alloys

$$W_e = W_L = \frac{P}{P+Q}$$

Weight fraction of the eutectic microconstituent

$$W_{\alpha'} = \frac{Q}{P+Q}$$

Weight fraction of the primary α.

$$W_\alpha = \frac{Q+R}{P+Q+R}$$

Weight fraction of total α.

$$W_\beta = \frac{P}{P+Q+R}$$

Weight fraction of β.

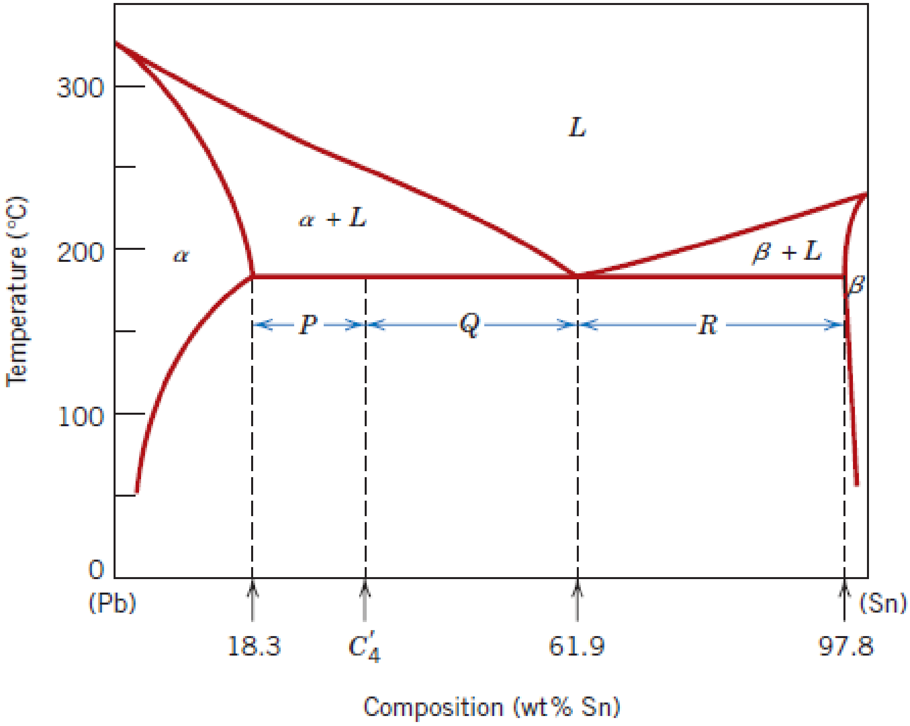


Figure 9.18 The lead–tin phase diagram used in computations for relative amounts of primary α and eutectic microconstituents for an alloy of composition C'_4.

Eutectoid and Peritectic Reactions

- At *E* (eutectoid point): eutectoid reaction takes place on cooling; one solid transforms into 2 other solids.

$$\delta \underset{\text{heating}}{\overset{\text{cooling}}{\Leftrightarrow}} \gamma + \varepsilon$$

- At *P* (peritectic point): peritectic reaction takes place on cooling; a solid and a liquid transform into another solid.

$$\delta + L \underset{\text{heating}}{\overset{\text{cooling}}{\Leftrightarrow}} \varepsilon$$

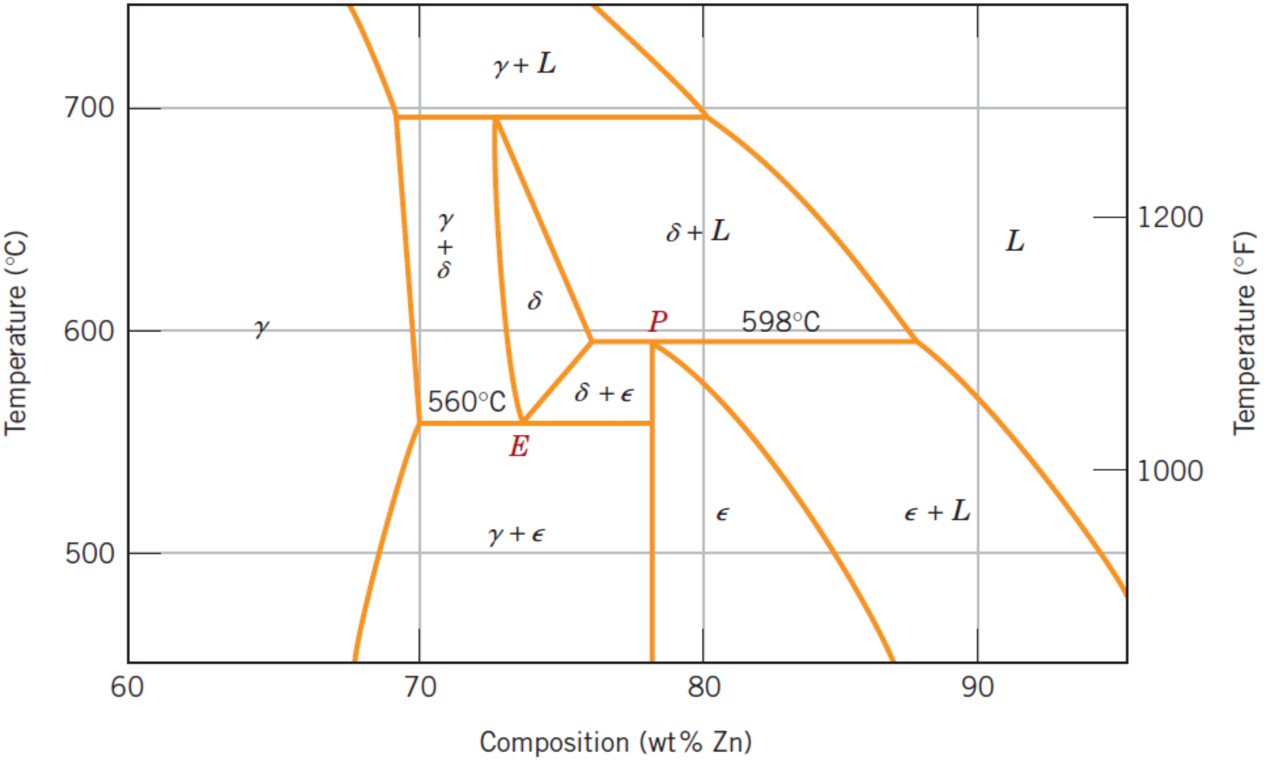


Figure 9.21 A region of the copper–zinc phase diagram that has been enlarged to show eutectoid and peritectic invariant points, labeled *E* (560 °C, 74 wt% Zn) and *P* (598 °C, 78.6 wt% Zn), respectively.

Congruent and Incongruent Transformations

- ***Congruent transformation***: no compositional alterations upon transformation.
  - E.g.; solidification of pure metals, allotropic transformations, etc.
  - Incongruent: Eutectoid and eutectic reactions, melting of an alloy, etc.

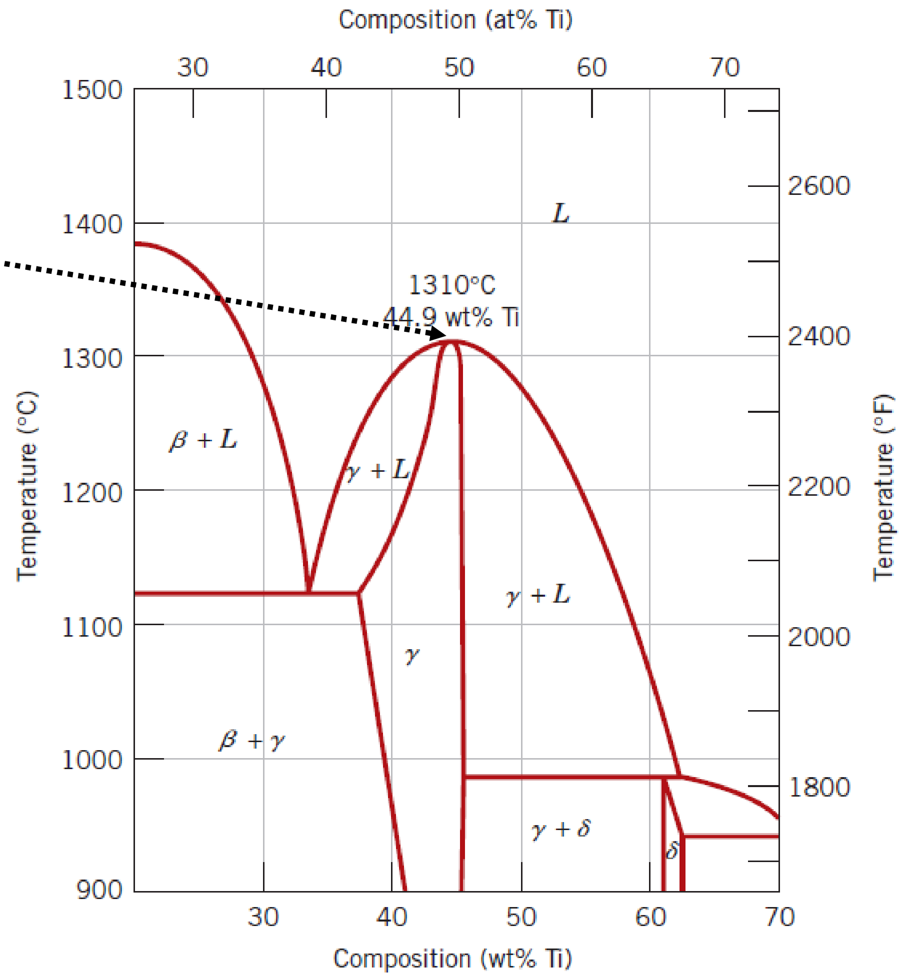


Figure 9.22 A portion of the Ni–Ti phase diagram on which is shown a congruent melting point for the γ-phase solid solution at 1310 °C and 44.9 wt% Ti.

The Gibbs Phase Rule

- ***Gibbs Phase Rule***: a rule that represents a criterion for the number of phases that will coexist within a system at equilibrium; expressed by:

$$P + F = C + N$$

P: the number of phases present.

F: *number of degrees of freedom* or the number of externally controlled variables (e.g., temperature, pressure, composition) which must be specified to completely define the state of the system.
Alternatively, *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: the number of noncompositional variables (e.g., temperature and pressure).

The Gibbs Phase Rule

- ***Gibbs Phase Rule***: applying to the copper–silver system, Fig. 9.7.
  - 1. Pressure is constant = 1 atm, so *N* = 1 (1—temperature is the only noncompositional variable).
  - 2. *C* = 2, since we have Cu and Ag.
  - Hence: $P + F = 3 \Rightarrow F = 3 - P$
  - Considering single-phase fields, *P* = 1. $\Rightarrow F = 2$
  - This means that to completely describe the characteristics of any alloy that exists within one of these phase fields, we must specify two parameters; these are composition and temperature.

The Gibbs Phase Rule

- ***Gibbs Phase Rule***: applying to the copper–silver system, Fig. 9.7.
  - 1. Pressure is constant = 1 atm, so *N* = 1 (1—temperature is the only noncompositional variable).
  - 2. *C* = 2, since we have Cu and Ag.
  - Hence: $P + F = 3 \quad \Rightarrow \quad F = 3 - P$
  - Considering two-phase fields, *P* = 2. $\quad \Rightarrow \quad F = 1$
  - Thus, it is necessary to specify either temperature or the composition of one of the phases to completely define the system.

The Gibbs Phase Rule

- ***Gibbs Phase Rule***: applying to the copper–silver system, Fig. 9.7.
  - 1. Pressure is constant = 1 atm, so *N* = 1 (1—temperature is the only noncompositional variable).
  - 2. *C* = 2, since we have Cu and Ag.
  - Hence: $P + F = 3 \Rightarrow F = 3 - P$
  - Considering three phases, *P* = 3. $\Rightarrow F = 0$
  - This means that the compositions of all three phases as well as the temperature are fixed (eutectic point).

The Iron – Carbon (Carbide: Fe_3C) System

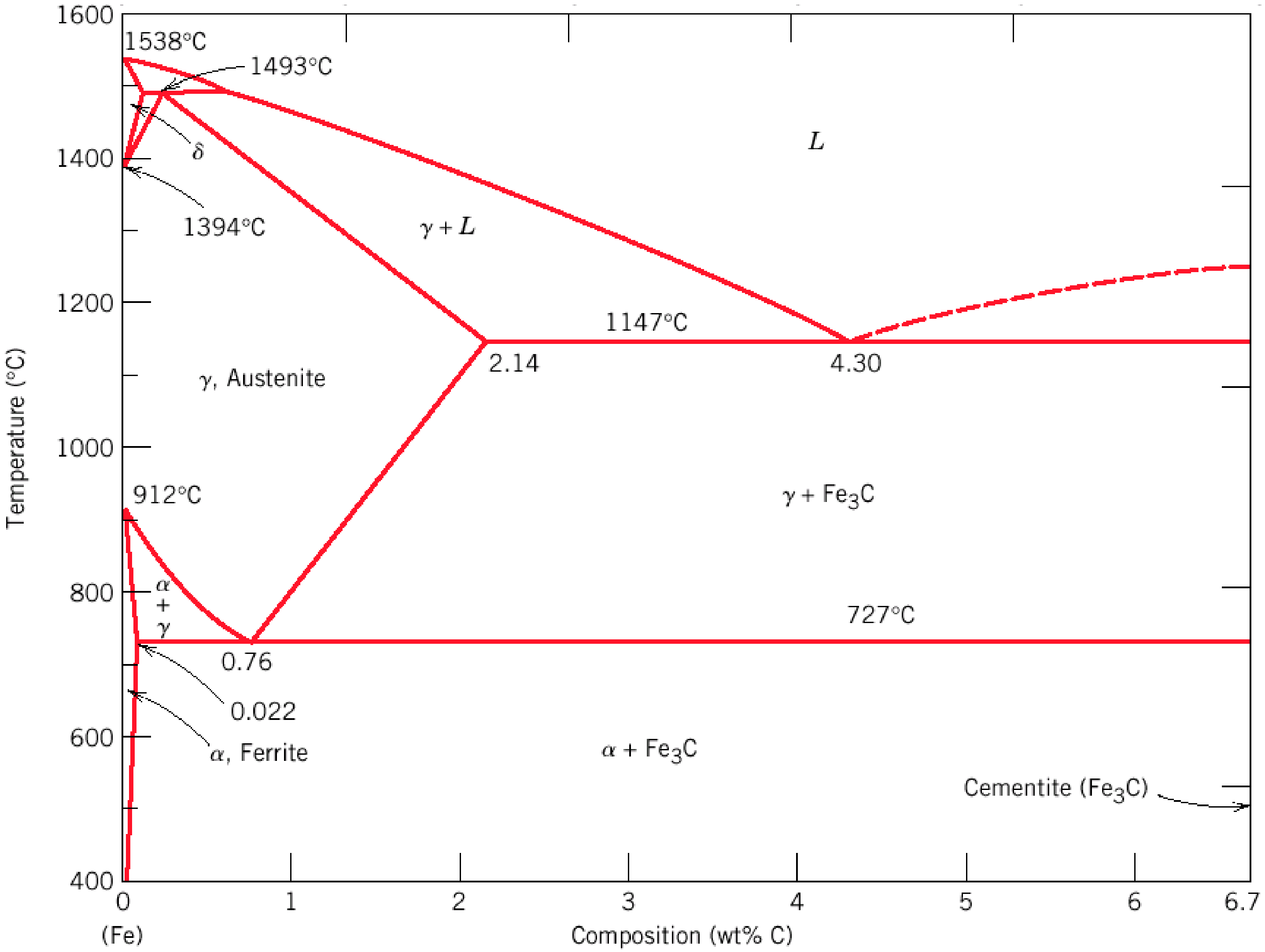


Figure 9.24 The iron–iron carbide phase diagram.

The Iron – Carbon (Carbide: Fe_3C) System

- **α-Fe (ferrite) - solid solution of C in BCC Fe**
  - Stable up to ~910 °C.
  - The maximum solubility of C in α-Fe is ~0.022 wt%
  - Transforms to FCC γ-Fe at ~910 °C.
  - When subjected to quenching, C can remain in the α solid solution, but soon precipitation of phases commences, by an aging treatment.
  - Ferrite is plastic, and in the annealed state it has large elongation (~40%).
  - Ferrite is soft (Brinell hardness is 65-130).
  - Ferrite is strongly magnetic up to 770 ºC.

- γ-Fe (austenite) - **solid solution of C in FCC Fe**
  - The maximum solubility of C in γ-Fe is ~2.14 wt %.
  - Transforms to BCC δ-Fe at ~1400 °C.
  - Austenite is soft but harder than ferrite, ductile and its elongation is similar to ferrite.
  - Lower conductivity of heat and electricity as compared to ferrite and is paramagnetic.

The Iron – Carbon (Carbide: Fe_3C) System

- δ-Fe (**ferrite**) - **solid solution of C in BCC Fe**
  - Same crystal structure as α-Fe and is also called ferrite.
  - Stable only above ~1400 °C
  - Solubility of C in δ-Fe is 5 times higher than in α-Fe.

- **Fe_3C (iron carbide or cementite)**
  - Cementite is an intermetallic compound and is almost always present in a metastable state.
  - Cementite is present even in relatively slowly cooled alloys; a long holding at elevated temperatures is required to decompose cementite to α-iron and graphite.
  - Cementite is brittle and exhibits great hardness (Brinell hardness ~800).
  - It is weakly magnetic up to 210 °C, poor conductor of heat and electricity and has a complicated rhombic lattice.

- Liquid solution forms at ~1538 ºC in pure iron; this temperature decreases on alloying with C and increases as C content reaches 4.3 wt.%.

The Iron – Carbon (Carbide: Fe_3C) System

- The eutectoid reaction is the transformation of one solid into two other solids. In the case of Fe-C system it represents the decomposition of the austenite into ferrite and cementite on cooling.

- The eutectoid reaction takes place at 727 °C and 0.76 wt. %C

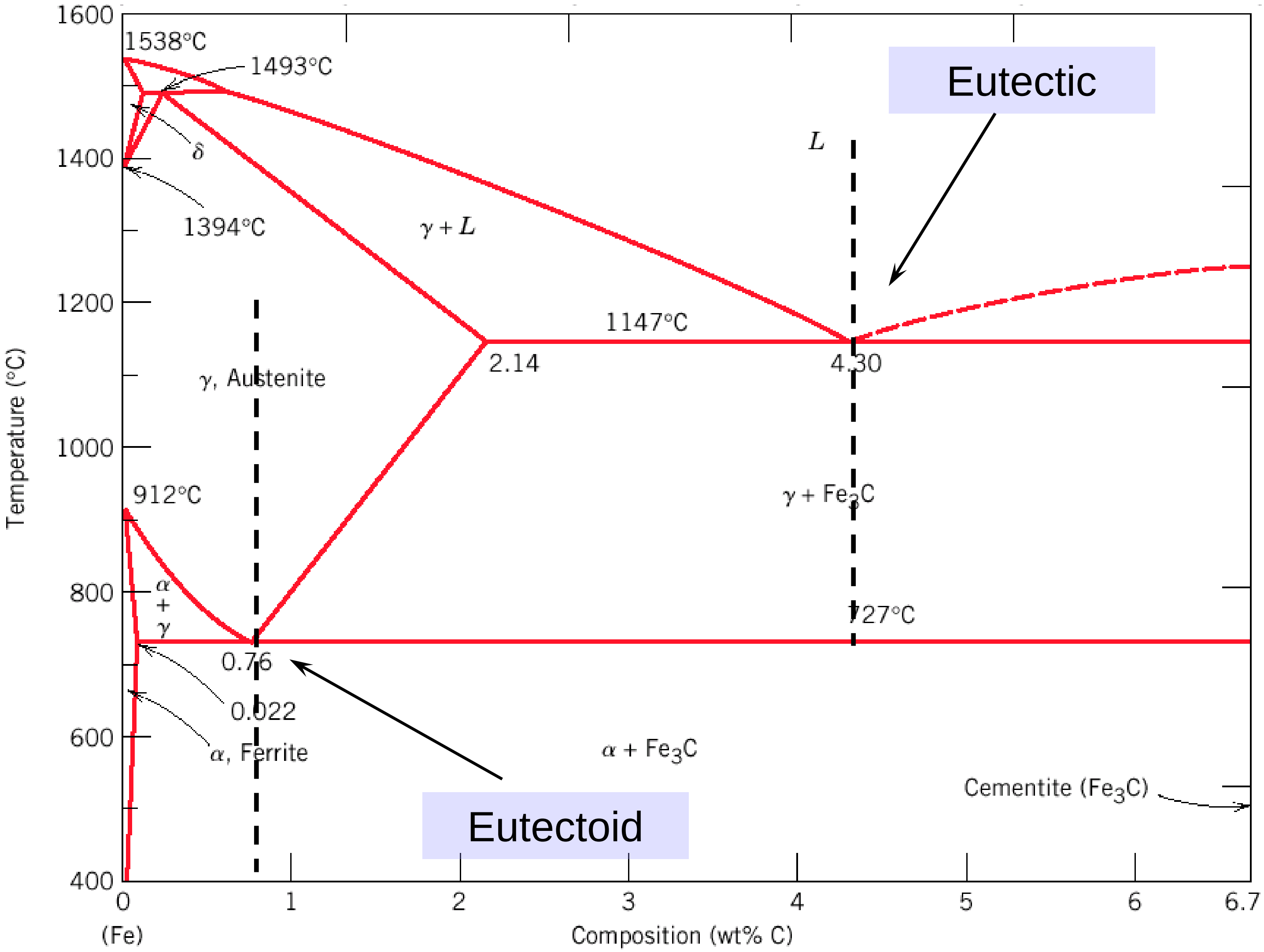
$$\gamma(0.76\ \text{wt\% C}) \rightarrow \alpha\ (0.022\ \text{wt\% C}) + Fe_3C$$

- The eutectic reaction on the other hand, is the transformation of one liquid into two solids. In the case of Fe-C system it represents the transformation of the liquid into austenite and cementite on cooling.

- The eutectic reaction takes place at 1147 °C and 4.3 wt. %C.

$$\text{Liq.} \rightarrow \gamma + Fe_3C$$

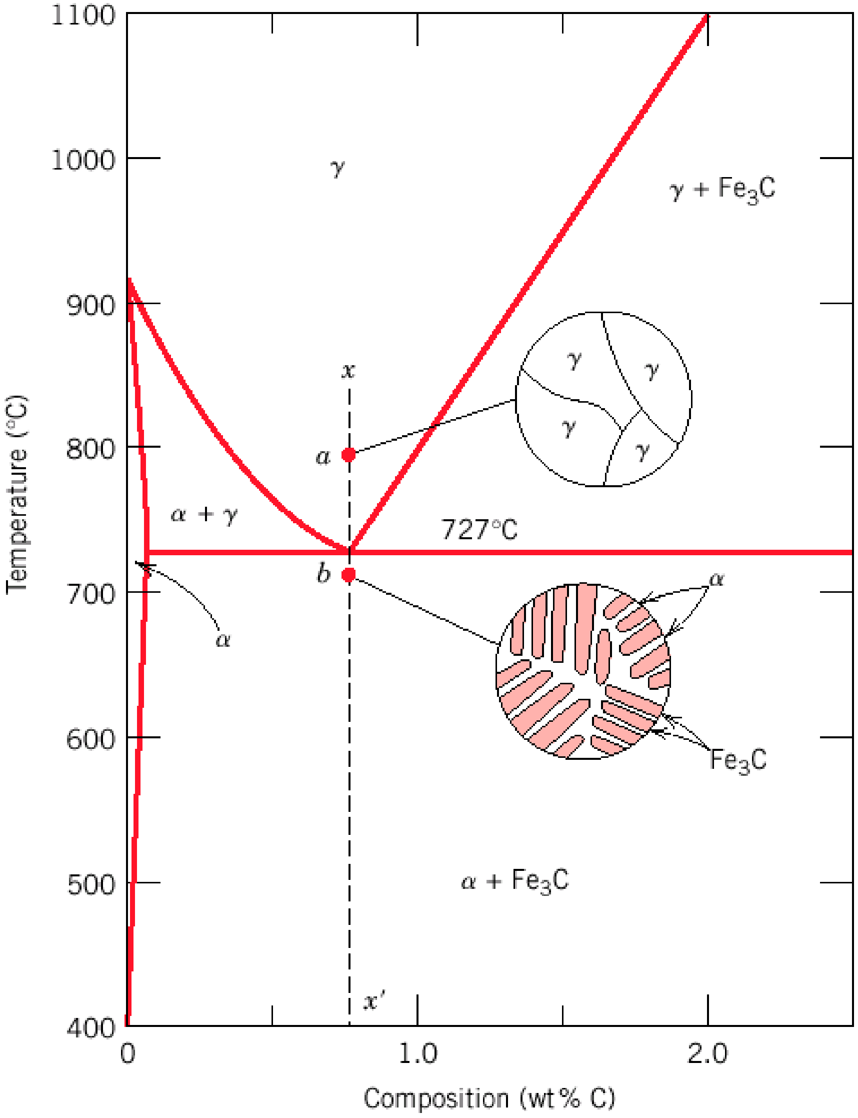
The Iron – Carbon (Carbide: Fe_3C) System



Eutectic

Eutectoid

The Iron – Carbon (Carbide: Fe_3C) System



The transformation from austenite to ferrite is hampered due to presence of C in austenite.

FCC: more space for C atoms. Higher solubility.

During transformation from γ to α, almost all C precipitates as Fe_3C from the austenite.

[1] $\gamma \rightarrow \alpha$

[2] Precipitation of C in the form of Fe_3C.

[3] Coagulation of the carbides.

The first two processes occur almost simultaneously, with the formation of a lamellar mixture of ferrite and cementite.

In γ: C is distributed randomly, thus Fe_3C and ferrite nucleate at C-rich and -depleted regions, respectively.

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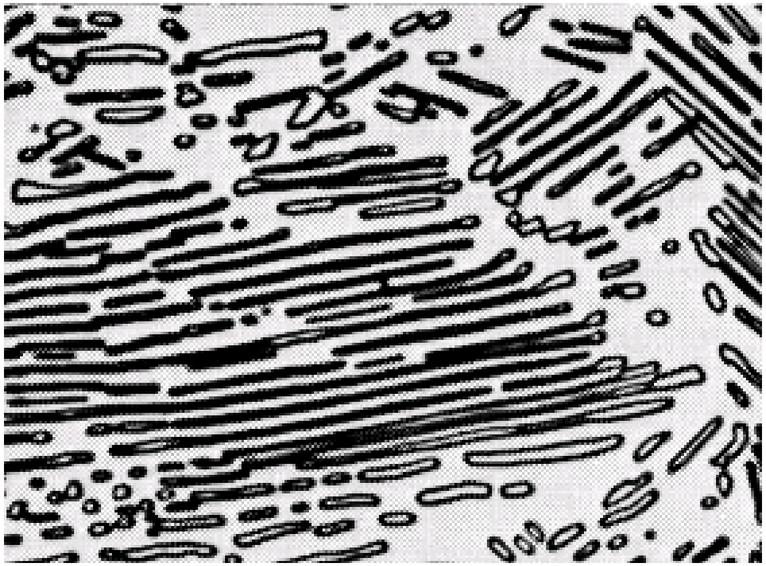

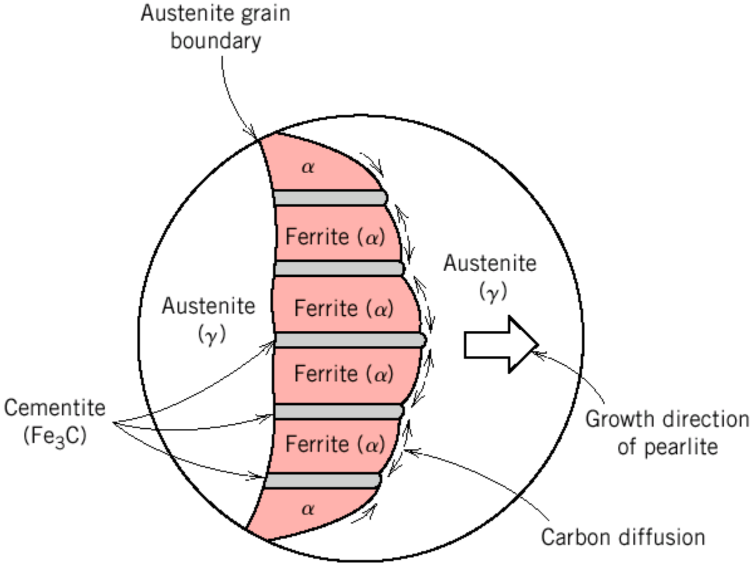

Pearlite: is a layered structure of ferrite and cementite. It forms if steel in the austenite region were allowed to cool slowly. (Simultaneous mixture of α and Fe_3C)

An annealed structure, hence soft (low physical properties).

Pearlite nuclei appear on defects such as grain boundaries. Its diffusion rate increases as cooling temp. is decreased (plate-to-plate distance decreases and fineness increases).

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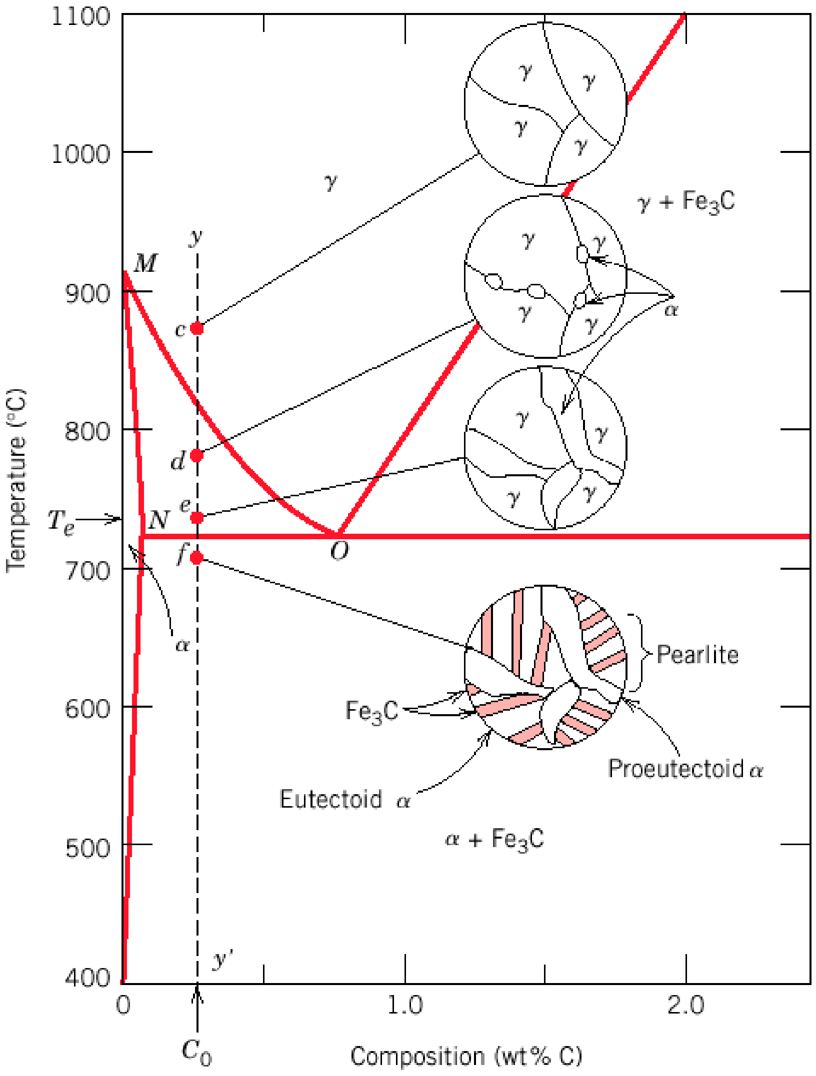


In hypoeutectoid steel, proeutectoid ferrite forms at *d*; the rest of austenite transforms into eutectoid ferrite and cementite.

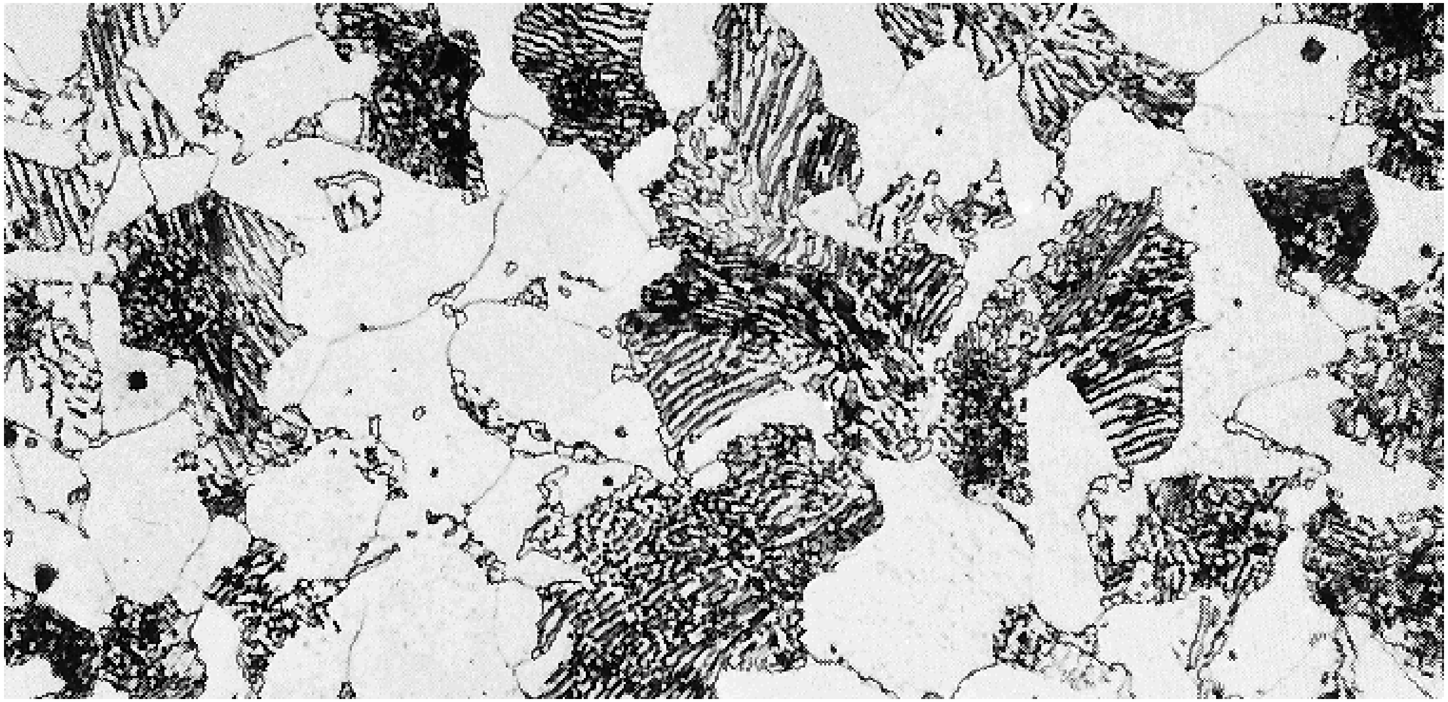
Hypoeutectoid reaction takes place when:

$0.022 < C \text{ wt.\%} < 0.76$

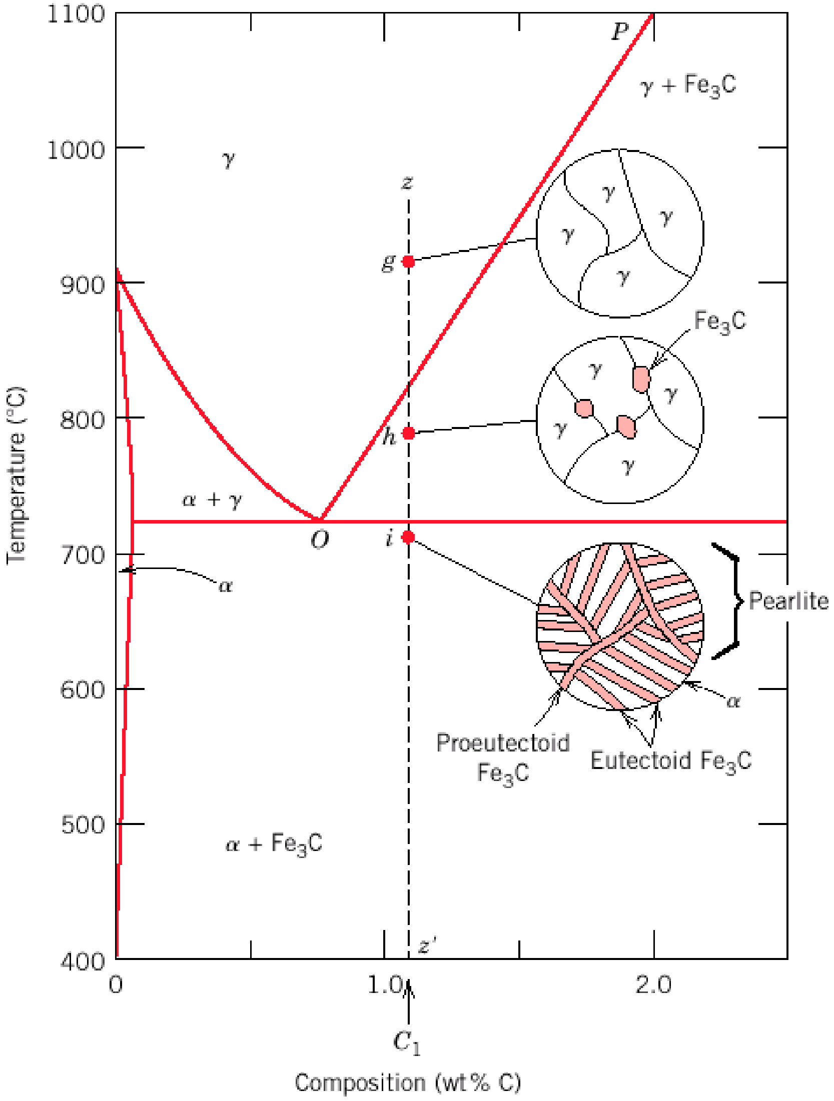
$\gamma \rightarrow \alpha_{(proeutectoid)} + \gamma \rightarrow \alpha_{(proeutectoid)} + \alpha_{(eutectoid)} + Fe_3C_{(eutectoid)}$

The Iron – Carbon (Carbide: Fe_3C) System

In this micrograph, proeutectoid α is the large white grains while eutectoid α is the white regions between the black plates (cementite).



The Iron – Carbon (Carbide: Fe_3C) System



In hypereutectoid steel, proeutectoid cementite forms at *h*; the rest of austenite transforms into eutectoid ferrite and cementite.

Hypereutectoid reaction takes place when:

$0.76 < C \text{ wt.\%} < 2.14$

$$\gamma \rightarrow Fe_3C_{(proeutectoid)} + \gamma \rightarrow Fe_3C_{(proeutectoid)} + Fe_3C_{(eutectoid)} + \alpha_{(eutectoid)}$$

The Iron – Carbon (Carbide: Fe_3C) System

In this micrograph, proeutectoid cementite is the large white areas while black and white plates represent eutectoid cementite and eutectoid α.