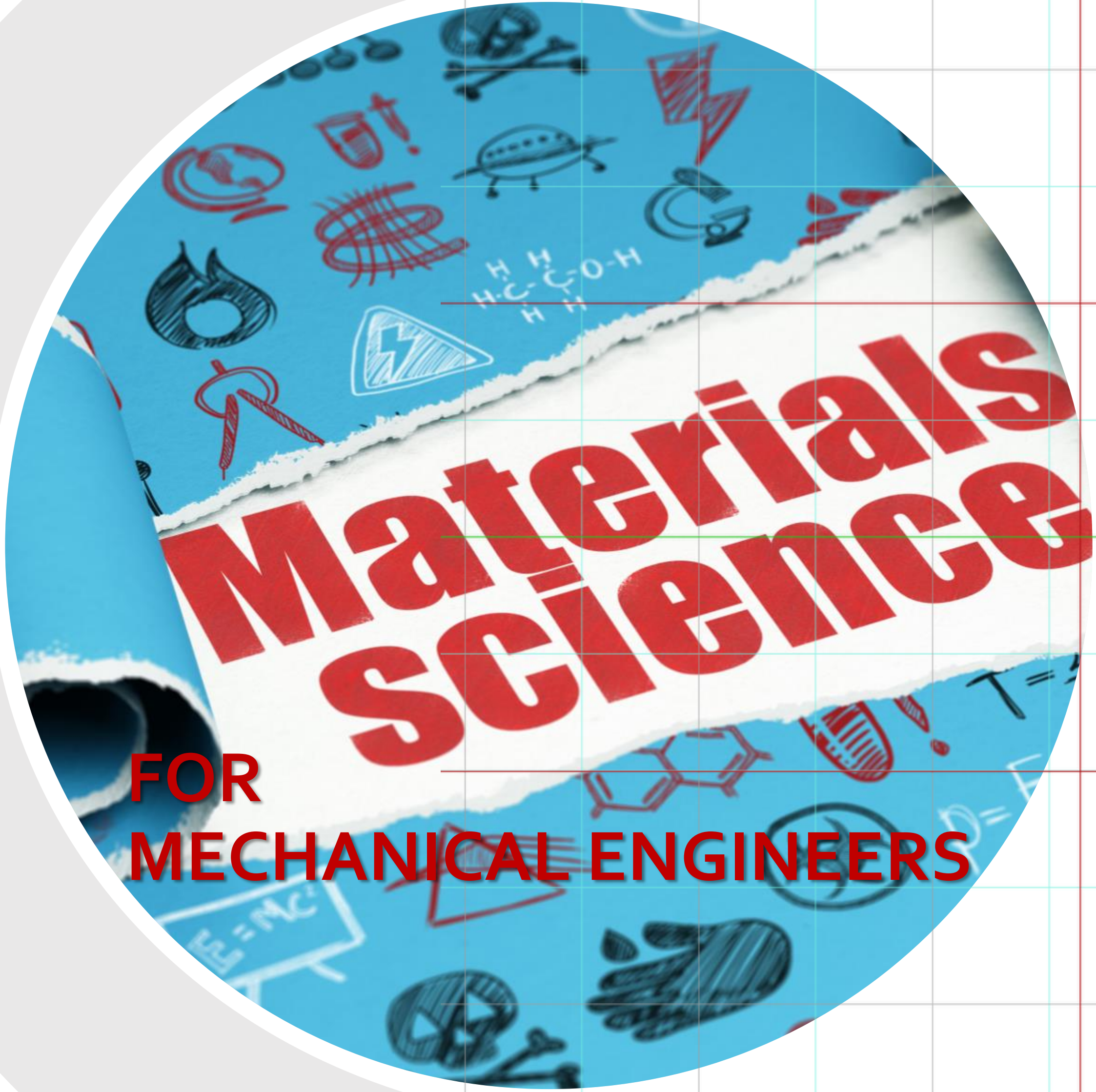


FOR
MECHANICAL ENGINEERS

Phase Diagrams

SPRING 2022-2023

INTRODUCTION

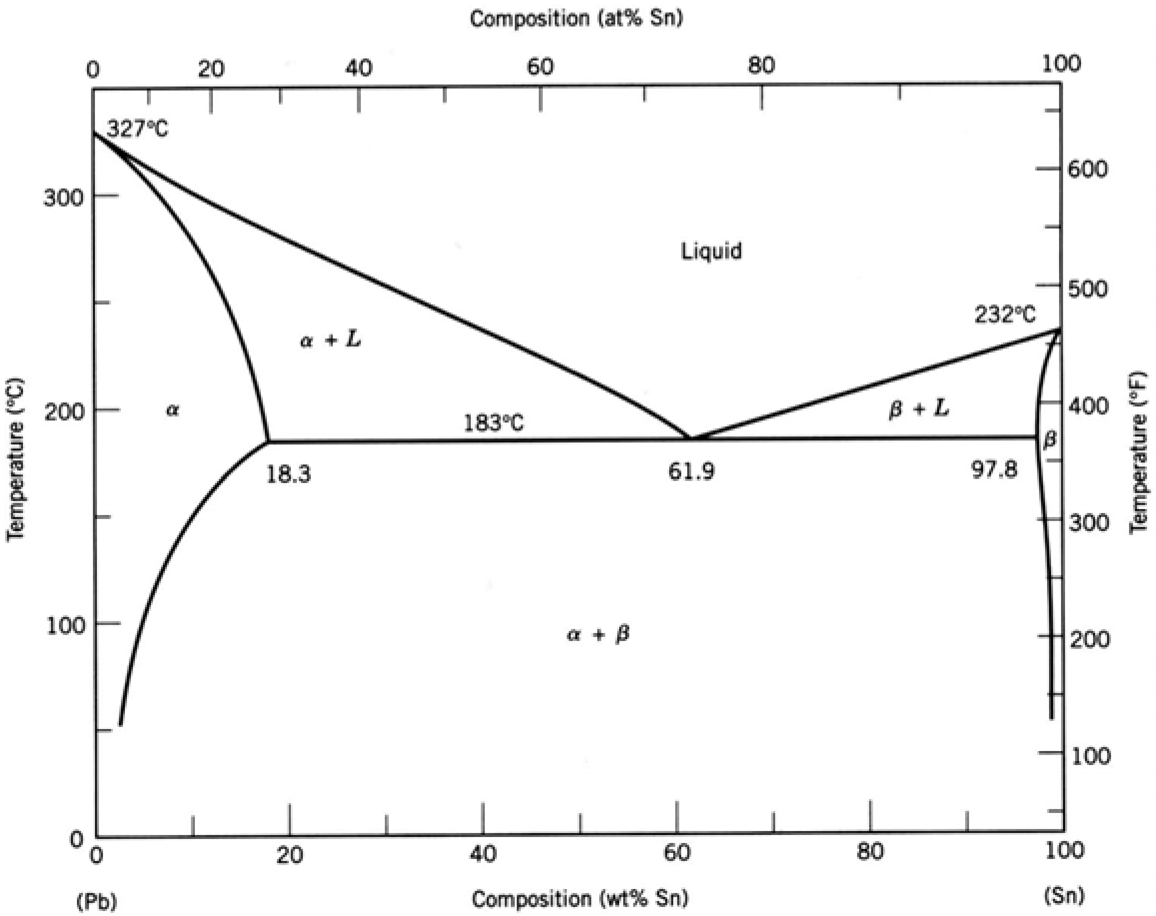
What is a phase diagram?

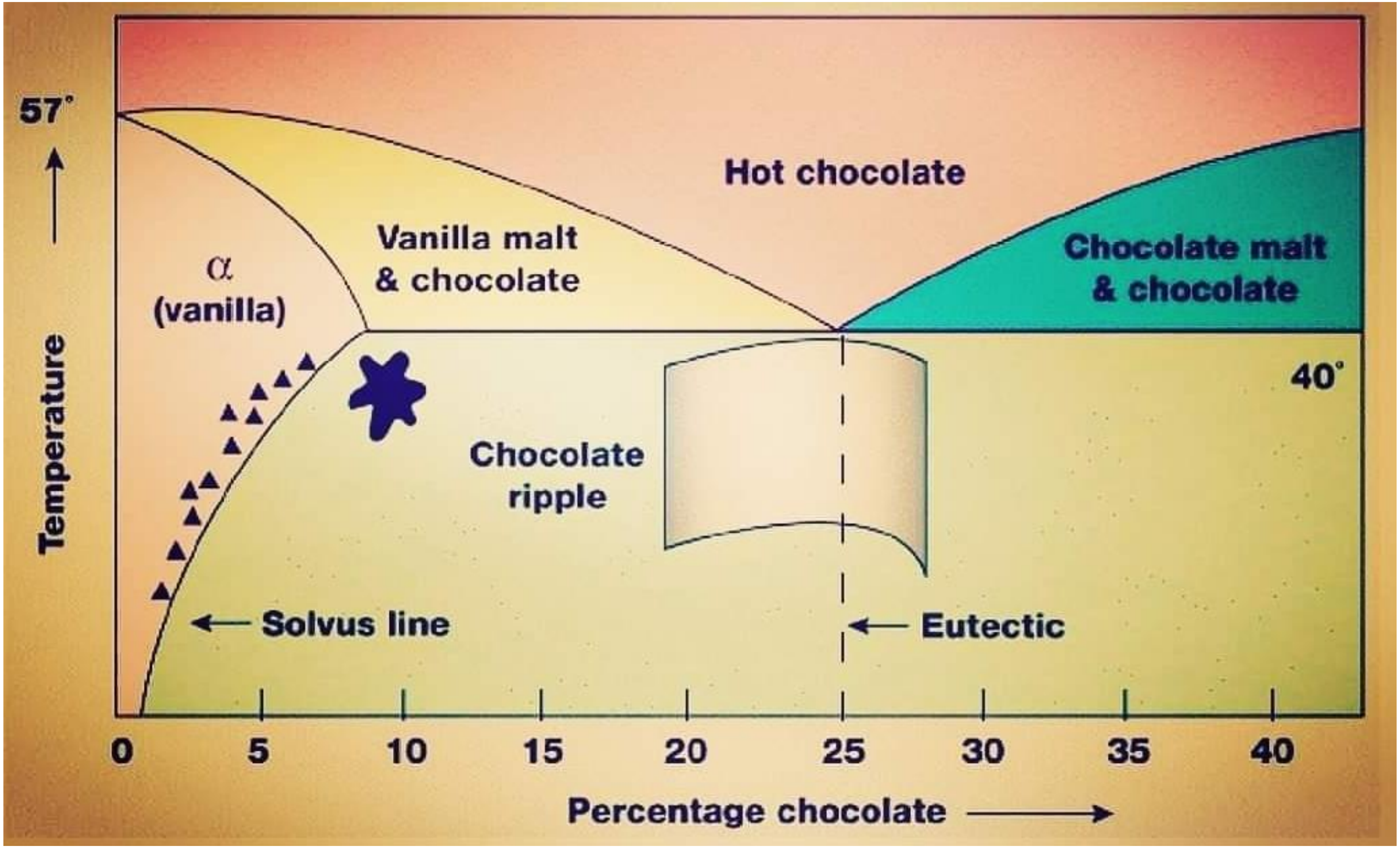
A diagram representing the limits of stability of the various phases in a chemical system at equilibrium, with respect to variables such as composition and temperature.

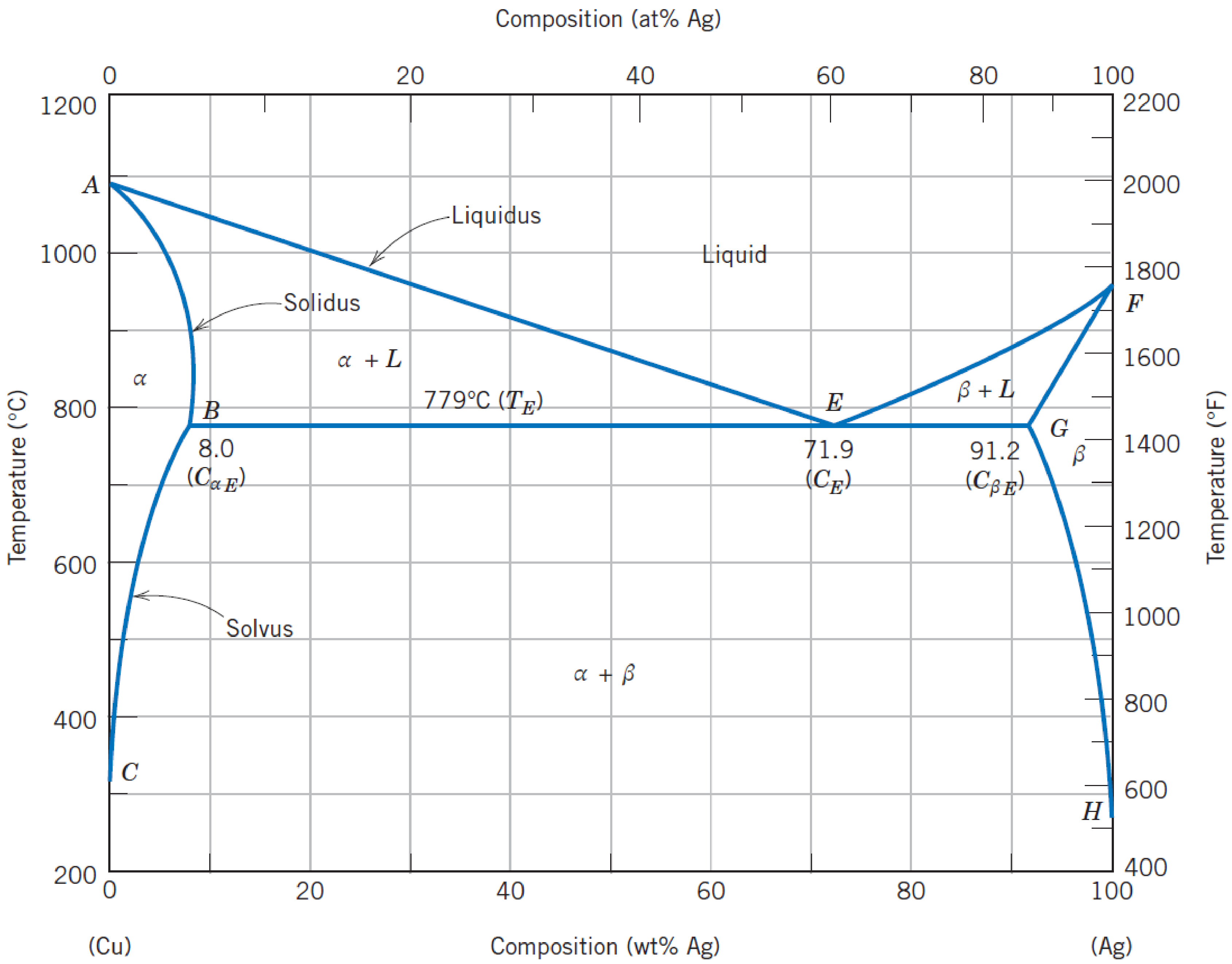
Why do we need a phase diagram?

Phase diagrams are the indispensable tools in the field of metallurgy. They provide a medium for understanding the different possible phases of pure metals and alloys under the influence of external agents such as temperature and pressure.

The understanding of phase diagrams for alloy systems is extremely important because there is a strong correlation between microstructure and mechanical properties, and the development of microstructure of an alloy is related to the characteristics of its phase diagram. In addition, phase diagrams provide valuable information about melting, casting, crystallization, and other phenomena.




57°
Temperature
Hot chocolate
Vanilla malt & chocolate
α (vanilla)
Chocolate malt & chocolate
40°
Chocolate ripple
Solvus line
Eutectic
0
5
10
15
20
25
30
35
40
Percentage chocolate


Composition (at% Ag)
0
20
40
60
80
100
1200
1000
800
600
400
200
2200
2000
1800
1600
1400
1200
1000
800
600
400
Temperature (°C)
Temperature (°F)
A
Liquidus
Liquid
Solidus
α
α + L
B
779°C (T_E)
E
β + L
F
G
β
8.0
($C_{\alpha E}$)
71.9
(C_E)
91.2
($C_{\beta E}$)
Solvus
α + β
C
H
0
20
40
60
80
100
(Cu)
Composition (wt% Ag)
(Ag)

INTRODUCTION

Learning Objectives

1. (a) Schematically sketch simple isomorphous and eutectic phase diagrams. (b) On these diagrams, label the various phase regions. (c) Label liquidus, solidus, and solvus lines.

2. Given a binary phase diagram, the composition of an alloy, and its temperature; and assuming that the alloy is at equilibrium; determine the following:
(a) what phase(s) is (are) present,
(b) the composition(s) of the phase(s), and
(c) the mass fraction(s) of the phase(s).

3. For some given binary phase diagram, do the following:
(a) locate the temperatures and compositions of all eutectic, eutectoid, peritectic, and congruent phase transformations;
And (b) write reactions for all these transformations for either heating or cooling.

4. Given the composition of an iron–carbon alloy containing between 0.022 and 2.14 wt% C, be able to
(a) specify whether the alloy is hypoeutectoid or hypereutectoid,
(b) name the proeutectoid phase,
(c) compute the mass fractions of proeutectoid phase and pearlite, and
(d) make a schematic diagram of the microstructure at a temperature just below the eutectoid.

INTRODUCTION

It is necessary to establish a foundation of definitions and basic concepts relating to alloys, phases, and equilibrium before delving into the interpretation and utilization of phase diagrams.

The term **component** is frequently used in this discussion;
components are pure metals and/or compounds of which an alloy is composed. For example, in a copper–zinc brass, the components are Cu and Zn. *Solute* and *solvent*, which are also common terms.

Another term used in this context is **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).

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.

To illustrate this concept, consider the sugar–water ($C_{12}H_{22}O_{11}$*–*H_2O*) system. Initially, as sugar is added to water, a sugar–water solution or syrup forms. As more sugar is introduced, the solution becomes more concentrated, until the solubility limit is reached or the solution becomes saturated with sugar. At this time, the solution is not capable of dissolving any more sugar, and further additions simply settle to the bottom of the container. Thus, the system now consists of two separate substances: a sugar–water syrup liquid solution and solid crystals of undissolved sugar.*

This solubility limit of sugar in water depends on the temperature of the water and may be represented in graphical form on a plot of temperature along the ordinate and composition (in weight percent sugar) along the abscissa.

SOLUBILITY LIMIT

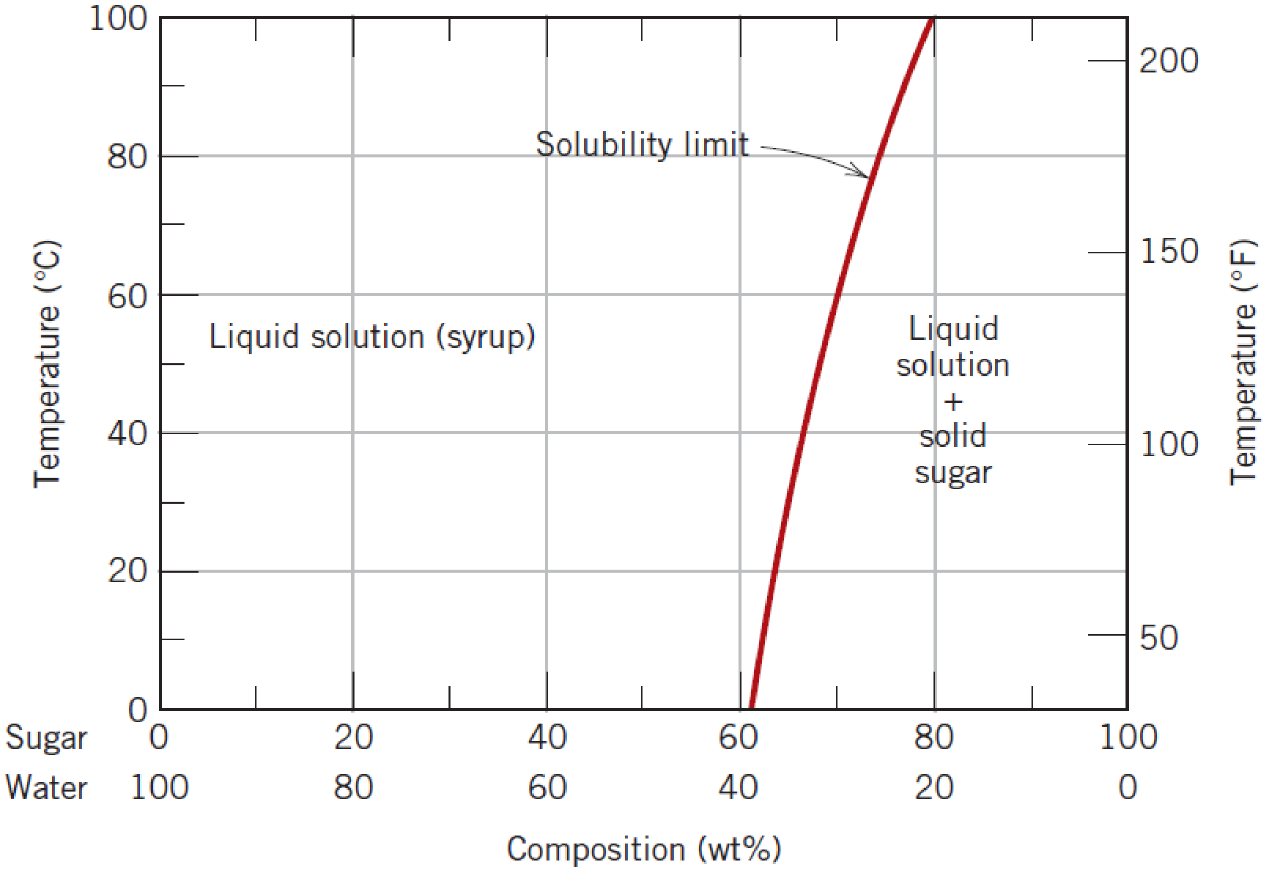
Along the composition axis, increasing sugar concentration is from left to right, and percentage of water is read from right to left.

Because only two components are involved (sugar and water), the sum of the concentrations at any composition will equal 100 wt%.

The solubility limit is represented as the nearly vertical line in the figure.

For compositions and temperatures to the left of the solubility line, only the syrup liquid solution exists; to the right of the line, syrup and solid sugar coexist.

The solubility limit at some temperature is the composition that corresponds to the intersection of the given temperature coordinate and the solubility limit line. For example, at 20°C, the maximum solubility of sugar in water is 65 wt%. The solubility limit increases slightly with rising temperature.



PHASES

Also critical to the understanding of phase diagrams is the concept of a **phase.**

A phase may be defined as 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. Each has different physical properties (one is a liquid, the other is a solid); furthermore, each is different chemically (i.e., has a different chemical composition); one is virtually pure sugar, the other is a solution of H_2O and $C_{12}H_{22}O_{11}$.

If more than one phase is present in a given system, each will have its own distinct properties, and a boundary separating the phases will exist, across which there will be a discontinuous and abrupt change in physical and/or chemical characteristics.

When two phases are present in a system, it is not necessary that there be a difference in both physical and chemical properties; a difference in one or the other set of properties is sufficient.

When water and ice are present in a container, two separate phases exist; they are physically dissimilar (one is a solid, the other is a liquid) but identical in chemical makeup.

Also, when a substance can exist in two or more polymorphic forms (e.g., having both FCC and BCC structures), each of these structures is a separate phase because their respective physical characteristics differ.

PHASES

Sometimes, a single-phase system is termed *homogeneous*. Systems composed of two or more phases are termed *mixtures* or *heterogeneous systems*.

Most metallic alloys and, for that matter, ceramic, polymeric, and composite systems are heterogeneous. Typically, the phases interact in such a way that the property combination of the multiphase system is different from, and more desirable than, either of the individual phases.

MICROSTRUCTURE

The physical properties and, in particular, the mechanical behaviour of a material often depend on the microstructure. Microstructure is subject to direct microscopic observation using optical or electron microscopes.

In metal alloys, microstructure is characterized by the number of phases present, their proportions, and the manner in which they are distributed or arranged.

The microstructure of an alloy depends on such variables as the alloying elements present, their concentrations, and the heat treatment of the alloy (i.e., the temperature, the heating time at temperature, and the rate of cooling to room temperature).

After appropriate polishing and etching, the different phases may be distinguished by their appearance. For example, for a two-phase alloy, one phase may appear light and the other phase dark. When only a single phase or solid solution is present, the texture is uniform, except for grain boundaries that may be revealed.

PHASE EQUILIBRIA

Equilibrium is another essential concept; it is best described in terms of a thermodynamic quantity called the **free energy.**

In brief, *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.

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.

The term **phase equilibrium,** often used in the context of this discussion, refers to equilibrium as it applies to systems in which more than one phase may exist.

Phase equilibrium is reflected by a constancy with time in the phase characteristics of a system.

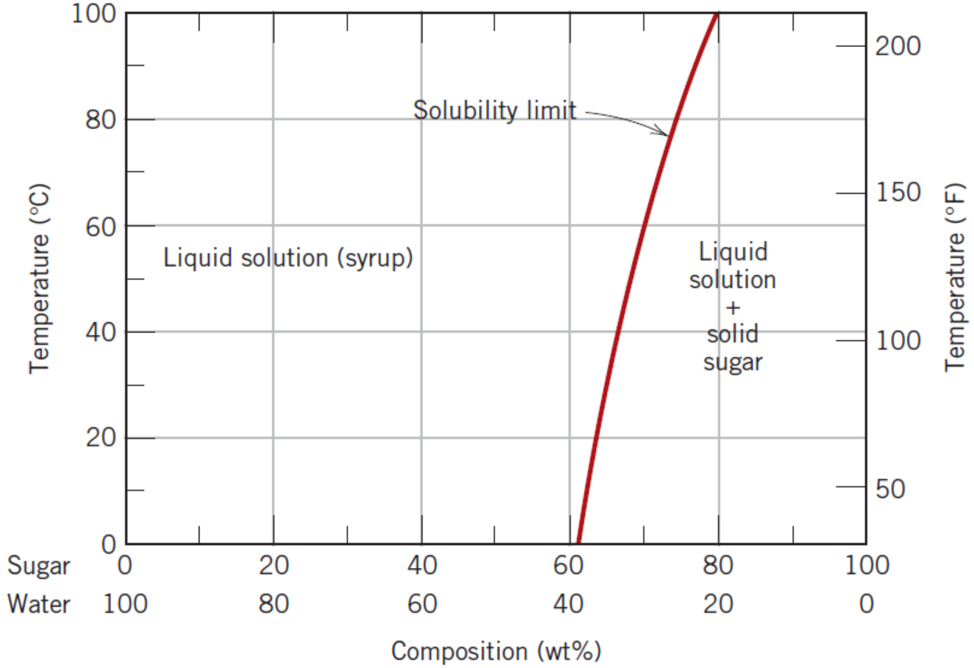
Suppose that a sugar–water syrup is contained in a closed vessel and the solution is in contact with solid sugar at 20°C.

PHASE EQUILIBRIA

If the system is at equilibrium, the composition of the syrup is 65 wt% sugar–35 wt% water, and the amounts and compositions of the syrup and solid sugar will remain constant with time.

If the temperature of the system is suddenly raised—say, to 100°C— this equilibrium or balance is temporarily upset and the solubility limit is increased to 80 wt% sugar.

Thus, some of the solid sugar will go into solution in the syrup. This will continue until the new equilibrium syrup concentration is established at the higher temperature.



This sugar–syrup example illustrates the principle of phase equilibrium using a liquid–solid system.

In many metallurgical and materials systems of interest, phase equilibrium involves just solid phases. In this regard the state of the system is reflected in the characteristics of the microstructure, which necessarily include not only the phases present and their compositions, but, in addition, the relative phase amounts and their spatial arrangement or distribution.

PHASE EQUILIBRIA

It is often the case, especially 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.

Often, metastable structures are of more practical significance than equilibrium ones. For example, some steel and aluminium alloys rely for their strength on the development of metastable microstructures during carefully designed heat treatments.

Thus it is important to understand not only equilibrium states and structures, but also the speed or rate at which they are established and the factors that affect that rate.

**Metastable state: when a state of equilibrium is never completely achieved as the rate of approach to equilibrium is extremely slow.*

ONE-COMPONENT (OR UNARY) PHASE DIAGRAMS

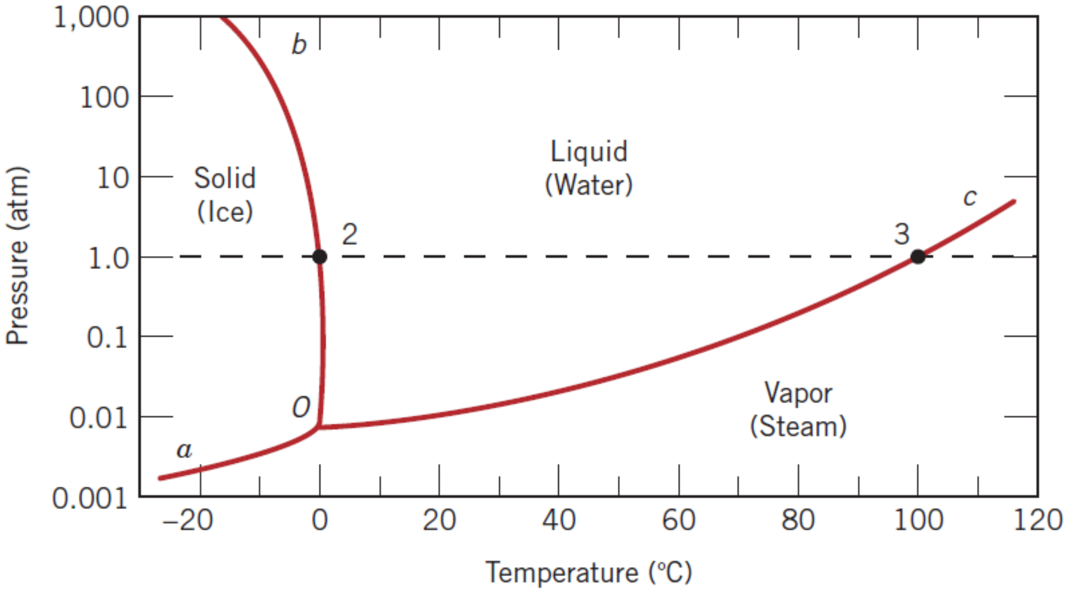
Much of the information about the control of the phase structure of a particular system is conveniently and concisely displayed in what is called a **phase diagram,** also often termed an *equilibrium diagram.*

Three externally controllable parameters affect phase structure— temperature, pressure, and composition—and phase diagrams are constructed when various combinations of these parameters are plotted against one another.

Perhaps the simplest and easiest type of phase diagram to understand is that for a one-component system, in which composition is held constant (i.e., the phase diagram is for a pure substance); this means that pressure and temperature are the variables.

This one-component phase diagram (or *unary phase diagram,* sometimes also called a *pressure–temperature* [or *P–T*] *diagram*) is represented as a two-dimensional plot of pressure (ordinate, or vertical axis) versus temperature (abscissa, or horizontal axis).

Most often, the pressure axis is scaled logarithmically.

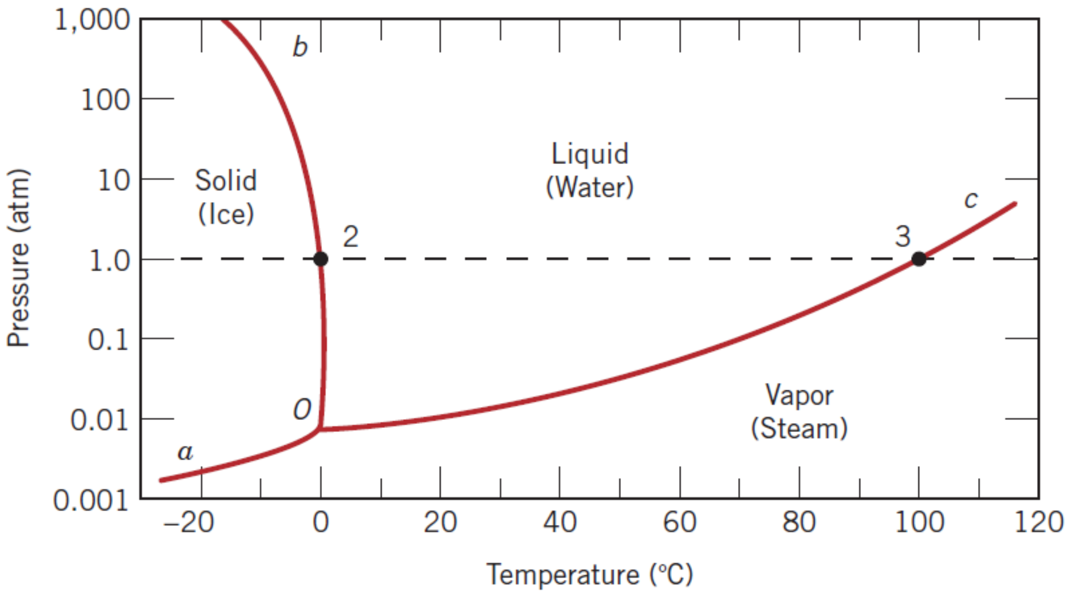


ONE-COMPONENT (OR UNARY) PHASE DIAGRAMS

Regions for three different phases—solid, liquid, and vapor—are defined on the plot.

Each of the phases exist under equilibrium conditions over the temperature–pressure ranges of its corresponding area.

The three curves shown on the plot (labeled *aO*, *bO*, and *cO*) are phase boundaries; at any point on one of these curves, the two phases on either side of the curve are in equilibrium (or coexist) with one another.



Equilibrium between solid and vapor phases is along curve *aO*; it is likewise for the solid–liquid boundary, curve *bO*, and the liquid–vapor boundary, curve *cO*. Upon crossing a boundary (as temperature and/or pressure is altered), one phase transforms into another.

For example, at 1 atm pressure, during heating the solid phase transforms to the liquid phase (i.e., melting occurs) at the point labelled 2 (i.e., the intersection of the dashed horizontal line with the solid–liquid phase boundary); this point corresponds to a temperature of 0°C.

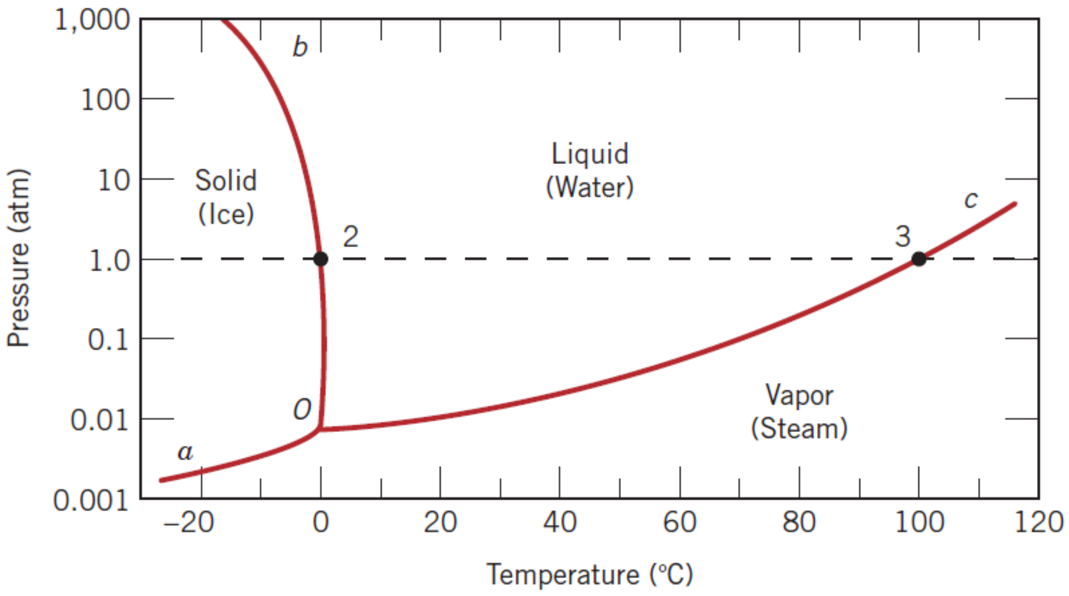
The reverse transformation (liquid-to-solid, or *solidification*) takes place at the same point upon cooling.

ONE-COMPONENT (OR UNARY) PHASE DIAGRAMS

Similarly, at the intersection of the dashed line with the liquid–vapor phase boundary (point 3 at 100°C) the liquid transforms into the vapor phase (or *vaporizes*) upon heating; condensation occurs for cooling.

Finally, solid ice sublimes or vaporizes upon crossing the curve labelled *aO*.

As may also be noted, all three of the phase boundary curves intersect at a common point, which is labelled *O* (for this H_2O system, at a temperature of 273.16 K and a pressure of 6.04×10^{-3} atm).



This means that at this point only, all of the solid, liquid, and vapor phases are simultaneously in equilibrium with one another. Appropriately, this, and any other point on a *P–T* phase diagram where three phases are in equilibrium, is called a *triple point*; sometimes it is also termed an *invariant point* inasmuch as its position is distinct, or fixed by definite values of pressure and temperature.

Any deviation from this point by a change of temperature and/or pressure will cause at least one of the phases to disappear.

Pressure–temperature phase diagrams for a number of substances have been determined experimentally, which also have solid-, liquid-, and vapor-phase regions.

BINARY PHASE DIAGRAMS

Another type of extremely common phase diagram is one in which temperature and composition are variable parameters and pressure is held constant—normally 1 atm.

If more than two components are present, phase diagrams become extremely complicated and difficult to represent.
An explanation of the principles governing and the interpretation of phase diagrams can be demonstrated using binary alloys even though most alloys contain more than two components.

Binary phase diagrams are maps that represent the relationships between temperature and the compositions and quantities of phases at equilibrium, which influence the microstructure of an alloy.

Many microstructures develop from *phase transformations*, the changes that occur when the temperature is altered (typically upon cooling).

This may involve the transition from one phase to another or the appearance or disappearance of a phase.

Binary phase diagrams are helpful in predicting phase transformations and the resulting microstructures, which may have equilibrium or nonequilibrium character.

BINARY PHASE DIAGRAMS

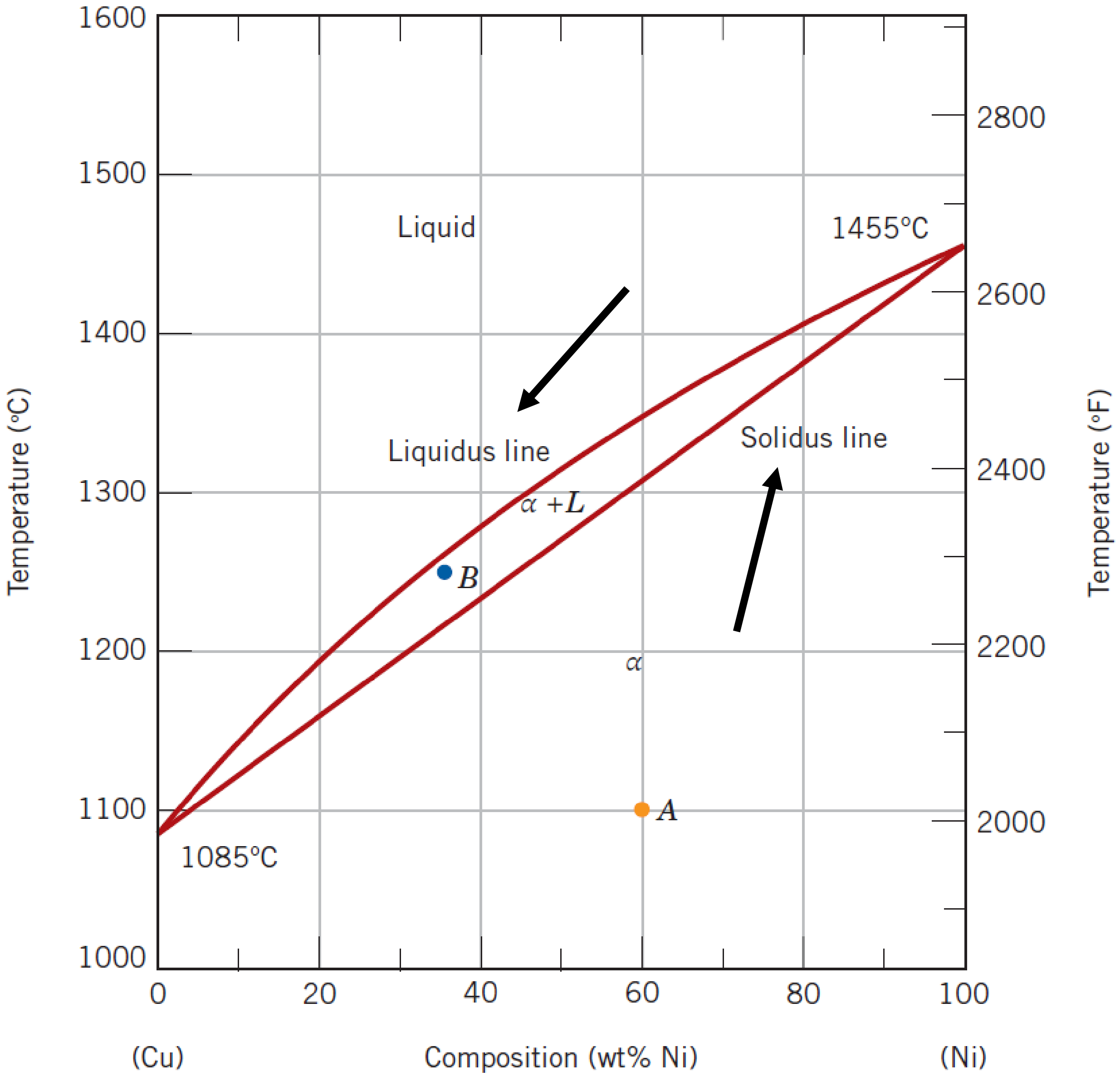
Possibly the easiest type of binary phase diagram to understand and interpret is the type that is characterized by the copper–nickel system .

Temperature is plotted along the ordinate, and the abscissa represents the composition of the alloy, in weight percent of nickel.

The composition ranges from 0 wt% Ni (100 wt% Cu) on the far left horizontal extreme 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 defined by the phase boundary lines.



BINARY PHASE DIAGRAMS

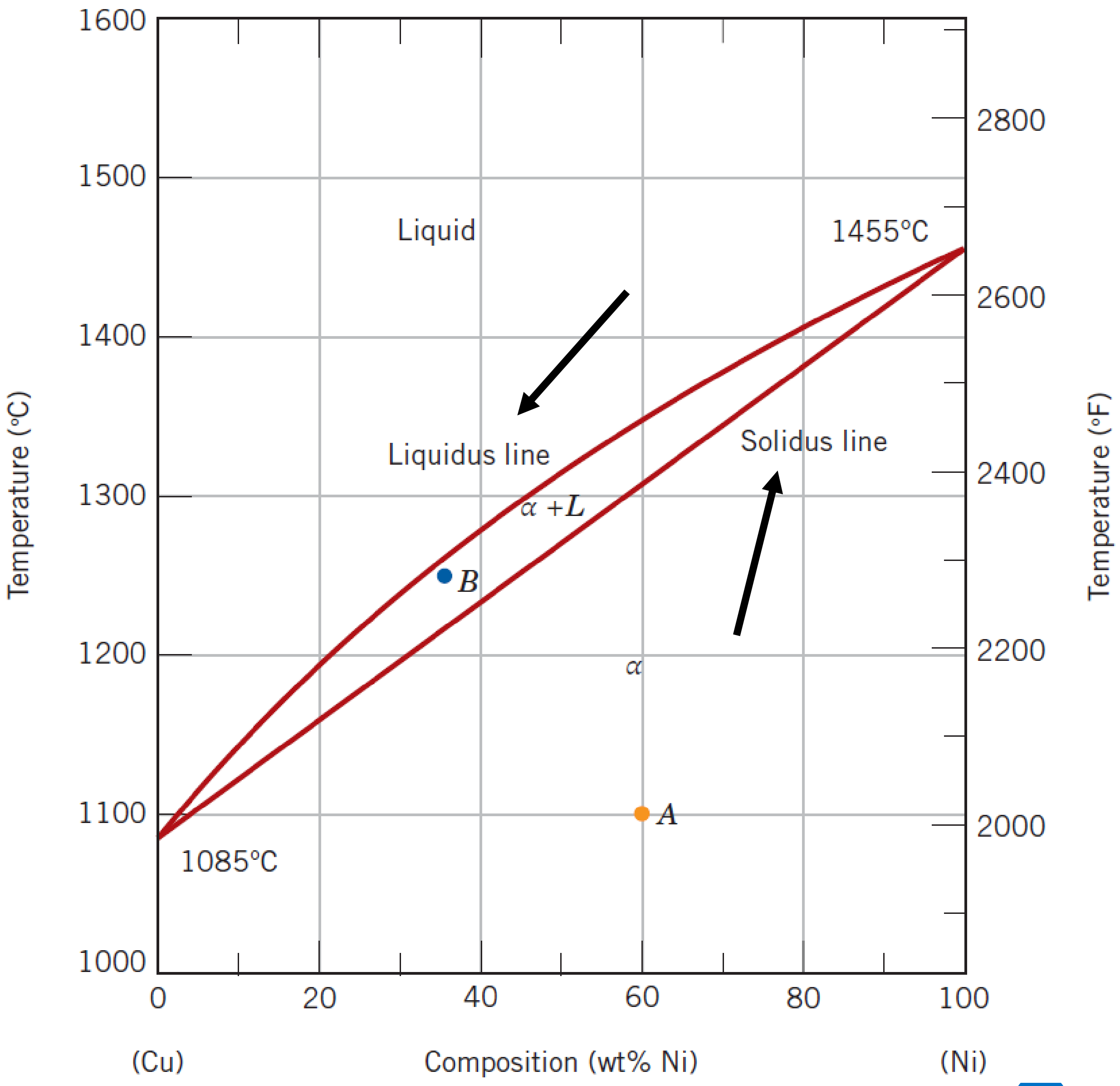
The liquid *L* is a homogeneous liquid solution composed of both copper and nickel.

The *α* phase is a substitutional solid solution consisting of both Cu and Ni atoms and has 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 electronegativities, and similar valences.

The copper–nickel system is termed **isomorphous** because of this complete liquid and solid solubility of the two components.



BINARY PHASE DIAGRAMS

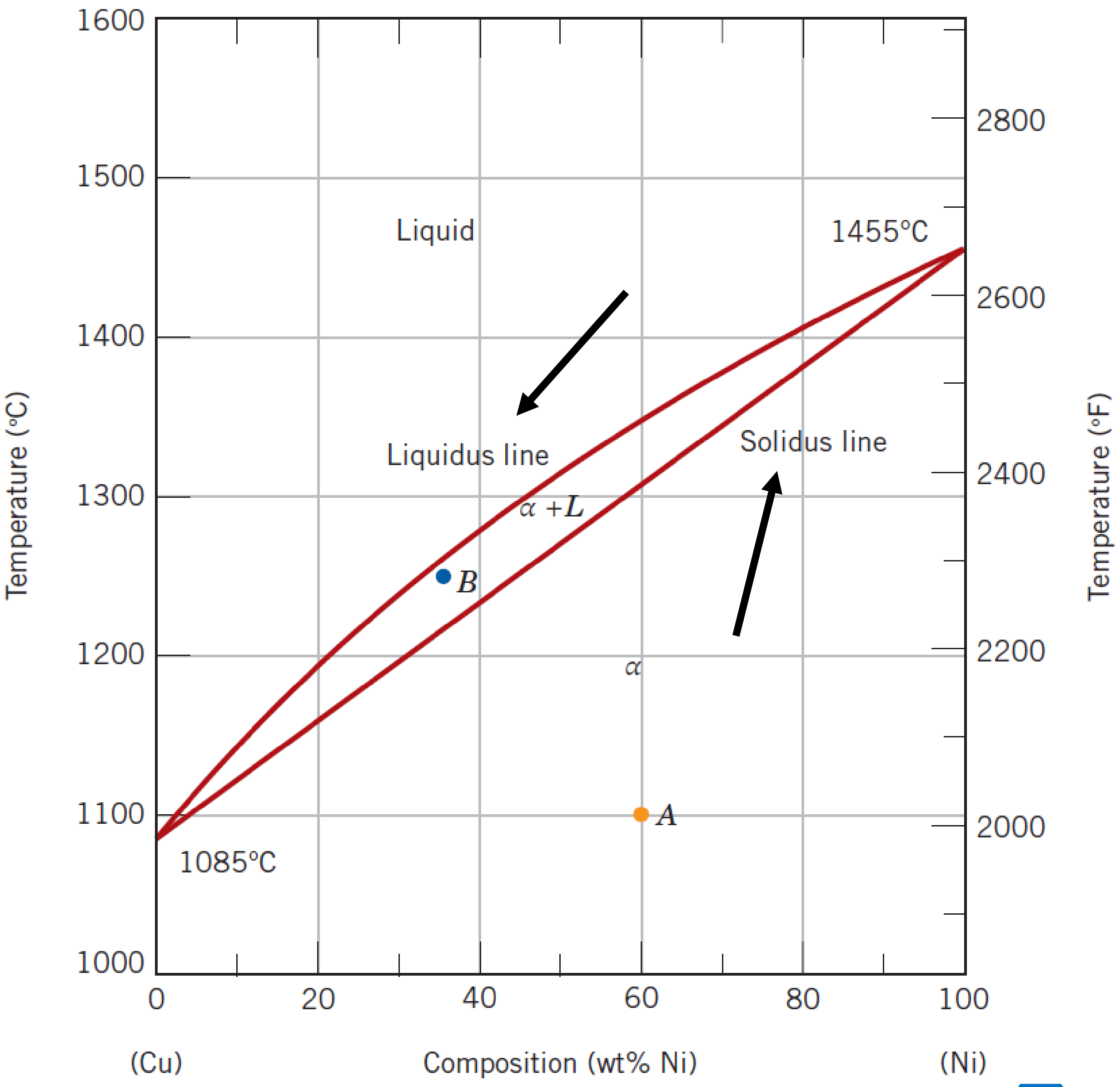
Some comments are in order regarding nomenclature: First, for metallic alloys, solid solutions are commonly designated by lowercase Greek letters (α, β, γ, etc.).

With regard to phase boundaries, the line separating the L and $\alpha + L$ phase fields is termed the *liquidus line*, as indicated in the Figure; 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.

The solidus and liquidus lines intersect at the two composition extremes; these correspond to the melting temperatures of the pure components.

For example, the melting temperatures of pure copper and nickel are 1085°C and 1455°C, respectively.



BINARY PHASE DIAGRAMS

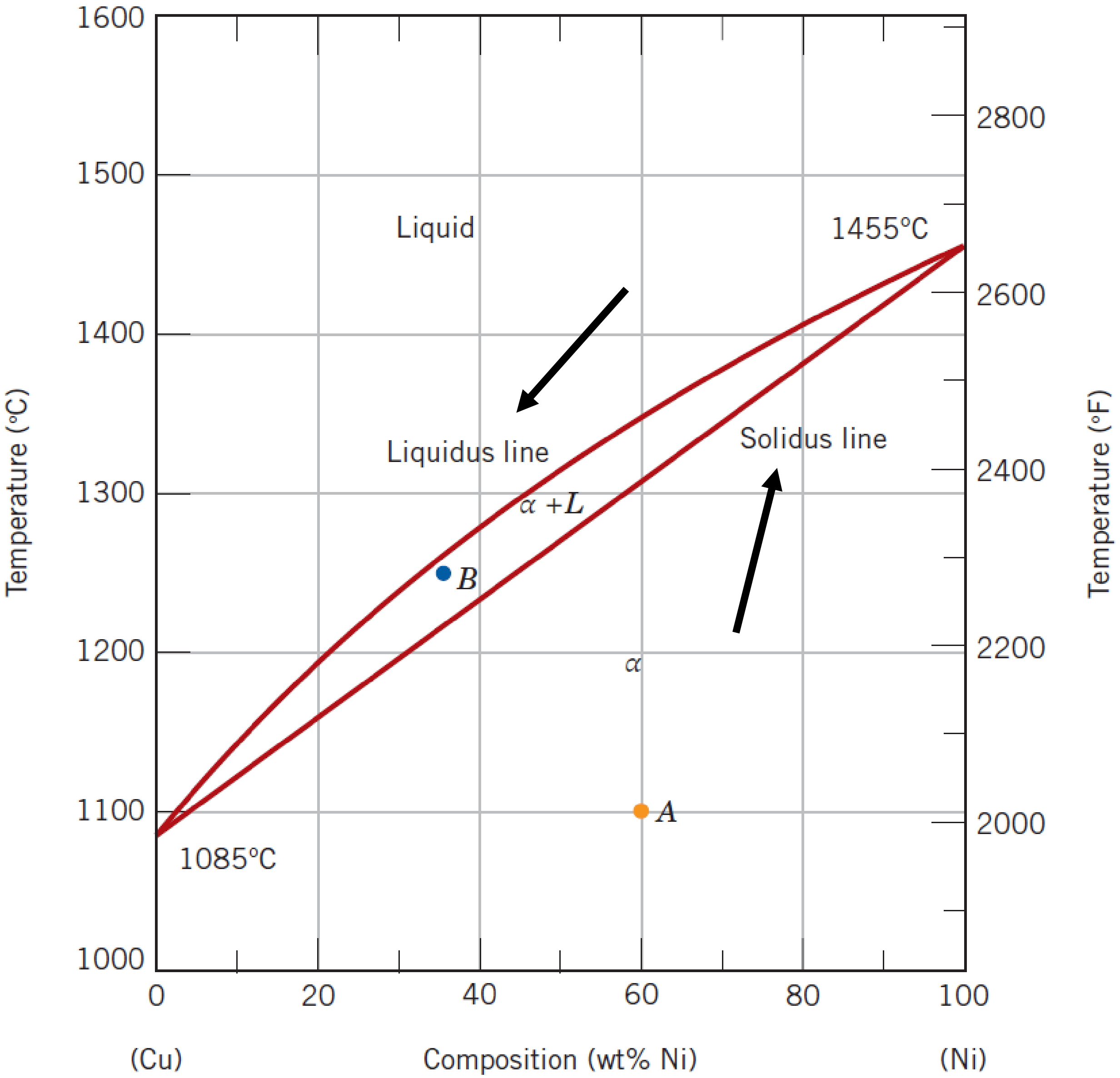
Heating pure copper corresponds to moving vertically up the left-hand temperature axis.

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 occurs over the range of temperatures between the solidus and liquidus lines; both solid *α* and liquid phases are in equilibrium within this temperature range.

For example, upon heating of an alloy of composition 50 wt% Ni–50 wt% Cu , 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 point the alloy is completely liquid.



INTERPRETATION OF PHASE DIAGRAMS

For a binary system of known composition and temperature at equilibrium, at least three kinds of information are available:

(1) the phases that are present,

(2) the compositions of these phases, and

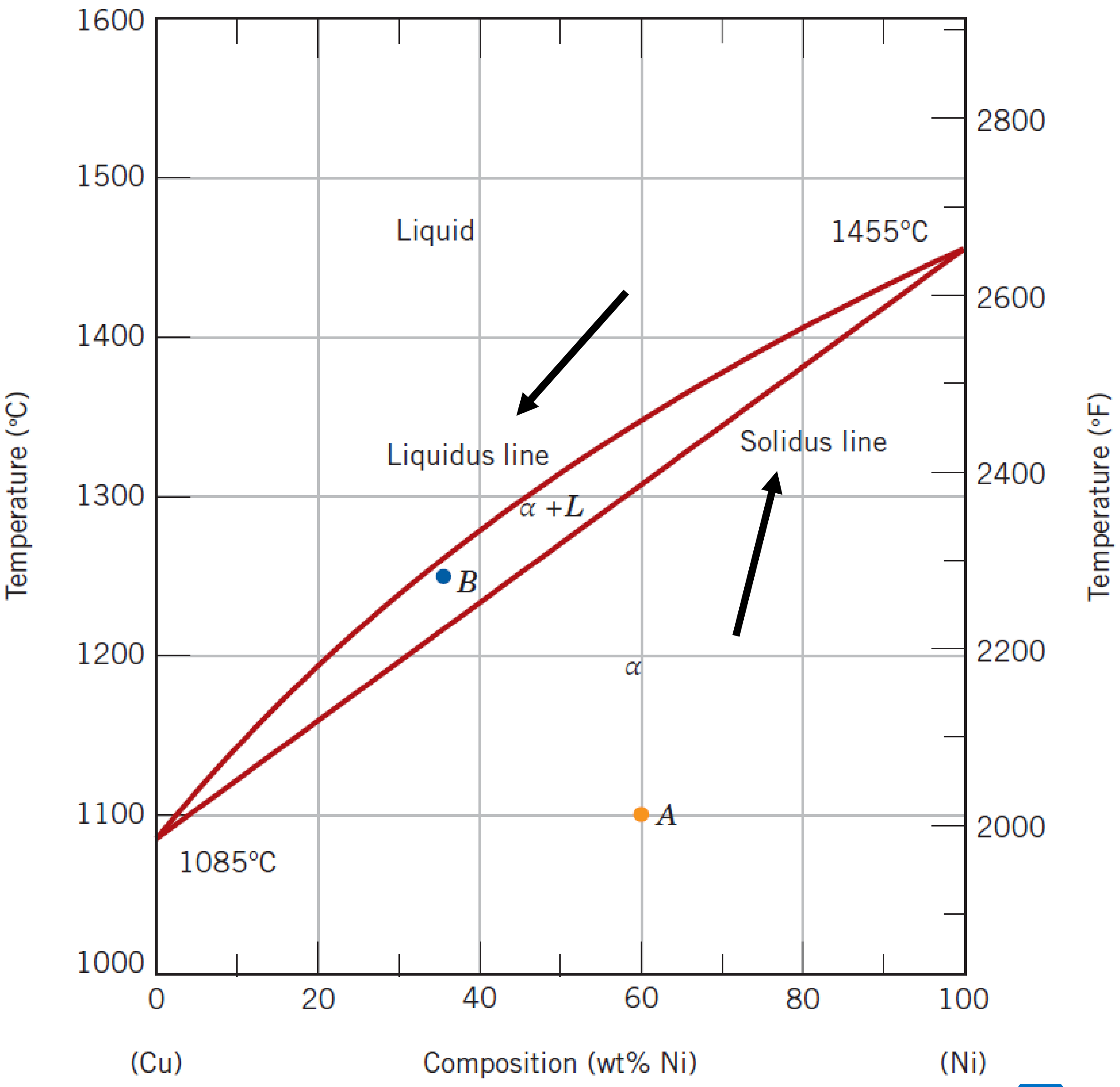
(3) the percentages or fractions of the phases.

The procedures for making these determinations will be demonstrated using the copper–nickel system.

Phases Present

The establishment of what phases are present is relatively simple. One just locates the temperature–composition point on the diagram and notes the phase(s) with which the corresponding phase field is labelled.

For example, an alloy of composition 60 wt% Ni–40 wt% Cu at 1100°C would be located at point *A*; because this is within the *α* region, only the single *α* phase will be present. However, a 35 wt% Ni–65 wt% Cu alloy at 1250°C (point *B*) consists of both *α* and liquid phases at equilibrium.



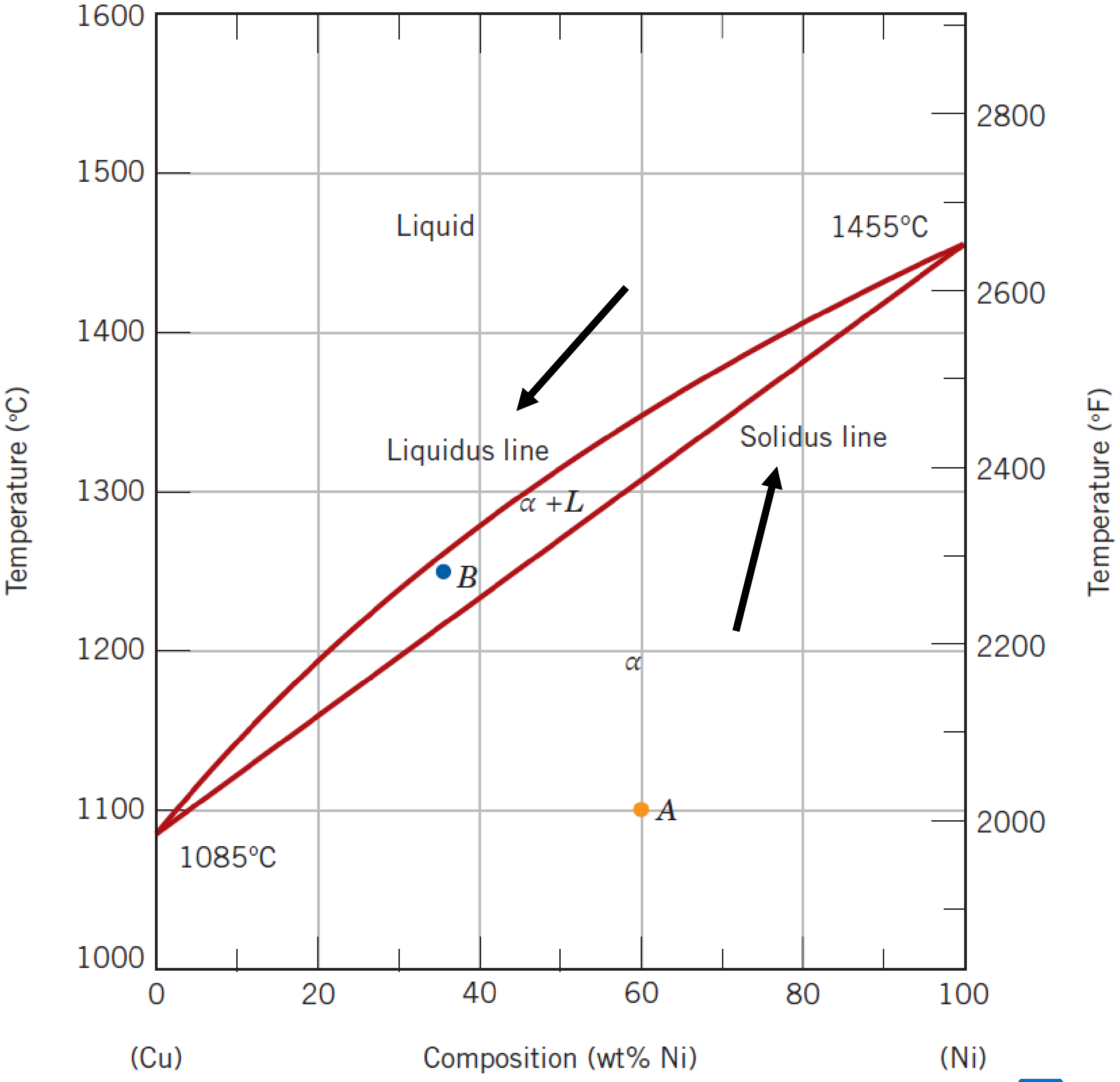
INTERPRETATION OF PHASE DIAGRAMS

Determination of Phase Compositions

The first step in the determination of phase compositions (in terms of the concentrations of the components) is to locate the temperature–composition point on the phase diagram.

Different methods are used for single- and two-phase regions. If only one phase is present, the procedure is trivial: The composition of this phase is simply the same as the overall composition of the alloy.

For example, consider the 60 wt% Ni–40 wt% Cu alloy at 1100°C (point *A*). At this composition and temperature, only the α phase is present, having a composition of 60 wt% Ni–40 wt% Cu.



INTERPRETATION OF PHASE DIAGRAMS

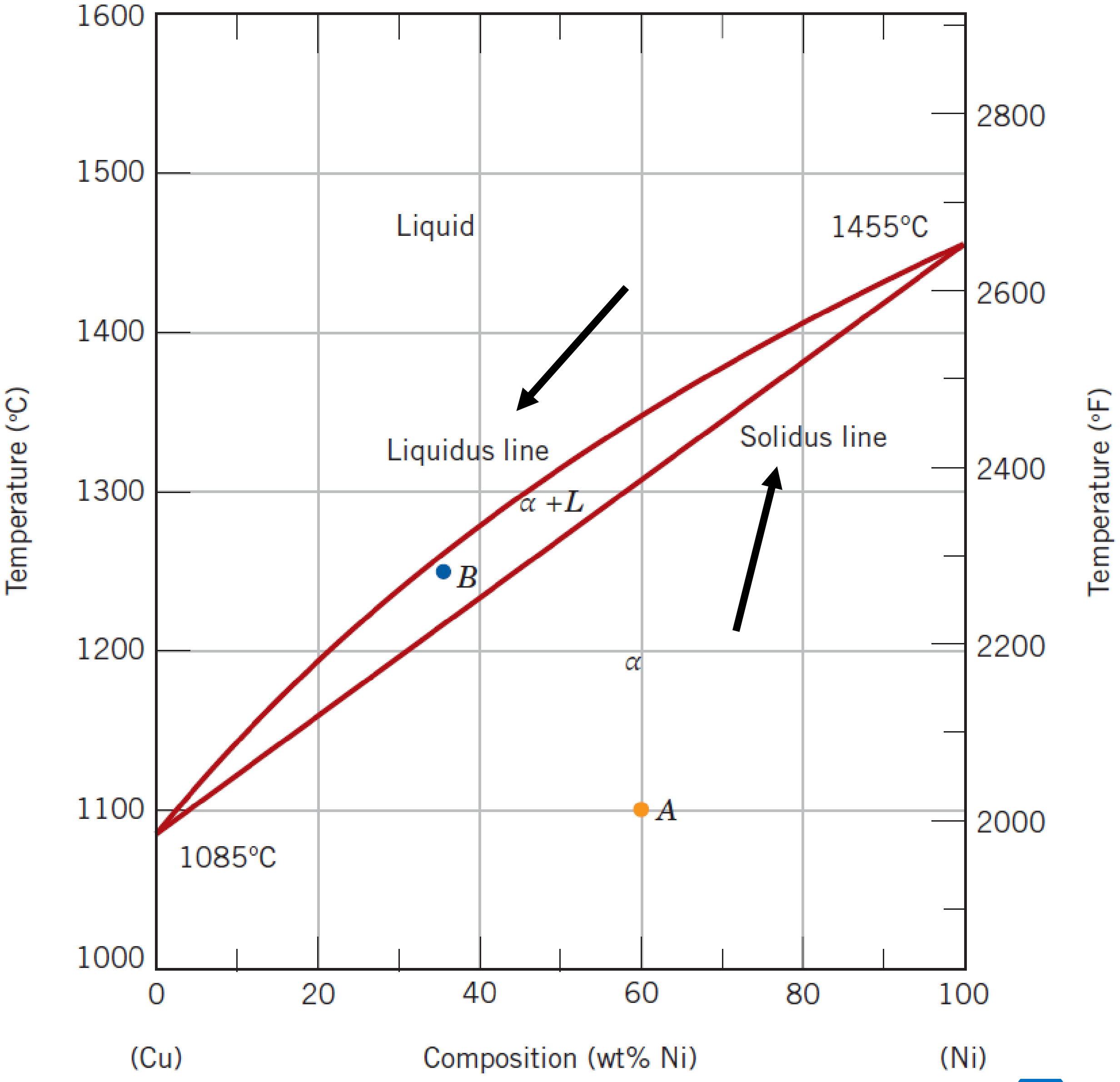
For an alloy having composition and temperature located in a two-phase region, the situation is more complicated.

In all two-phase regions (and in two-phase regions only), one may imagine a series of horizontal lines, one at every temperature; each of these is known as a **tie line,** or sometimes as an *isotherm*.

These tie lines extend across the two-phase region and terminate at the phase boundary lines on either side.

To compute the equilibrium concentrations of the two phases, the following procedure is used:

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.



INTERPRETATION OF PHASE DIAGRAMS

For example, consider again the 35 wt% Ni–65 wt% Cu alloy at 1250°C, located at point *B* and lying within the $\alpha + L$ region.

Thus, the problem is to determine the composition (in wt% Ni and Cu) for both the α and liquid phases.

The tie line is constructed across the $\alpha + L$ phase region, as shown.

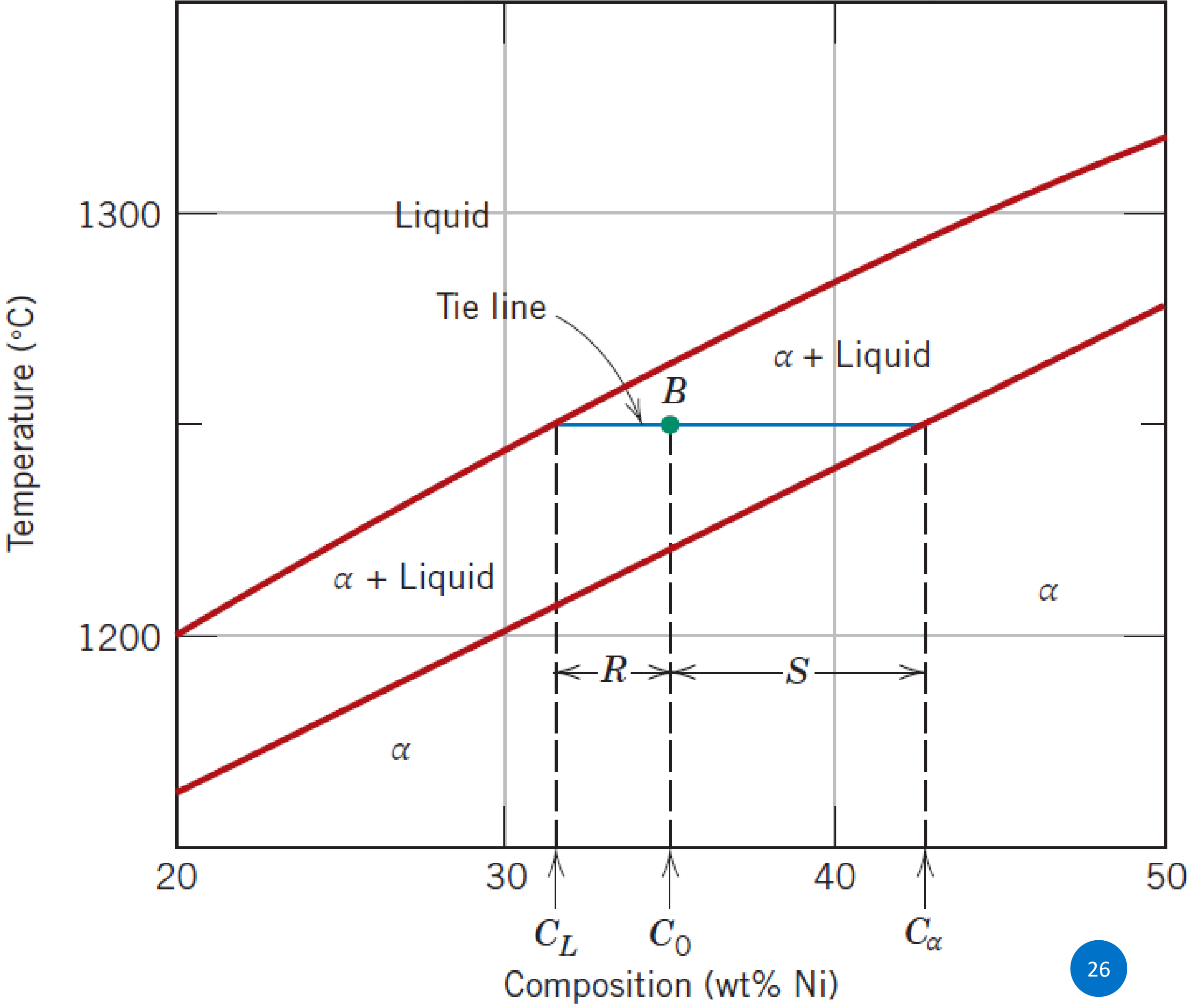
The perpendicular from the intersection of the tie line with the liquidus boundary meets the composition axis at 31.5 wt% Ni–68.5 wt% Cu, which is the composition of the liquid phase, C_L.

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.

(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.



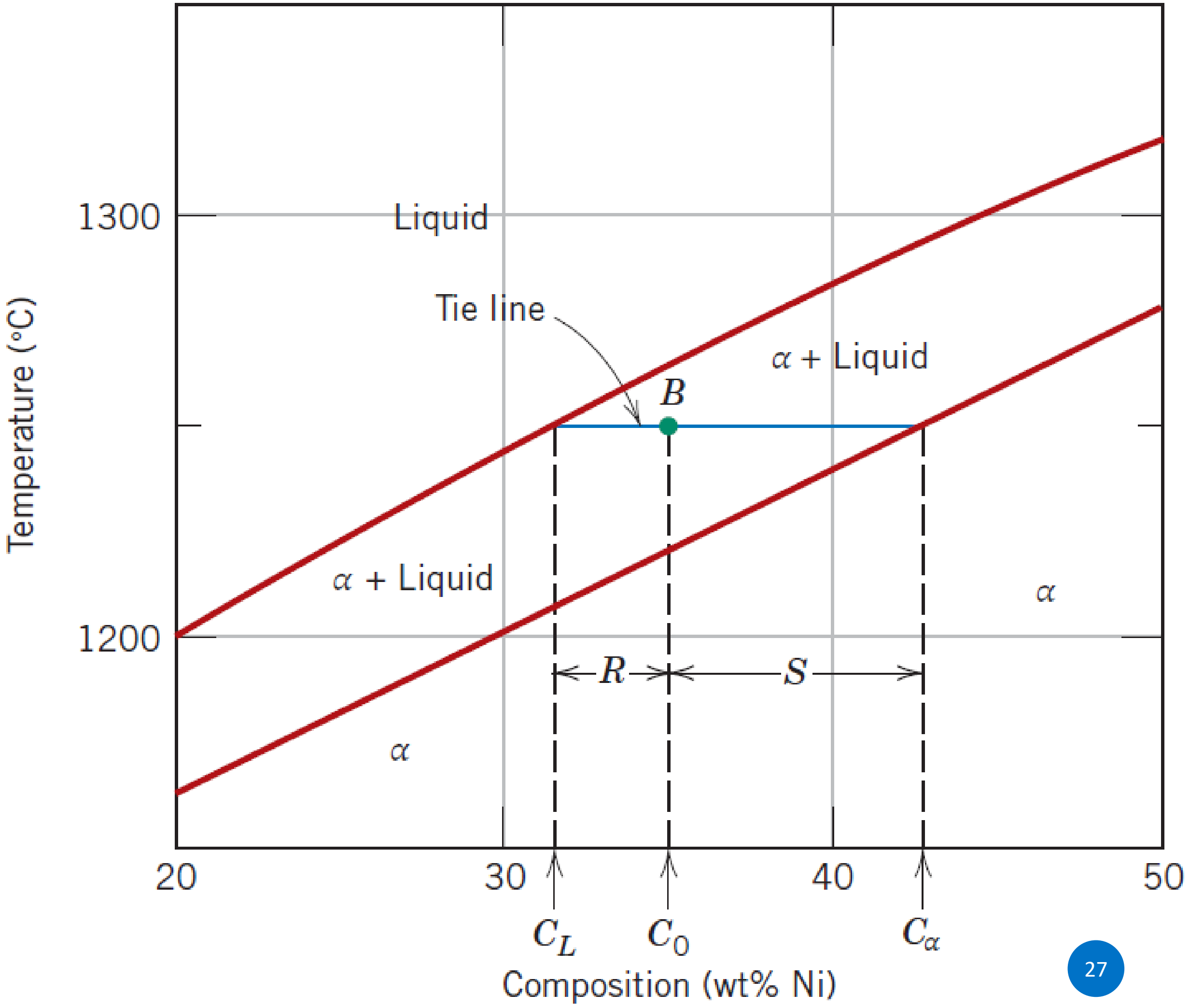
INTERPRETATION OF PHASE DIAGRAMS

(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.



INTERPRETATION OF PHASE DIAGRAMS

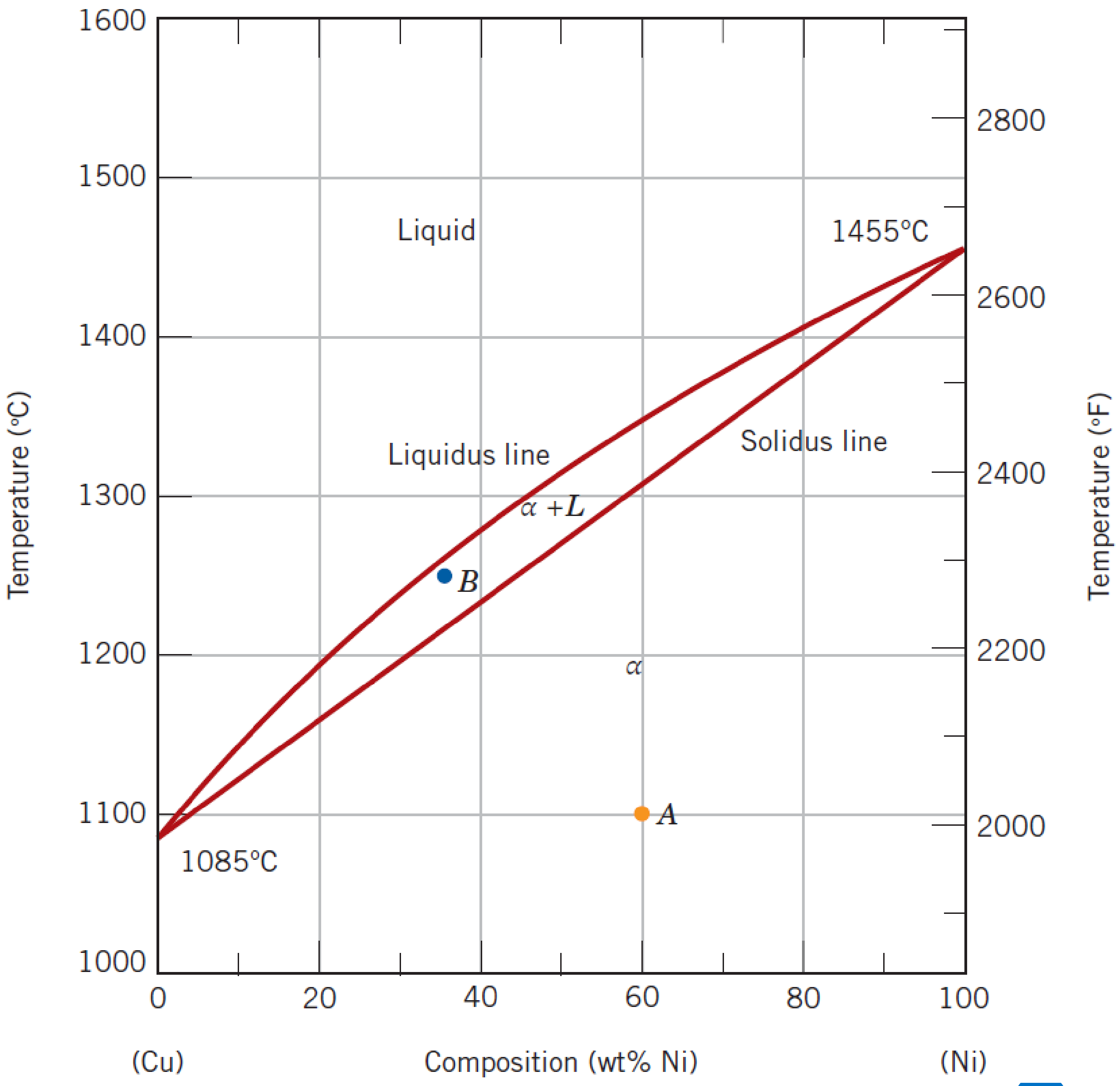
Determination of Phase Amounts

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

Again, the single- and two-phase situations must be treated separately. The solution is obvious in the single-phase region.

Because only one phase is present, the alloy is composed entirely of that phase—that is, the phase fraction is 1.0, or, alternatively, the percentage is 100%.

From the previous example for the 60 wt% Ni–40 wt% Cu alloy at 1100°C (point *A*), only the α phase is present; hence, the alloy is completely, or 100%, α.



INTERPRETATION OF PHASE DIAGRAMS

If the composition and temperature position is located within a two-phase region, things are more complex. The tie line must be used in conjunction with a procedure that is often called the **lever rule** (or the *inverse lever rule*), which is applied as follows:

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.
5. If phase percentages are desired, each phase fraction is multiplied by 100. When

the composition axis is scaled in weight percent, the phase fractions computed using the lever rule are *mass fractions*—the mass (or weight) of a specific phase divided by the total alloy mass (or weight).

The mass of each phase is computed from the product of each phase fraction and the total alloy mass.

In the use of the lever rule, tie line segment lengths may be determined either by direct measurement from the phase diagram using a linear scale, preferably graduated in millimetres, or by subtracting compositions as taken from the composition axis.

INTERPRETATION OF PHASE DIAGRAMS

Consider again the example shown, in which at 1250°C both α and liquid phases are present for a 35 wt% Ni–65 wt% Cu alloy.

The problem is to compute the fraction of each of the α and liquid phases.

The tie line is constructed that was used for the determination of α and L phase compositions.

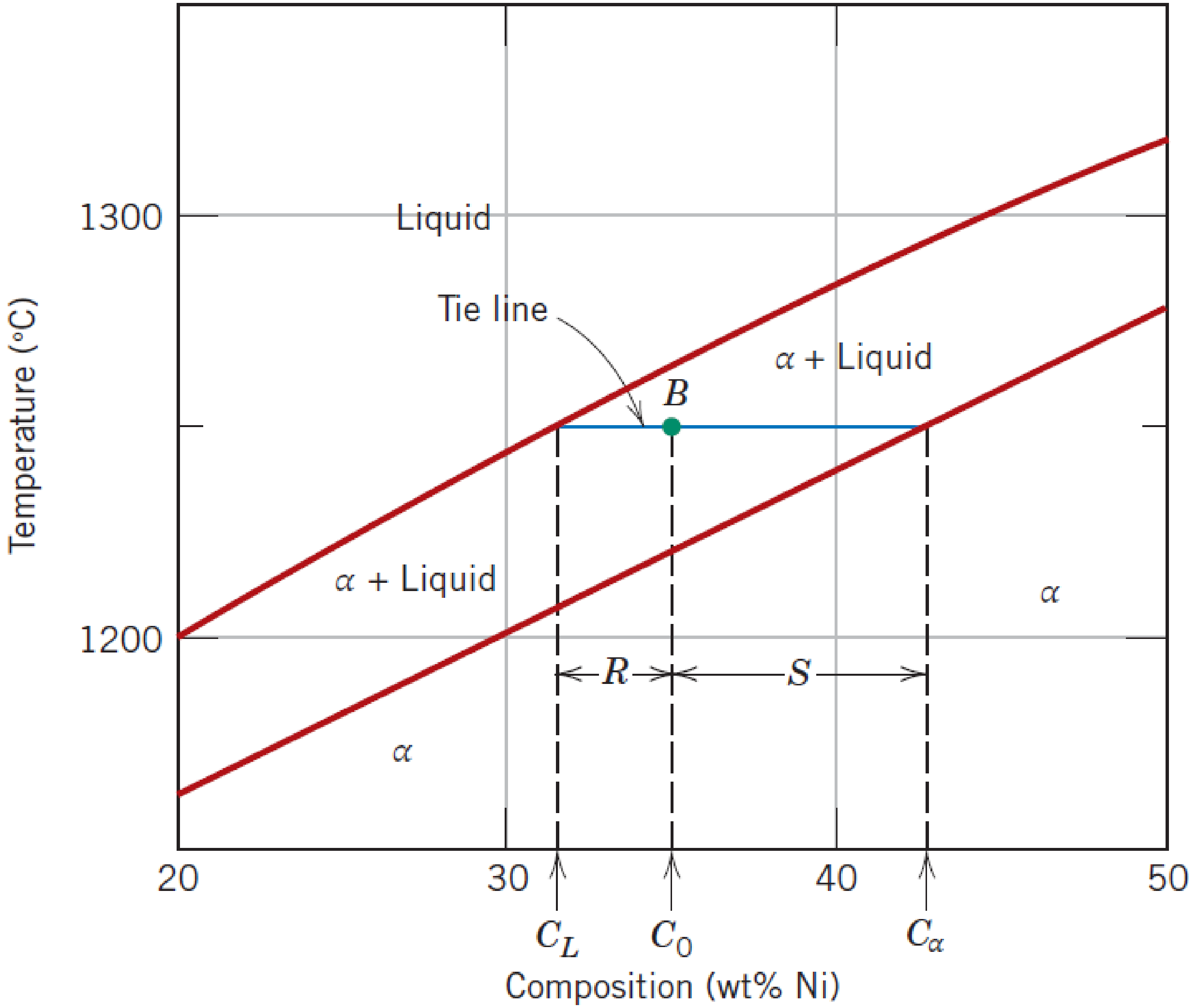
Let the overall alloy composition be located along the tie line and denoted as C_0, and let the mass fractions be represented by W_L and W_α for the respective phases.

From the lever rule, W_L may be computed according to

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

or, by subtracting compositions,

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



INTERPRETATION OF PHASE DIAGRAMS

Composition need be specified in terms of only one of the constituents for a binary alloy; for the preceding computation, weight percent nickel is used (i.e., C_0 = 35 wt% Ni, C_α = 42.5 wt% Ni, and C_L = 31.5 wt% Ni), and

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

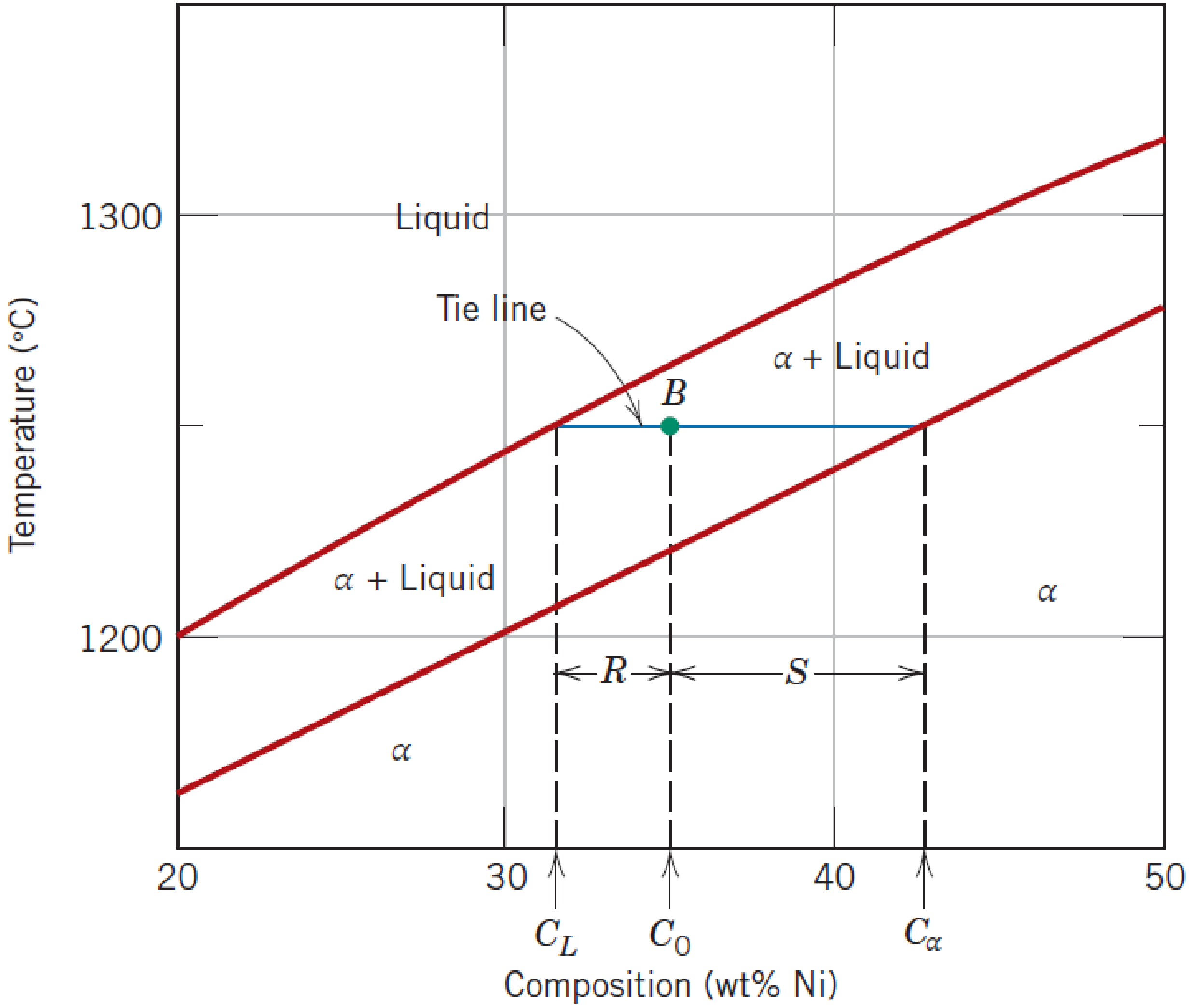
Similarly, for the α phase,

$$W_\alpha = \frac{R}{R + S}$$

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

$$= \frac{35 - 31.5}{42.5 - 31.5} = 0.32$$

Of course, identical answers are obtained if compositions are expressed in weight percent copper instead of nickel.



INTERPRETATION OF PHASE DIAGRAMS

The lever rule may be employed to determine the relative amounts or fractions of phases in any two-phase region for a binary alloy if the temperature and composition are known and if equilibrium has been established.

Compositions of phases are expressed in terms of weight precents of the components (e.g., wt% Cu, wt% Ni). For any alloy consisting of a single phase, the composition of that phase is the same as the total alloy composition.

If two phases are present, the tie line must be employed, the extremes of which determine the compositions of the respective phases.

With regard to *fractional phase amounts* (e.g., mass fraction of the α or liquid phase), when a single phase exists, the alloy is completely that phase. For a two-phase alloy, the lever rule is used, in which a ratio of tie line segment lengths is taken.

For multiphase alloys, it is often more convenient to specify relative phase amount in terms of volume fraction rather than mass fraction. Phase volume fractions are preferred because they (rather than mass fractions) may be determined from examination of the microstructure; furthermore, the properties of a multiphase alloy may be estimated
on the basis of volume fractions.

INTERPRETATION OF PHASE DIAGRAMS

For an alloy consisting of α and β phases, the volume fraction of the α phase, V_α, is defined as:

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta}$$

where v_α and v_β denote the volumes of the respective phases in the alloy. An analogous expression exists for V_β, and, for an alloy consisting of just two phases, it is the case that $V_\alpha + V_\beta = 1$.

On occasion, conversion from mass fraction to volume fraction (or vice versa) is desired. Equations that facilitate these conversions are as follows:

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}} \qquad V_\beta = \frac{\dfrac{W_\beta}{\rho_\beta}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}}$$

And:

$$W_\alpha = \frac{V_\alpha \rho_\alpha}{V_\alpha \rho_\alpha + V_\beta \rho_\beta} \qquad W_\beta = \frac{V_\beta \rho_\beta}{V_\alpha \rho_\alpha + V_\beta \rho_\beta}$$

The densities can be calculated as we learnt in chapter 4.

DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

Equilibrium Cooling

At this point it is instructive to examine the development of microstructure that occurs for isomorphous alloys during solidification.

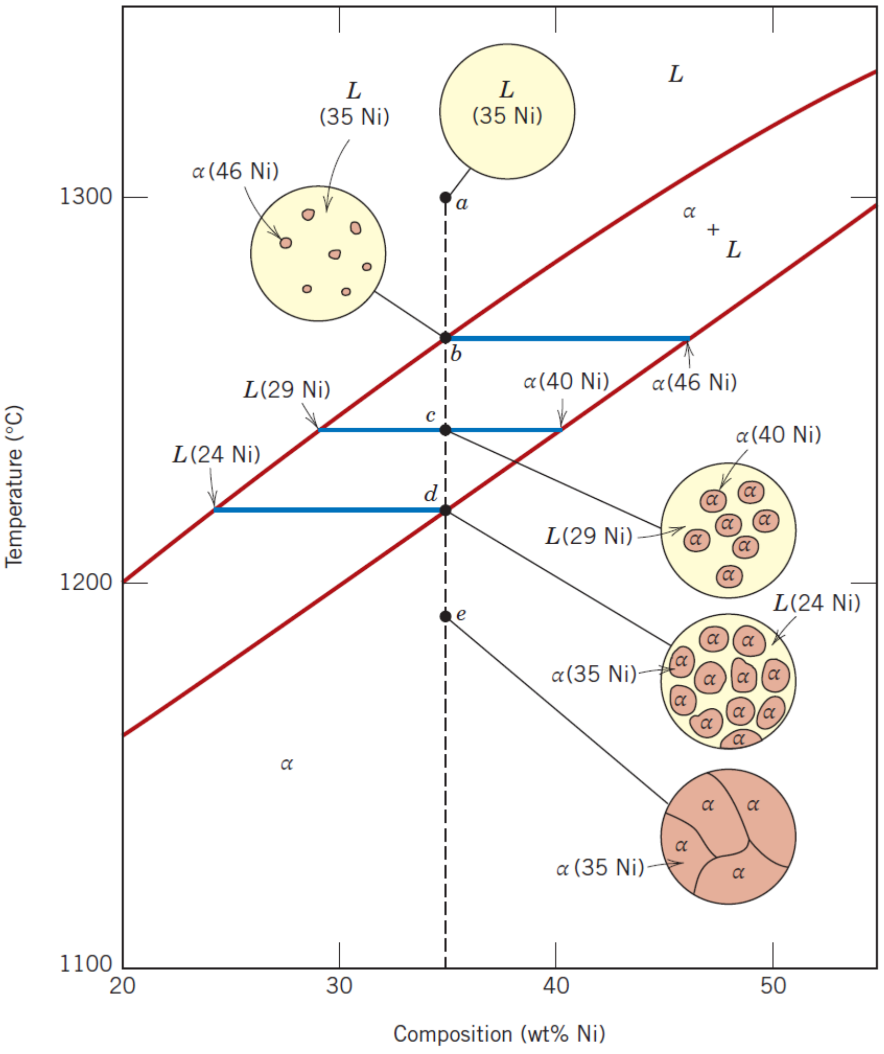
First treat the situation in which the cooling occurs very slowly, in that phase equilibrium is continuously maintained.

Consider the copper–nickel system, specifically an alloy of composition 35 wt% Ni–65 wt% Cu as it is cooled from 1300°C.

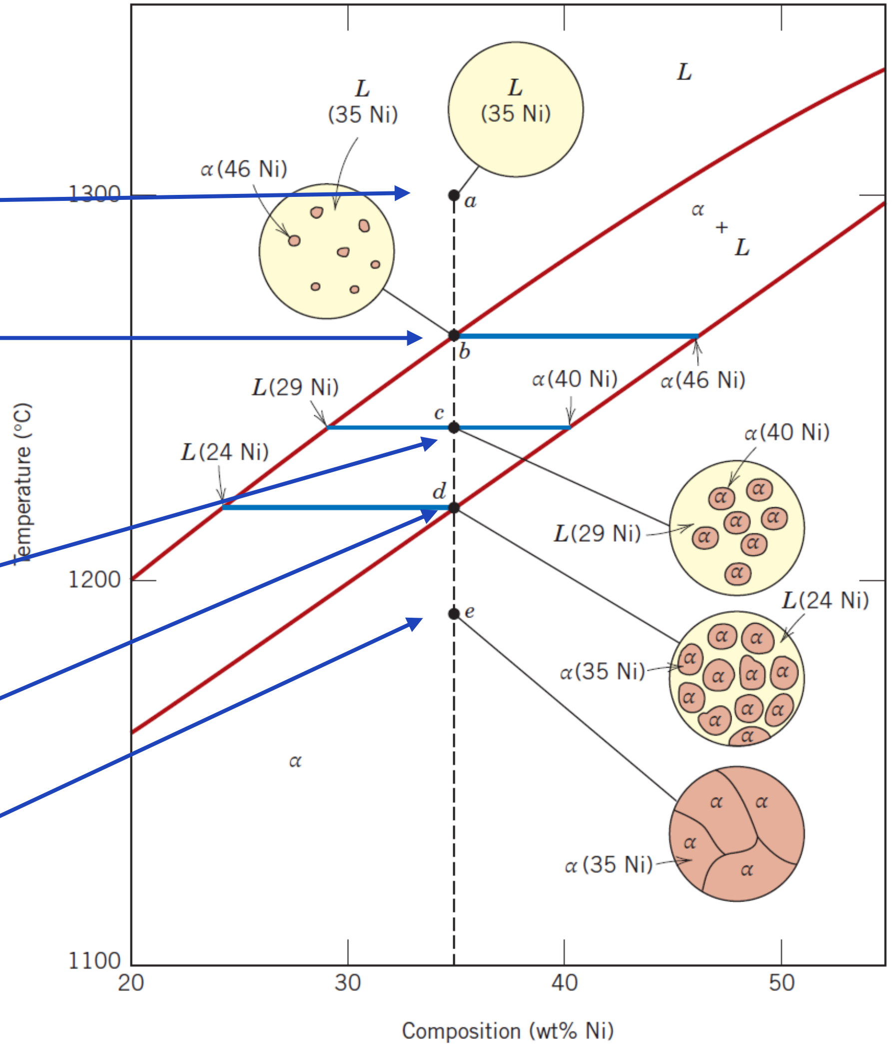
The region of the Cu–Ni phase diagram in the vicinity of this composition is shown.

Cooling of an alloy of this composition corresponds to moving down the vertical dashed line. At 1300°C, point *a*, the alloy is completely liquid (of composition 35 wt% Ni–65 wt% Cu) and has the microstructure represented by the circle inset in the figure.

As cooling begins, no microstructural or compositional changes will be realized until we reach the liquidus line (point *b*, ~1260°C).



DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS



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*.

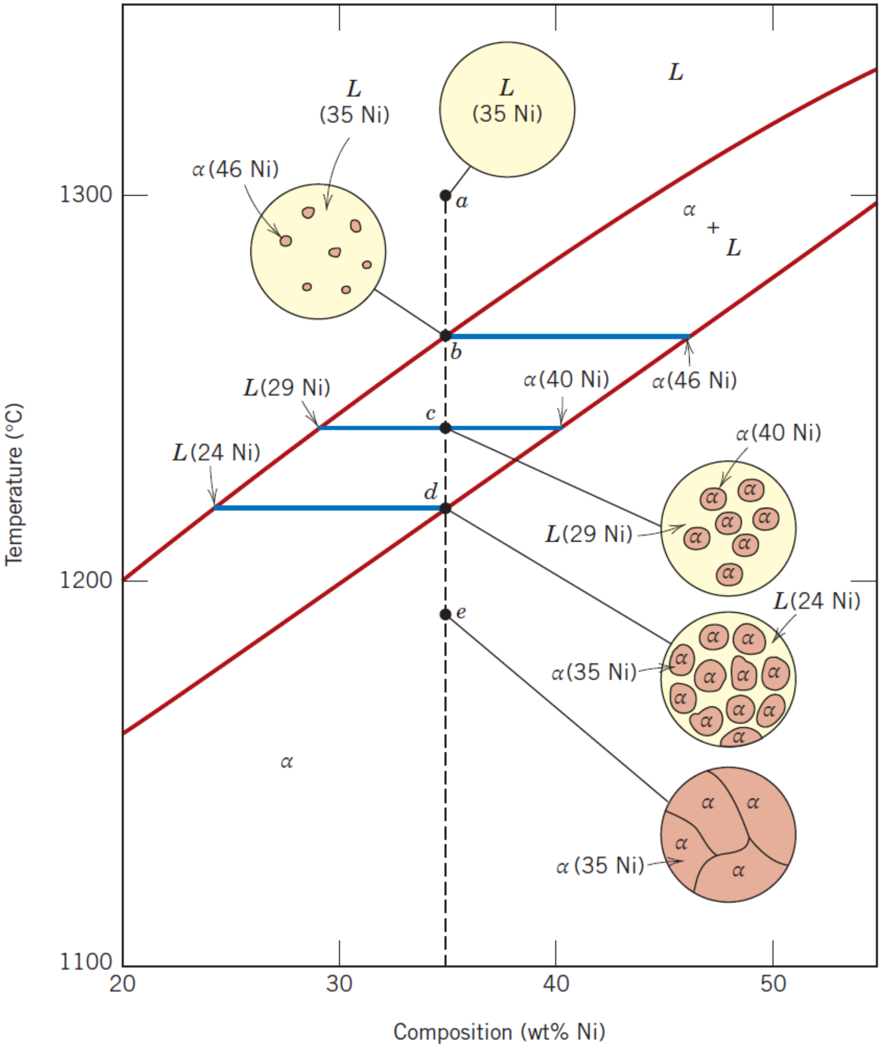
DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

At this point, the first solid α begins to form, which has a composition dictated by the tie line drawn at this temperature [i.e., 46 wt% Ni–54 wt% Cu, noted as α(46 Ni)]; the composition of liquid is still approximately 35 wt% Ni–65 wt% Cu [L(35 Ni)], which is different from that of the solid α.

With continued cooling, both compositions and relative amounts of each of the phases will change.

The compositions of the liquid and α phases will follow the liquidus and solidus lines, respectively. Furthermore, the fraction of the α phase will increase with continued cooling.

Note that the overall alloy composition (35 wt% Ni–65 wt% Cu) remains unchanged during cooling even though there is a redistribution of copper and nickel between the phases.



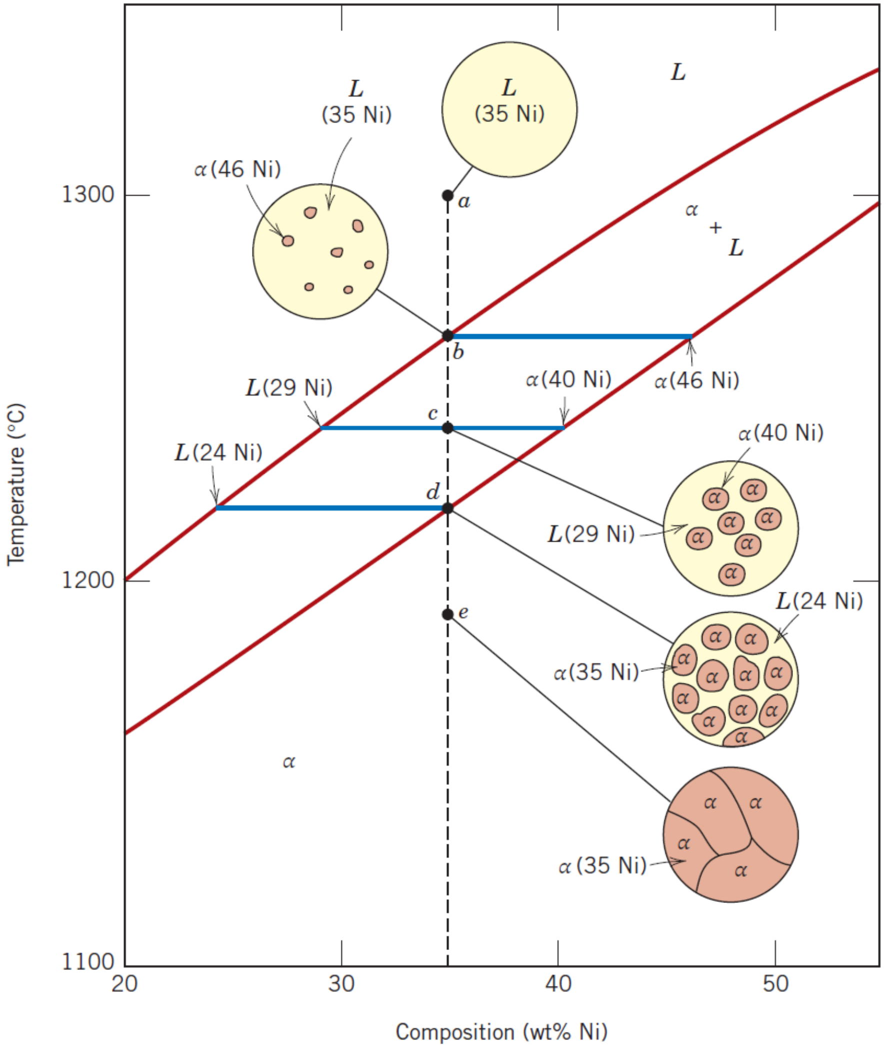
DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

At 1240°C, point *c*, the compositions of the liquid and α phases are 29 wt% Ni–71 wt% Cu [L(29 Ni)] and 40 wt% Ni–60 wt% Cu [α(40 Ni)], respectively.

The solidification process is virtually complete at about 1220°C, point *d*; the composition of the solid α is approximately 35 wt% Ni–65 wt% Cu (the overall alloy composition), whereas that of the last remaining liquid is 24 wt% Ni–76 wt% Cu.

Upon crossing the solidus line, this remaining liquid solidifies; the final product then is a polycrystalline α-phase solid solution that has a uniform 35 wt% Ni–65 wt% Cu composition (point *e*).

Subsequent cooling produces no microstructural or compositional alterations.



DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

Nonequilibrium Cooling

Conditions of equilibrium solidification and the development of microstructures, as described in the previous section, are realized only for extremely slow cooling rates.

The reason for this is that with changes in temperature, there must be readjustments in the compositions of the liquid and solid phases in accordance with the phase diagram (i.e., with the liquidus and solidus lines), as discussed.

These readjustments are accomplished by diffusional processes—that is, diffusion in both solid and liquid phases and also across the solid–liquid interface.

Because diffusion is a time-dependent phenomenon, to maintain equilibrium during cooling, sufficient time must be allowed at each temperature for the appropriate compositional readjustments. *Diffusion rates* (i.e., the magnitudes of the diffusion coefficients) are especially low for the solid phase and, for both phases, decrease with diminishing temperature.

In virtually all practical solidification situations, cooling rates are much too rapid to allow these compositional readjustments and maintenance of equilibrium; consequently, microstructures other than those previously described develop.

DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

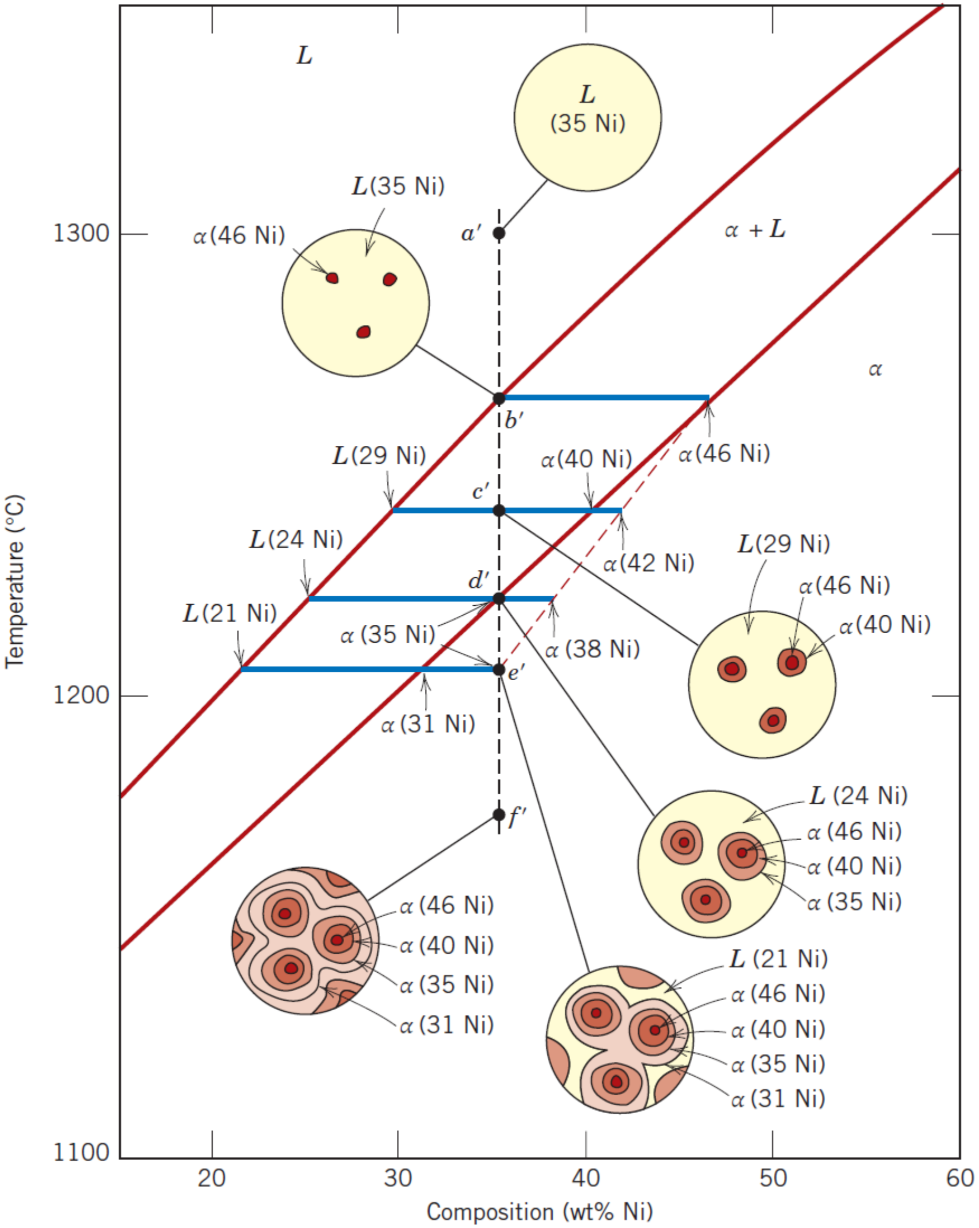
Some of the consequences of nonequilibrium solidification for isomorphous alloys will now be discussed by considering a 35 wt% Ni–65 wt% Cu alloy, the same composition that was used for equilibrium cooling in the previous section.

The portion of the phase diagram near this composition is shown; in addition, microstructures and associated phase compositions at various temperatures upon cooling are noted in the circular insets.

To simplify this discussion, it will be assumed that diffusion rates in the liquid phase are sufficiently rapid such that equilibrium is maintained in the liquid.

Begin cooling from a temperature of about 1300°C; this is indicated by point *a*′ in the liquid region.

This liquid has a composition of 35 wt% Ni–65 wt% Cu [noted as *L*(35 Ni) in the figure], and no changes occur while cooling through the liquid phase region (moving down vertically from point *a*′).



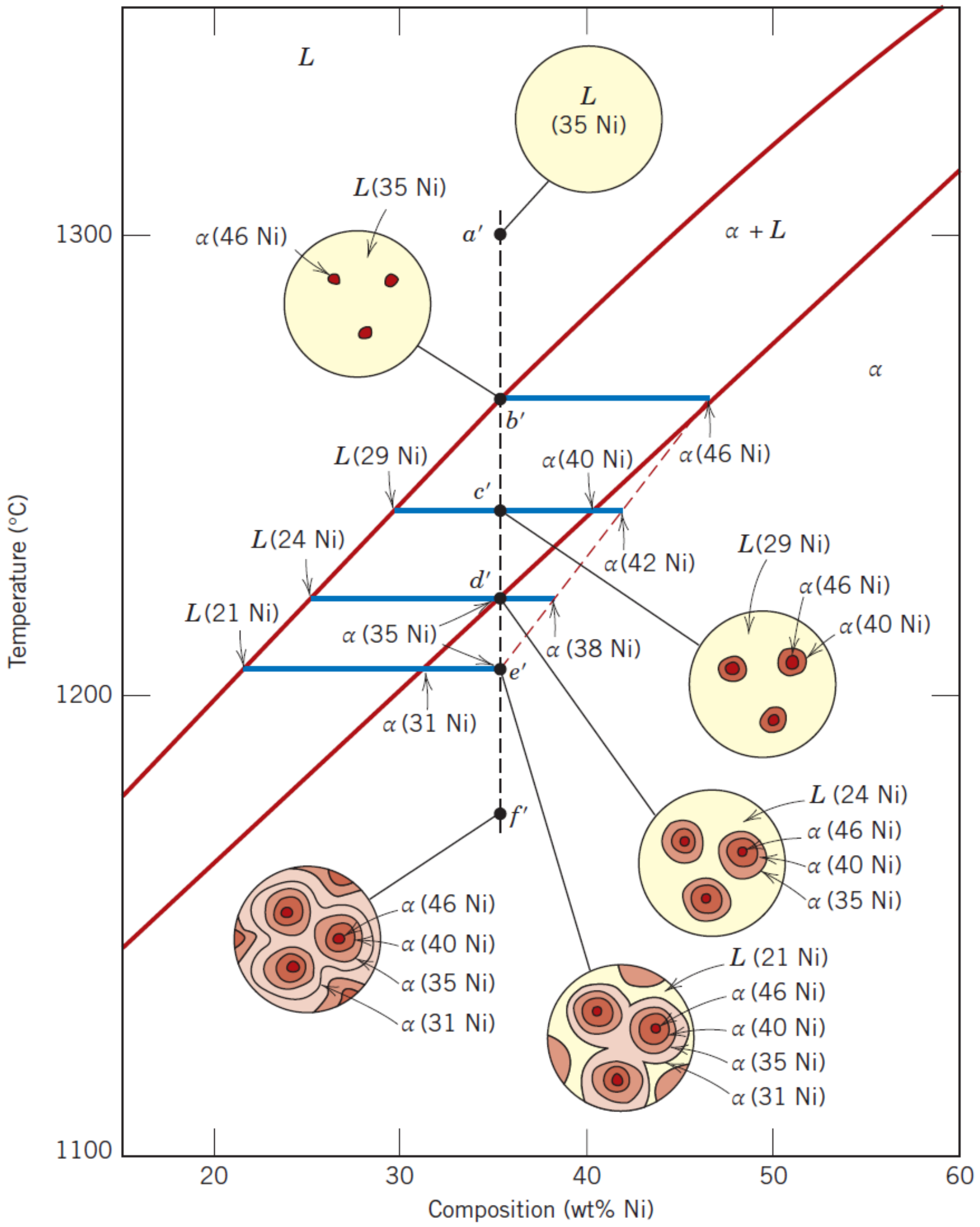
DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

At point b' (approximately 1260°C), α-phase particles begin to form, which, from the tie line constructed, have a composition of 46 wt% Ni–54 wt% Cu [α(46 Ni)].

Upon further cooling to point c' (about 1240°C), the liquid composition has shifted to 29 wt% Ni–71 wt% Cu; furthermore, at this temperature the composition of the α phase that solidified is 40 wt% Ni–60 wt% Cu [α(40 Ni)].

However, because diffusion in the solid α phase is relatively slow, the α phase that formed at point b' has not changed composition appreciably—that is, it is still about 46 wt% Ni—and the composition of the α grains has continuously changed with radial position, from 46 wt% Ni at grain centres to 40 wt% Ni at the outer grain perimeters.

Thus, at point c', the *average composition* of the solid α grains that have formed would be some volume-weighted average composition lying between 46 and 40 wt% Ni.



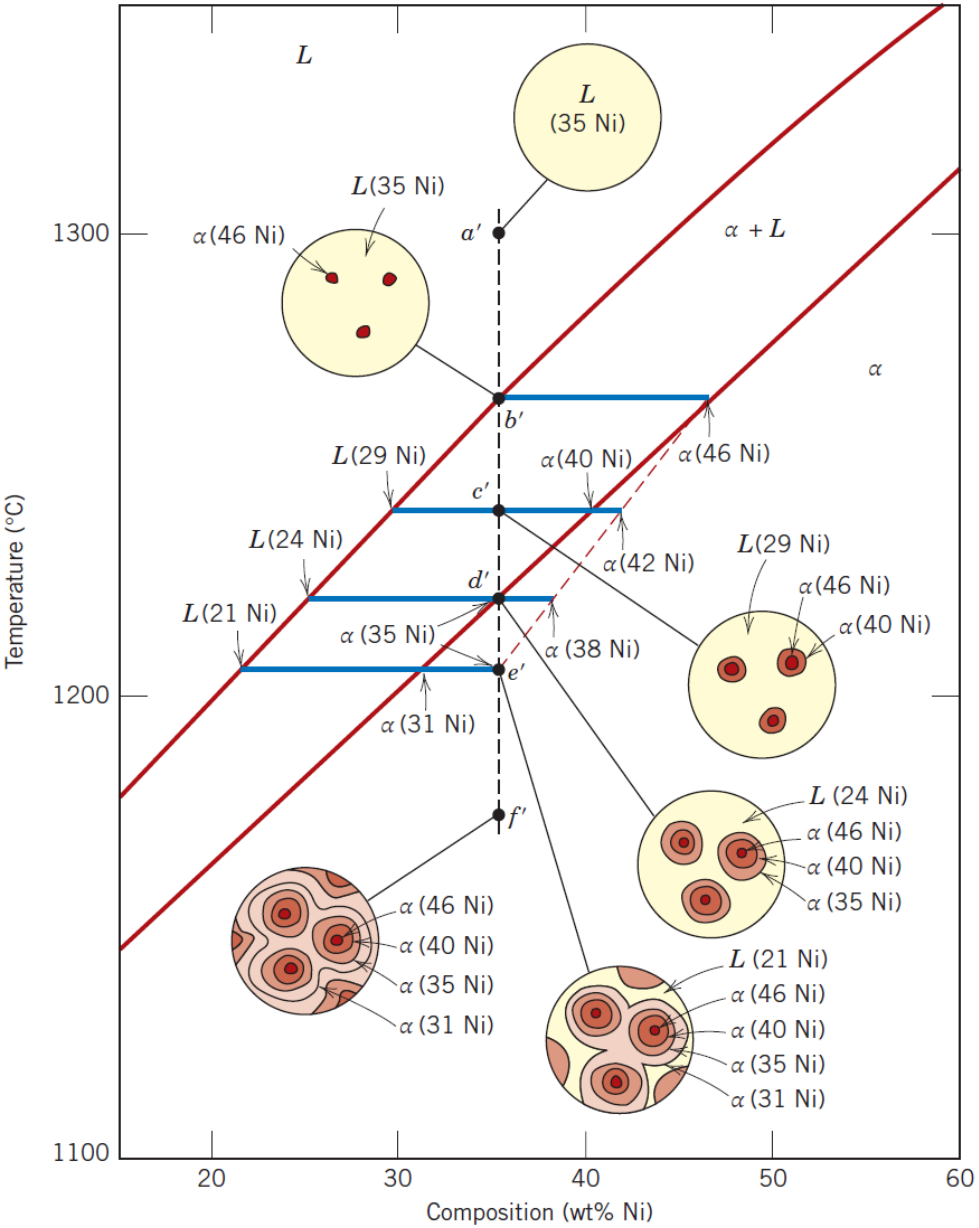
DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

For the sake of argument, let us take this average composition to be 42 wt% Ni–58 wt% Cu [α(42 Ni)].

Furthermore, we would also find that, on the basis of lever-rule computations, a greater proportion of liquid is present for these nonequilibrium conditions than for equilibrium cooling.

The implication of this nonequilibrium solidification phenomenon is that the solidus line on the phase diagram has been shifted to higher Ni contents—to the average compositions of the α phase (e.g., 42 wt% Ni at 1240°C)—and is represented by the dashed line in the figure.

There is no comparable alteration of the liquidus line inasmuch as it is assumed that equilibrium is maintained in the liquid phase during cooling because of sufficiently rapid diffusion rates.



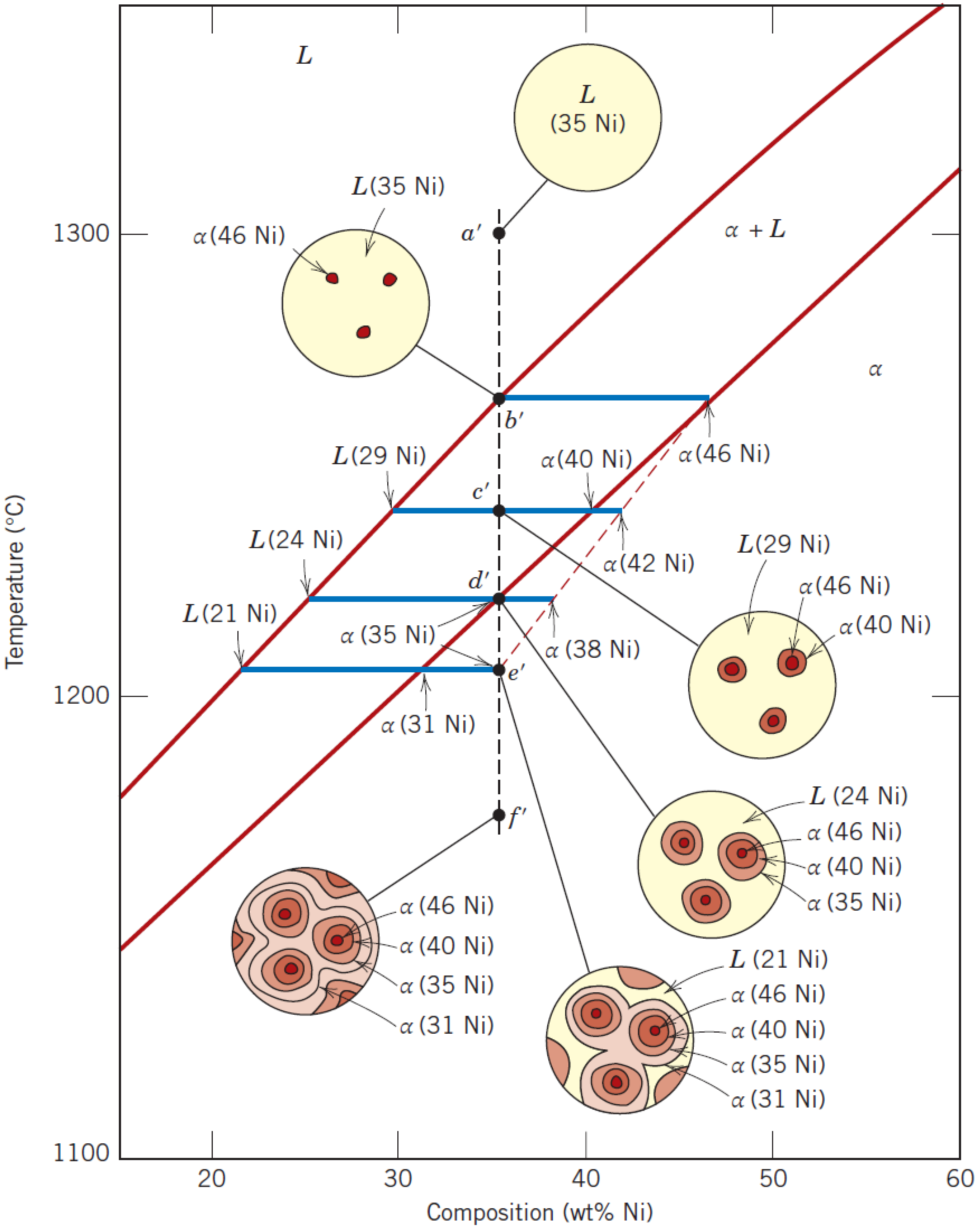
DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

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

Nonequilibrium solidification finally reaches completion at point *e′* (~1205°C).

The composition of the last α phase to solidify at this point is about 31 wt% Ni; the *average* composition of the α phase at complete solidification is 35 wt% Ni.

The inset at point *f ′* shows the microstructure of the totally solid material.



DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

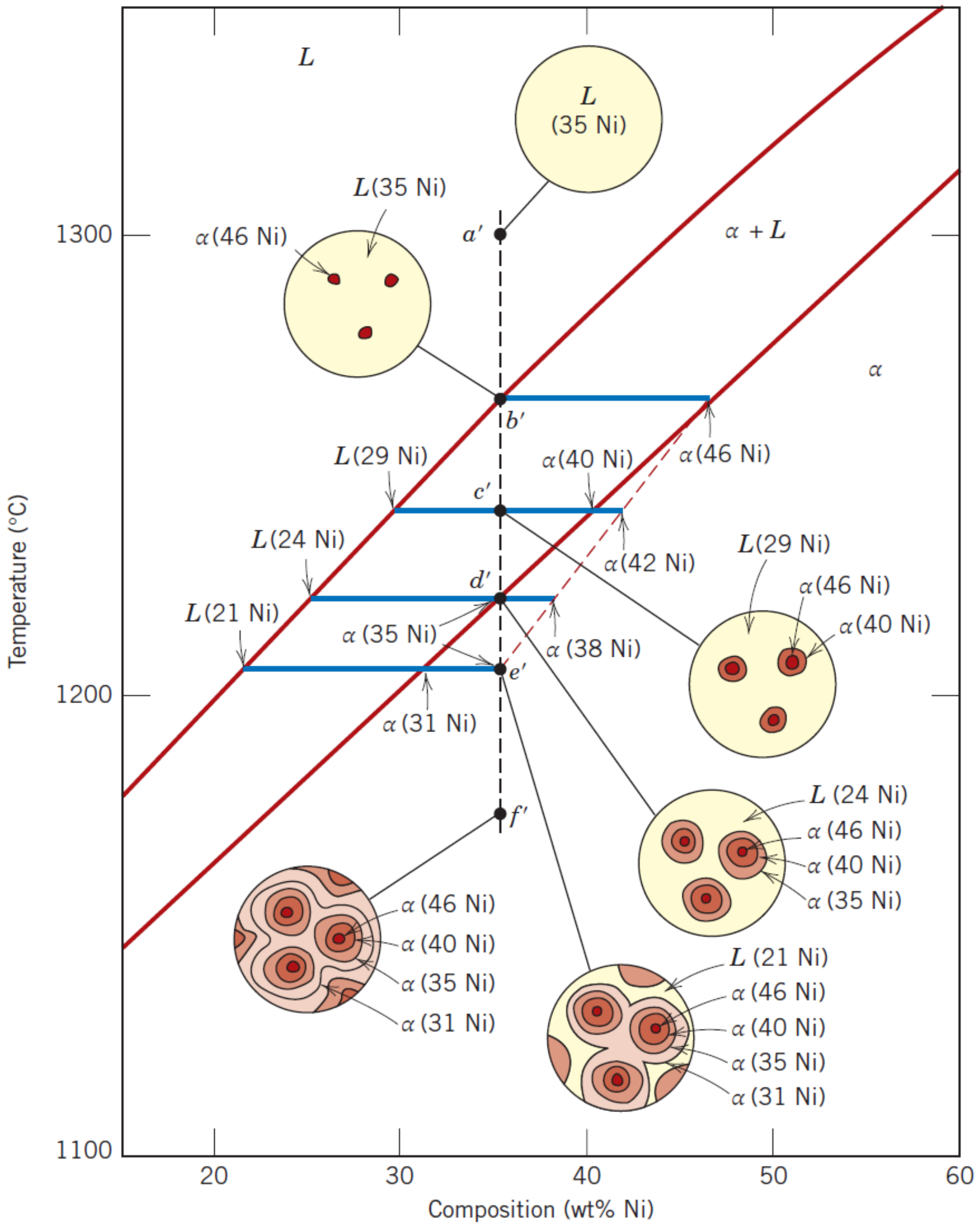
The degree of displacement of the nonequilibrium solidus curve from the equilibrium one depends on the rate of cooling; the slower the cooling rate, the smaller this displacement—that is, the difference between the equilibrium solidus and average solid composition is lower.

Furthermore, if the diffusion rate in the solid phase increases, this displacement decreases.

There are some important consequences for isomorphous alloys that have solidified under nonequilibrium conditions.

As discussed earlier, the distribution of the two elements within the grains is nonuniform, a phenomenon termed *segregation*—that is, concentration gradients are established across the grains that are represented by the insets of the figure.

The centre of each grain, which is the first part to freeze, is rich in the high-melting element (e.g., nickel for this Cu–Ni system), whereas the concentration of the low-melting element increases with position from this region to the grain boundary.



DEVELOPMENT OF MICROSTRUCTURE IN ISOMORPHOUS ALLOYS

This is termed a *cored* structure, which gives rise to less than the optimal properties.

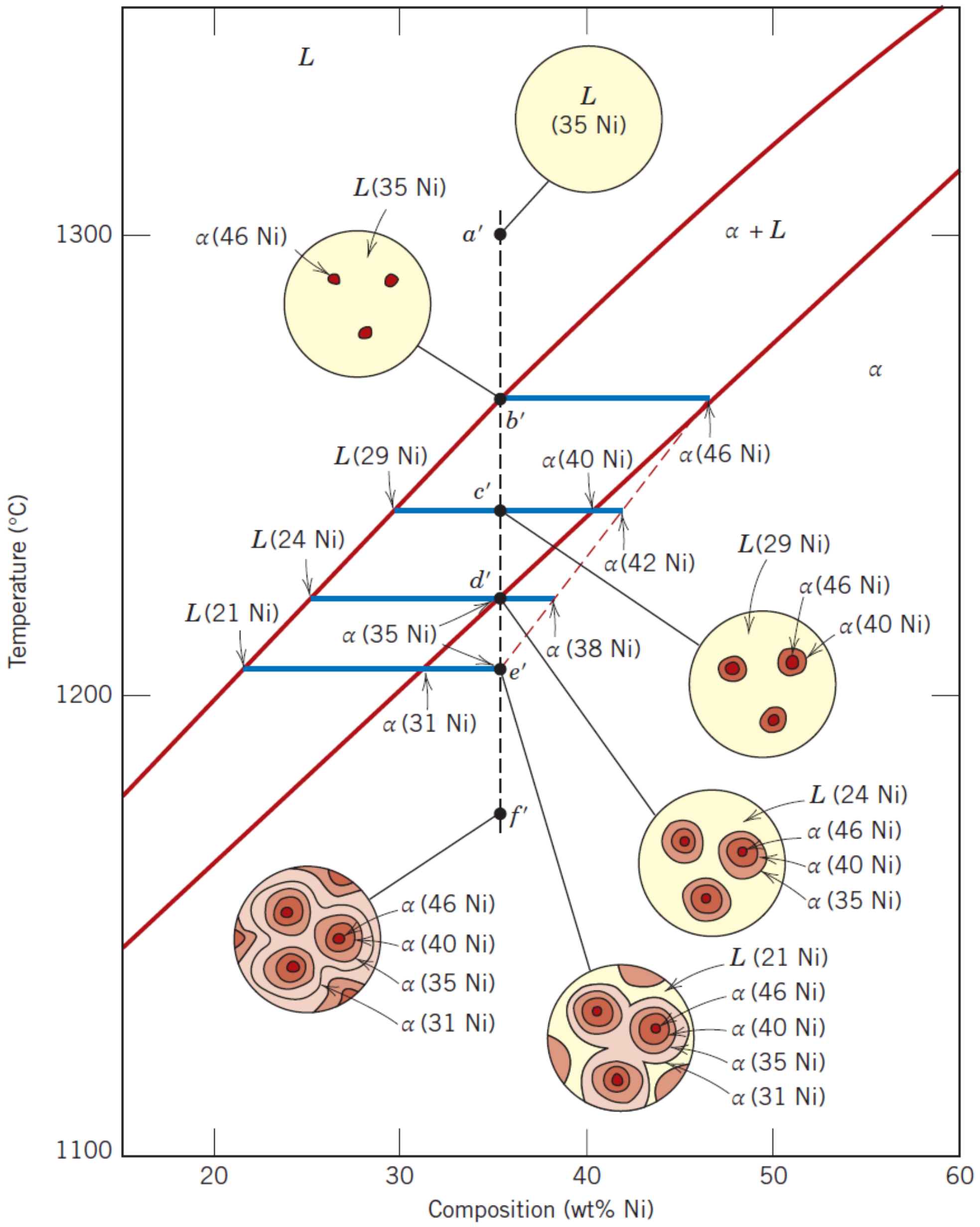
As a casting having a cored structure is reheated, grain boundary regions melt first because they are richer in the low-melting component.

This produces a sudden loss in mechanical integrity due to the thin liquid film that separates the grains.

Furthermore, this melting may begin at a temperature below the equilibrium solidus temperature of the alloy.

Coring may be eliminated by a homogenization heat treatment carried out at a temperature below the solidus point for the particular alloy composition.

During this process, atomic diffusion occurs, which produces compositionally homogeneous grains.



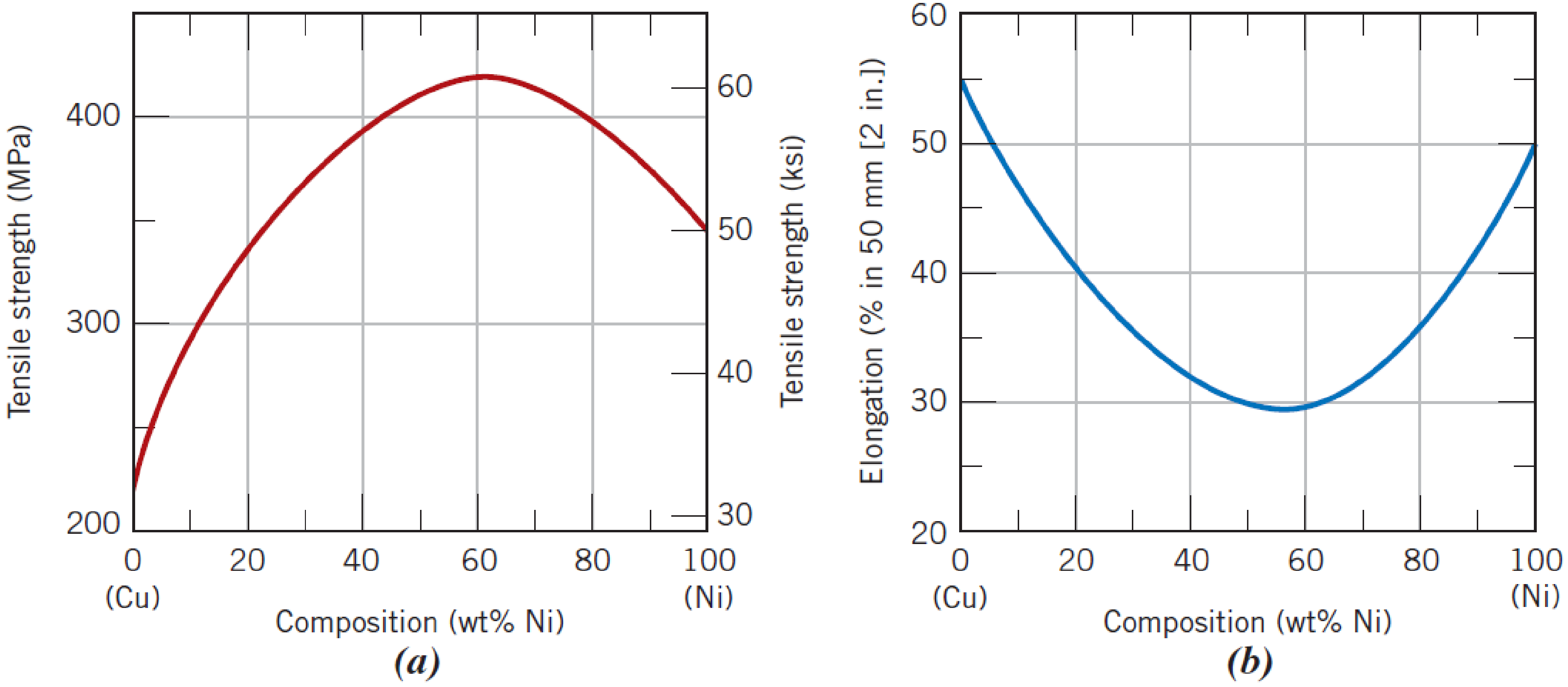
MECHANICAL PROPERTIES OF ISOMORPHOUS ALLOYS

For all temperatures and compositions below the melting temperature of the lowest melting component, only a single solid phase exists.

Therefore, each component experiences solid-solution strengthening or an increase in strength and hardness by additions of the other component.

This effect is demonstrated in (a) as tensile strength versus composition for the copper–nickel system at room temperature; at some intermediate composition, the curve necessarily passes through a maximum.

Plotted in (b) is the ductility (%EL) –composition behaviour, which is just the opposite of tensile strength —that is, ductility decreases with additions of the second component, and the curve exhibits a minimum.



BINARY EUTECTIC SYSTEMS

Another type of common and relatively simple phase diagram found for binary alloys is shown for the copper–silver system; this is known as a *binary eutectic phase diagram*.

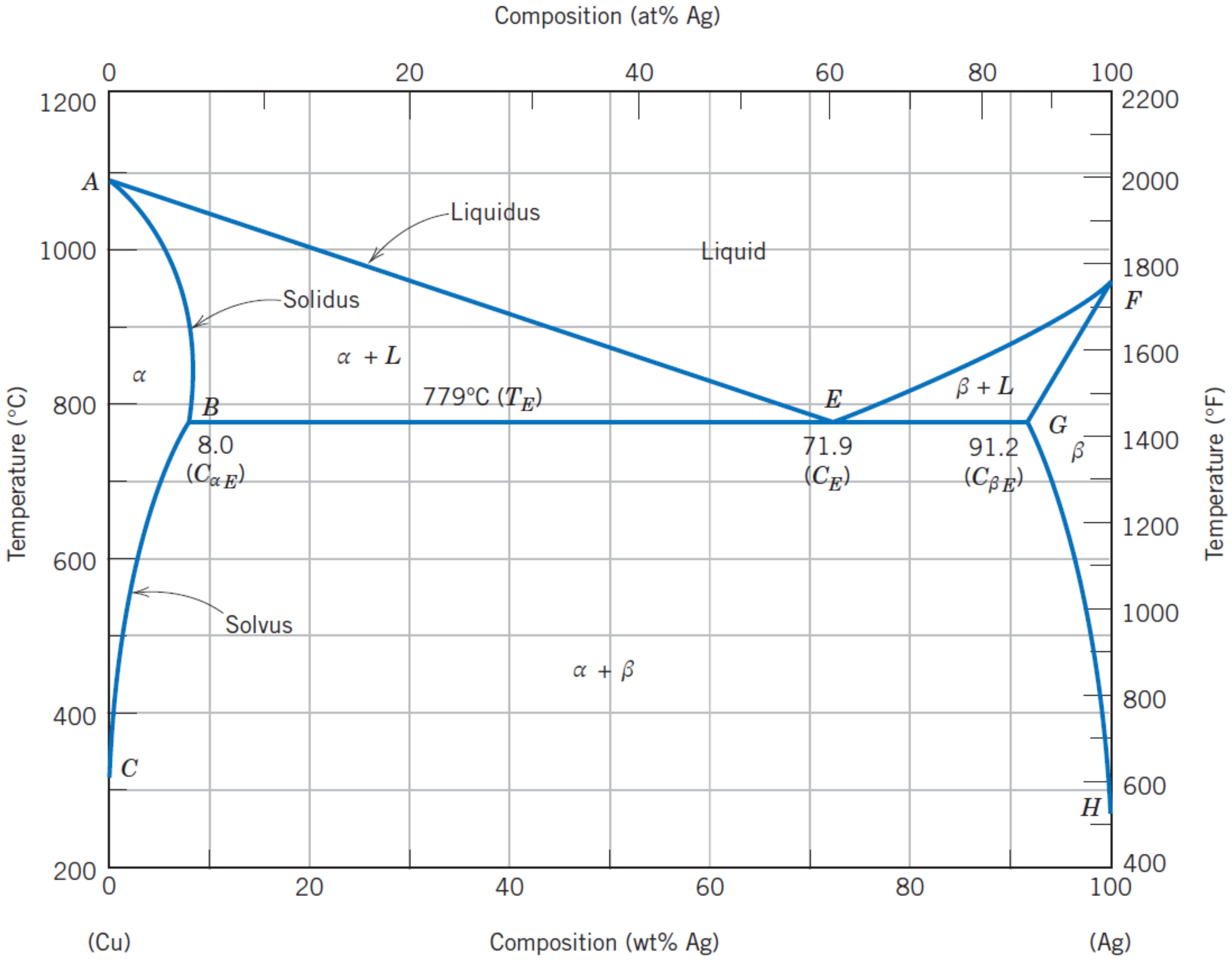
A number of features of this phase diagram are important and worth noting.

First, 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.

Pure copper and pure silver are also considered to be α and β phases, respectively.



A eutectic system is a homogeneous, solid mixture of two or more substances that form a super-lattice; the mixture either melts or solidifies at a lower temperature than the melting point of any of the individual substances. The phrase most commonly refers to a mixture of alloys

DEFINITIONS

A eutectic system from the Greek "εὐ" (eu = well) and "τήξις" (tēxis = melting) is a homogeneous mixture of substances that melts or solidifies at a single temperature that is lower than the melting point of any of the constituents.

This temperature is known as the eutectic temperature, and is the lowest possible melting temperature over all of the mixing ratios for the involved component species.

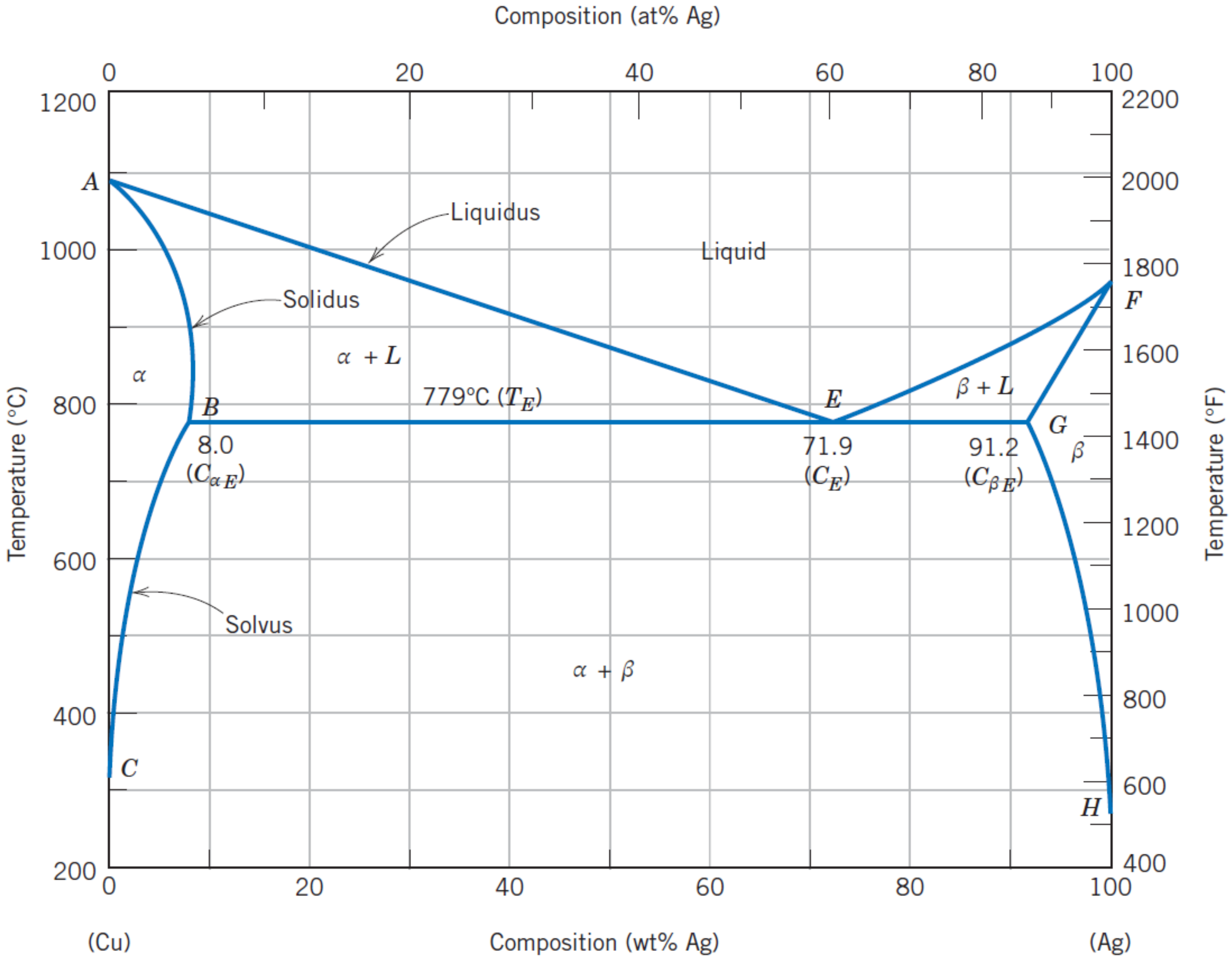
On a phase diagram, the eutectic temperature is seen as the eutectic point.

BINARY EUTECTIC SYSTEMS

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 dissolves 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, labelled *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.



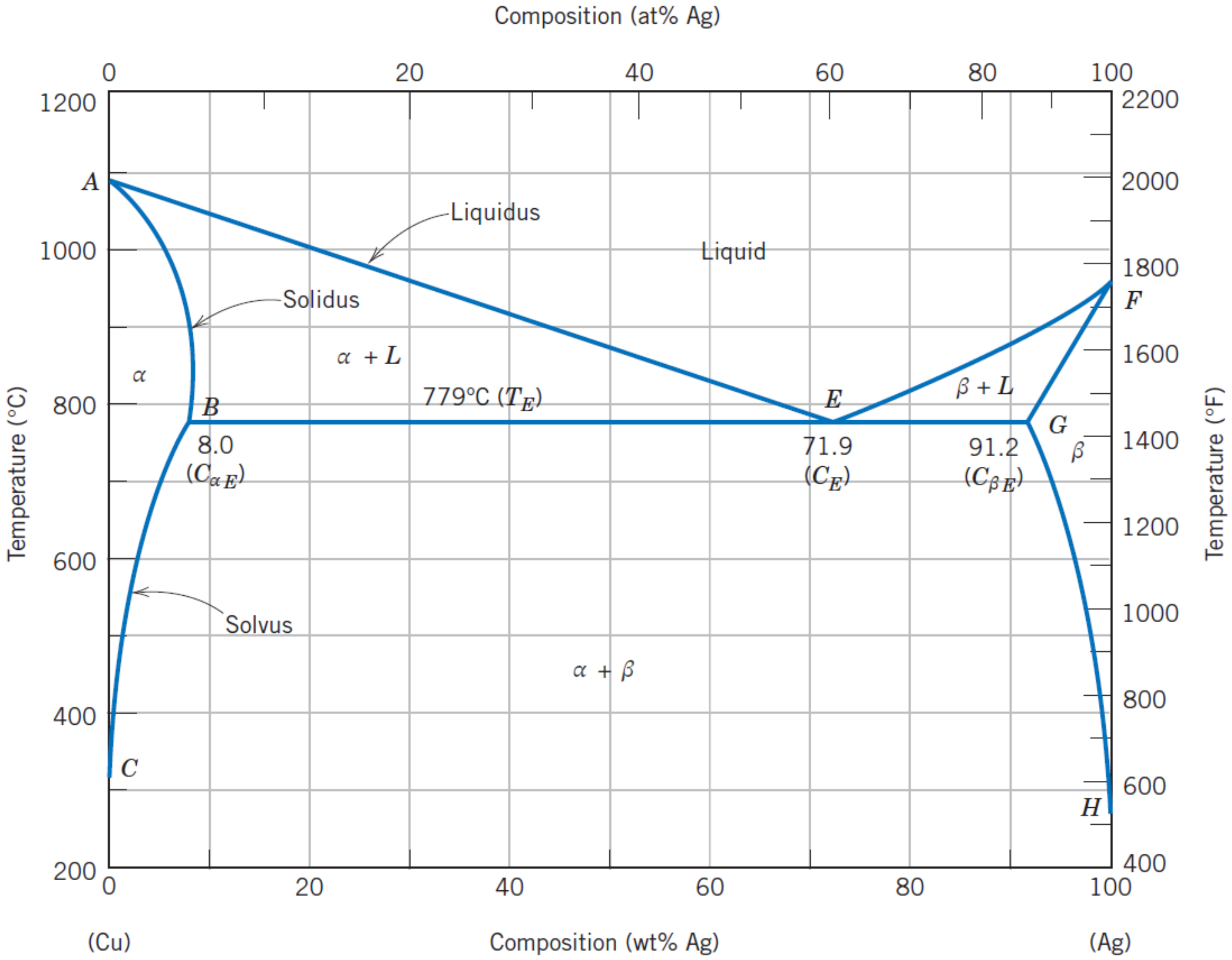
BINARY EUTECTIC SYSTEMS

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 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: $\alpha + L$, $\beta + L$, and $\alpha + \beta$.



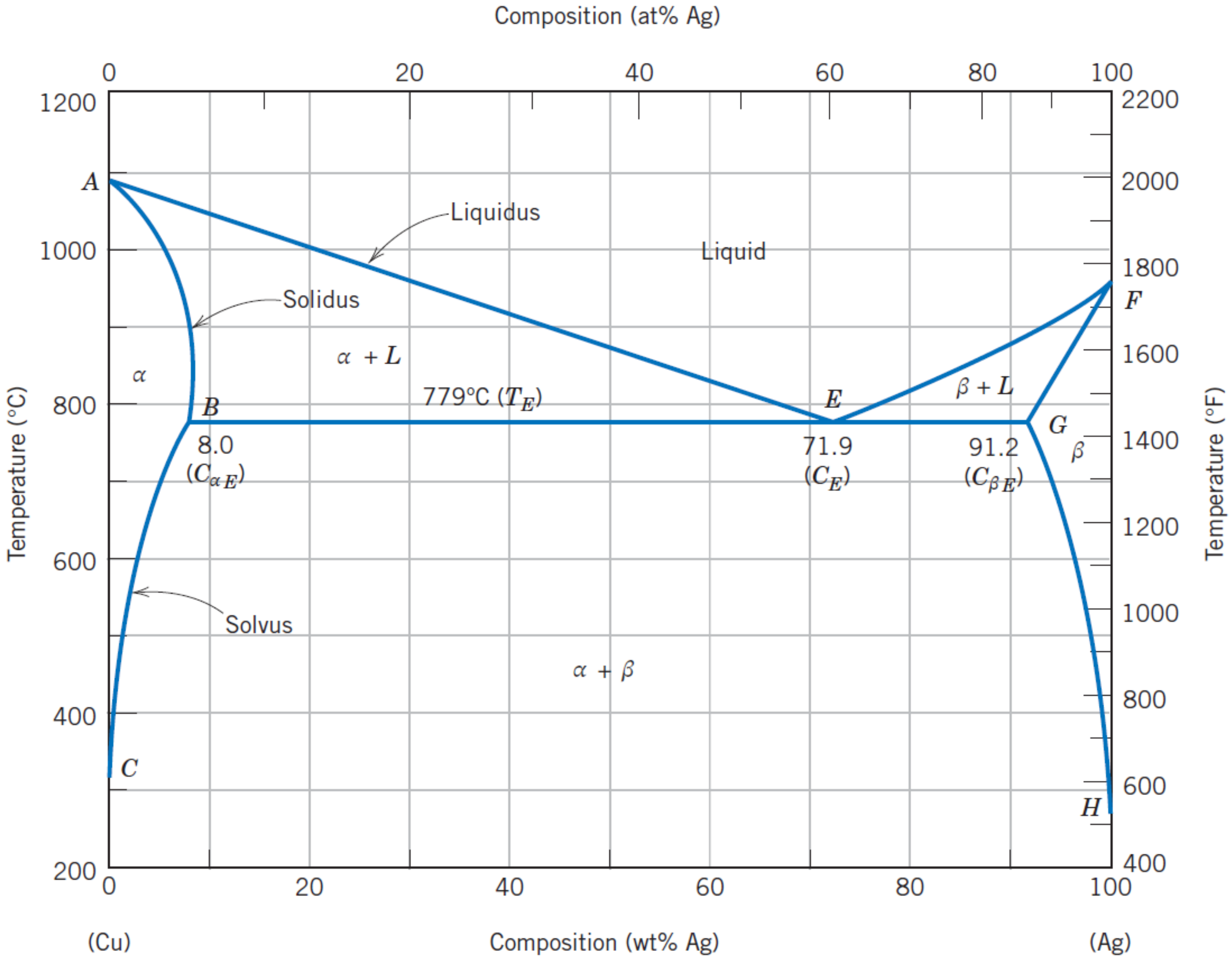
BINARY EUTECTIC SYSTEMS

The α- and β-phase solid solutions coexist for all compositions and temperatures within the $\alpha + \beta$ phase field; the α + liquid and β + 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*.



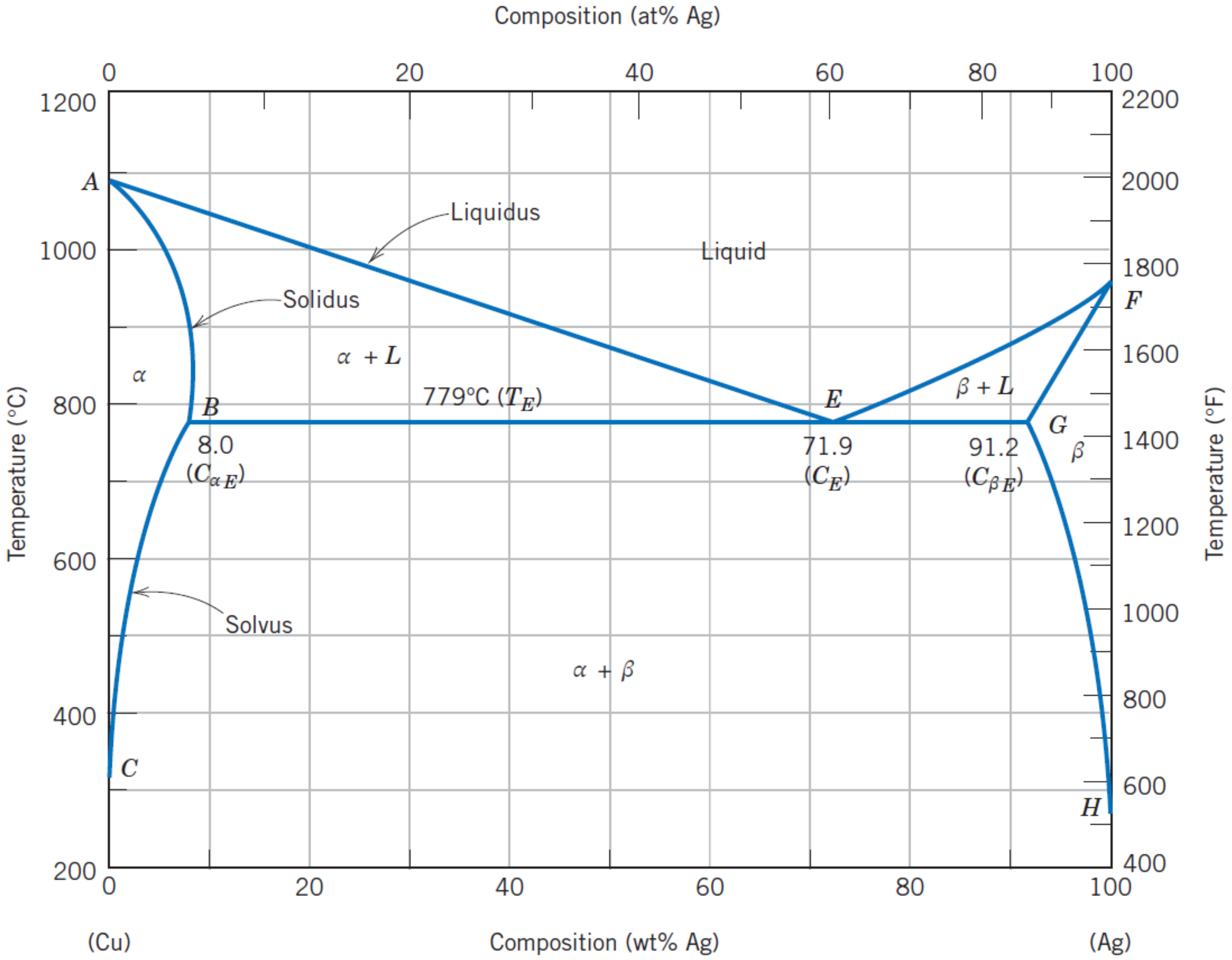
BINARY EUTECTIC SYSTEMS

These liquidus lines meet at the point *E* on the phase diagram, which point is designated by 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.

It should also be noted there is a horizontal isotherm at 779°C and represented by the line labelled *BEG* that also passes through point *E*.

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:

$$L(C_E) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$



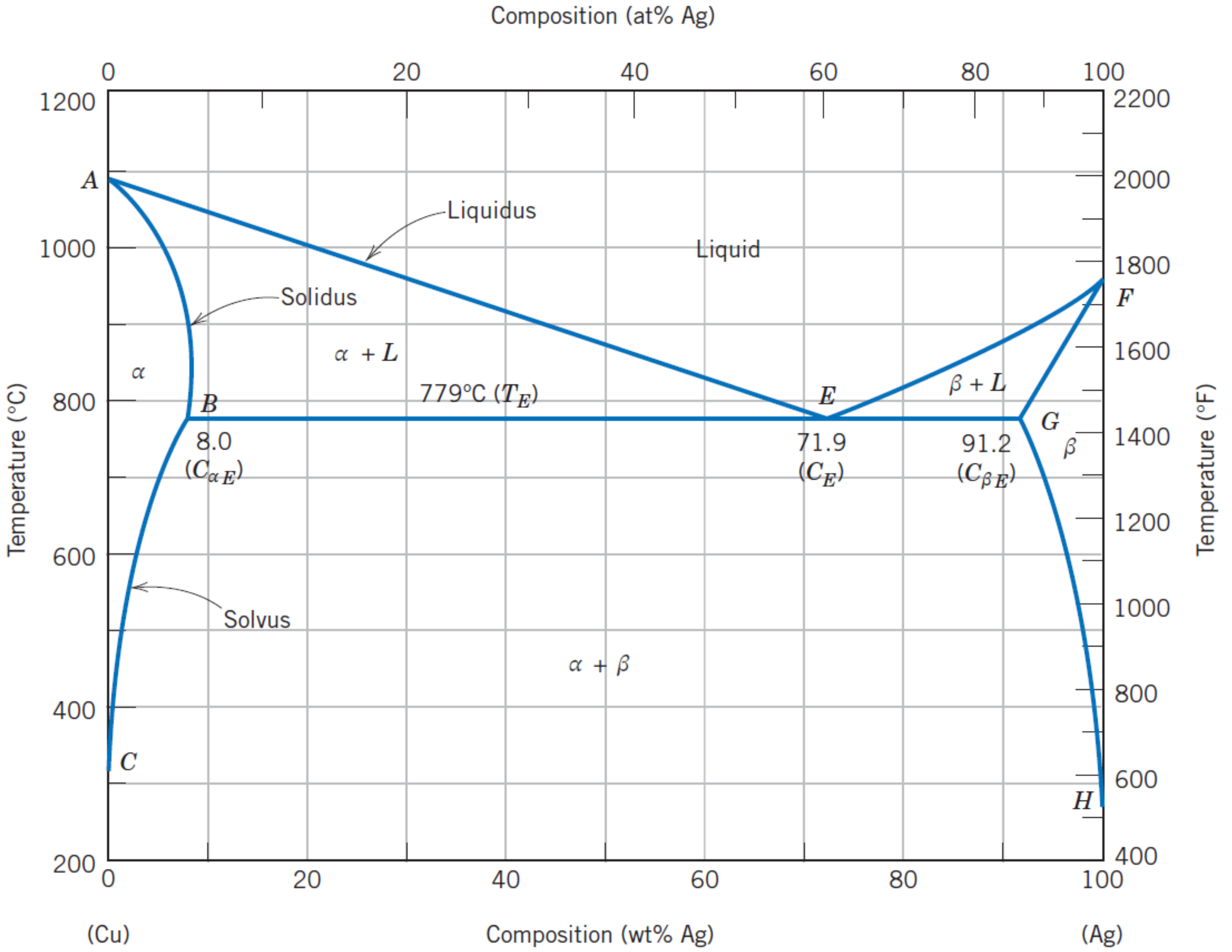
BINARY EUTECTIC SYSTEMS

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 point *E* on the diagram is called the *eutectic point;* furthermore, *CE* and *TE* represent the eutectic composition and temperature, respectively.

As also noted, $C\alpha E$ 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:

$$L(71.9\text{ wt\% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(8.0\text{ wt\% Ag}) + \beta(91.2\text{ wt\% Ag})$$



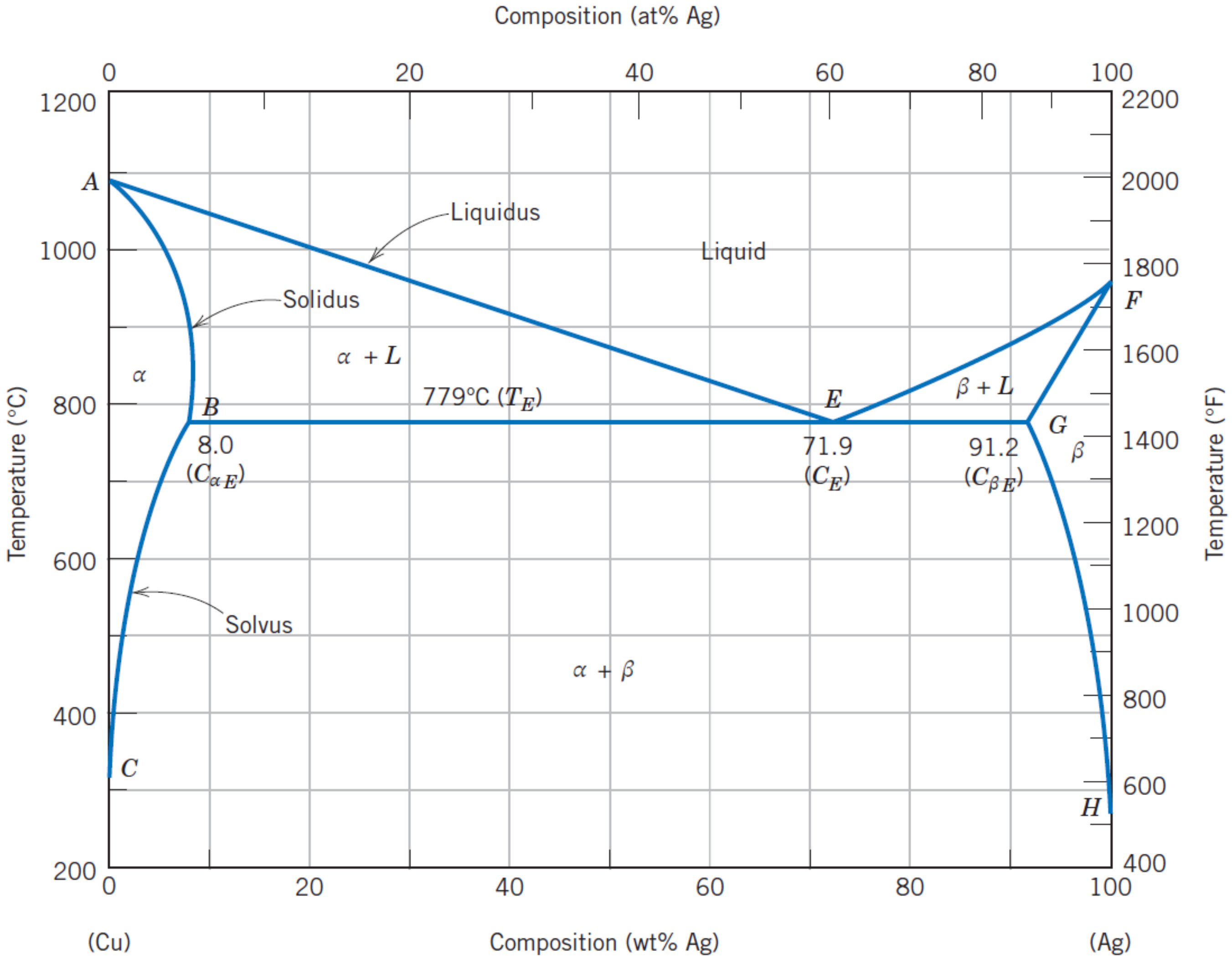
BINARY EUTECTIC SYSTEMS

This eutectic reaction is termed an *invariant reaction* inasmuch as it occurs under equilibrium conditions at a specific temperature (*TE*) and specific compositions (*CE*, *CαE* and *CβE*), which are constant (i.e., invariable) for a specific binary system.

Furthermore, the horizontal solidus line *BEG* at *TE* is sometimes 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.



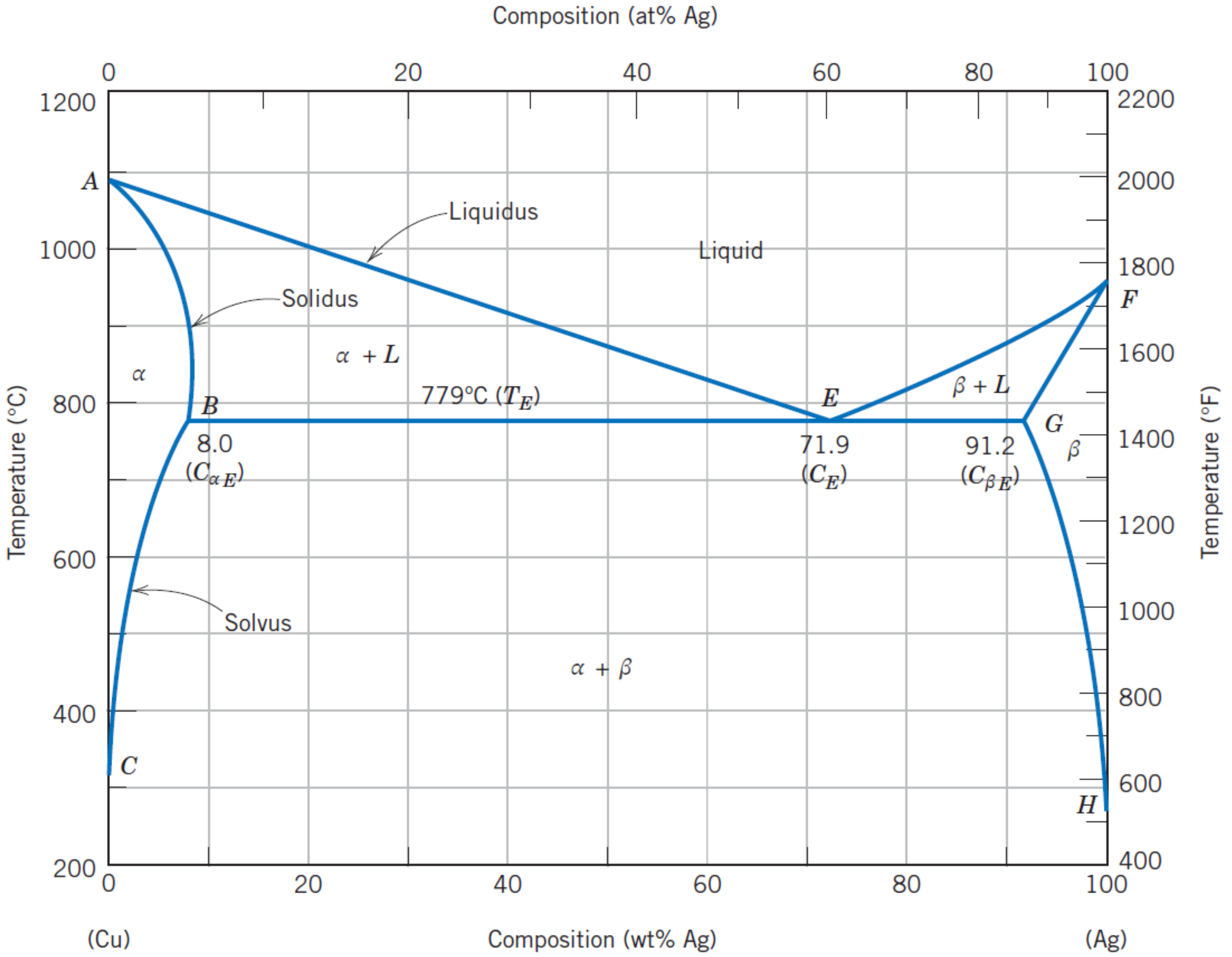
BINARY EUTECTIC SYSTEMS

Because of this eutectic reaction, phase diagrams similar to that shown are termed *eutectic phase diagrams;* components exhibiting this behaviour make up 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 presented so far (Ni-Cu, and Ag-Cu).

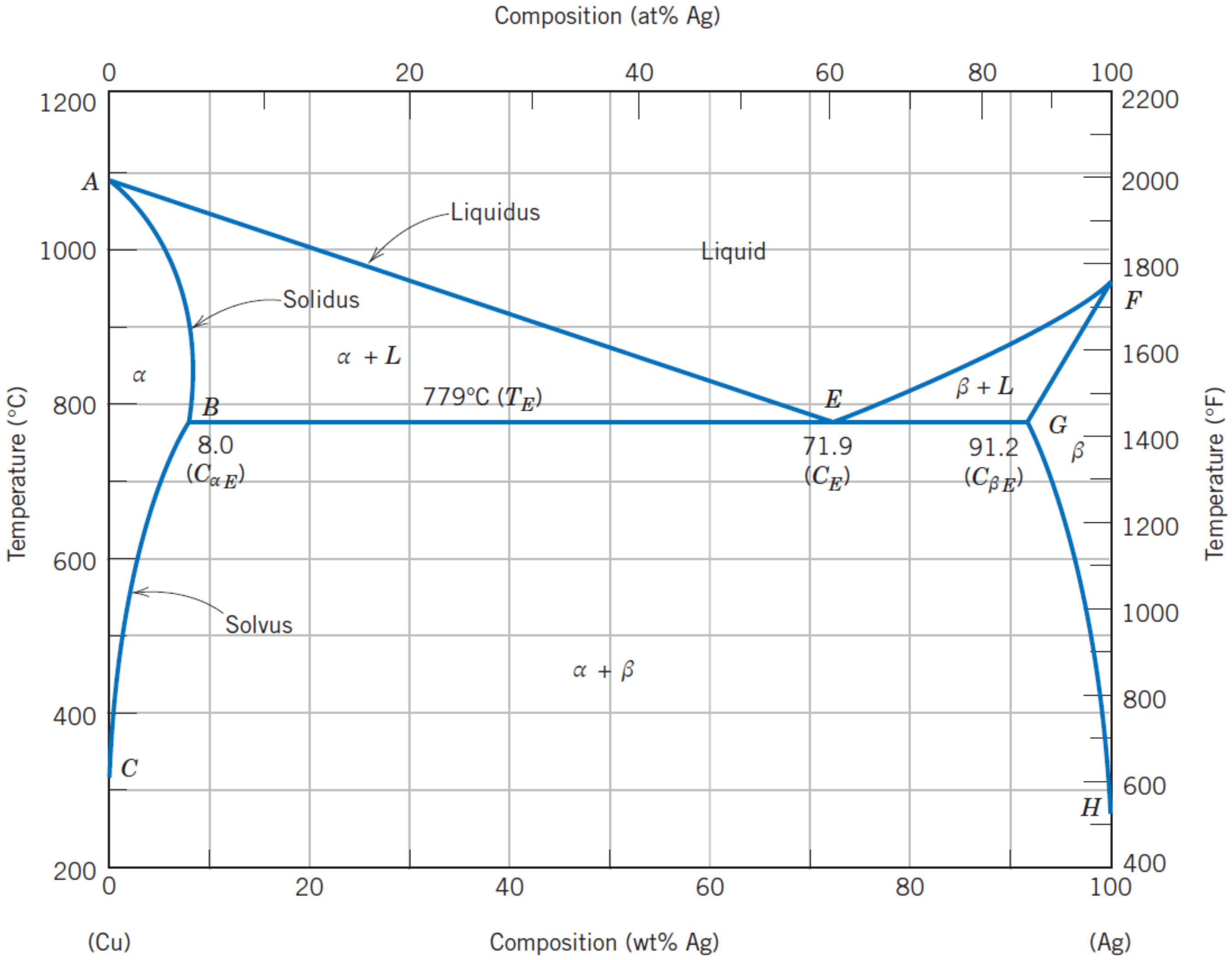
For a eutectic system, three phases (α, β, and L) may be in equilibrium, but only at points along the eutectic isotherm.



BINARY EUTECTIC SYSTEMS

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 the shown figure.



BINARY EUTECTIC SYSTEMS

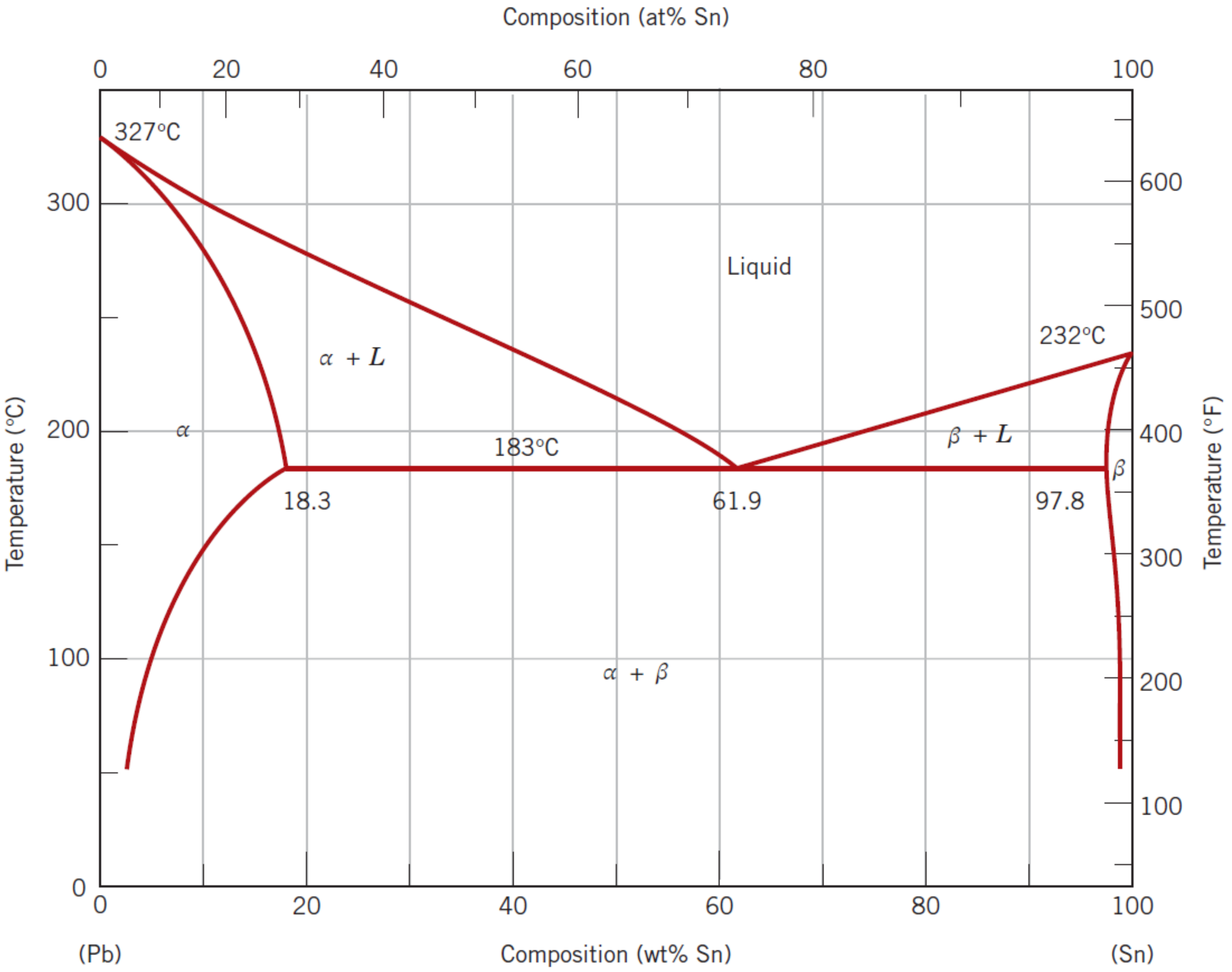
Another common eutectic system is that for lead and tin; the phase diagram has a general shape similar to that for copper–silver.

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; for β, tin is the solvent and lead is the solute.

The eutectic 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 are different for the copper–silver and lead–tin systems, as may be observed by comparing their phase diagrams.

On occasion, low-melting-temperature alloys are prepared having near-eutectic compositions. A familiar example is 60–40 solder, which contains 60 wt% Sn and 40 wt% Pb.



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 because it is easily melted.

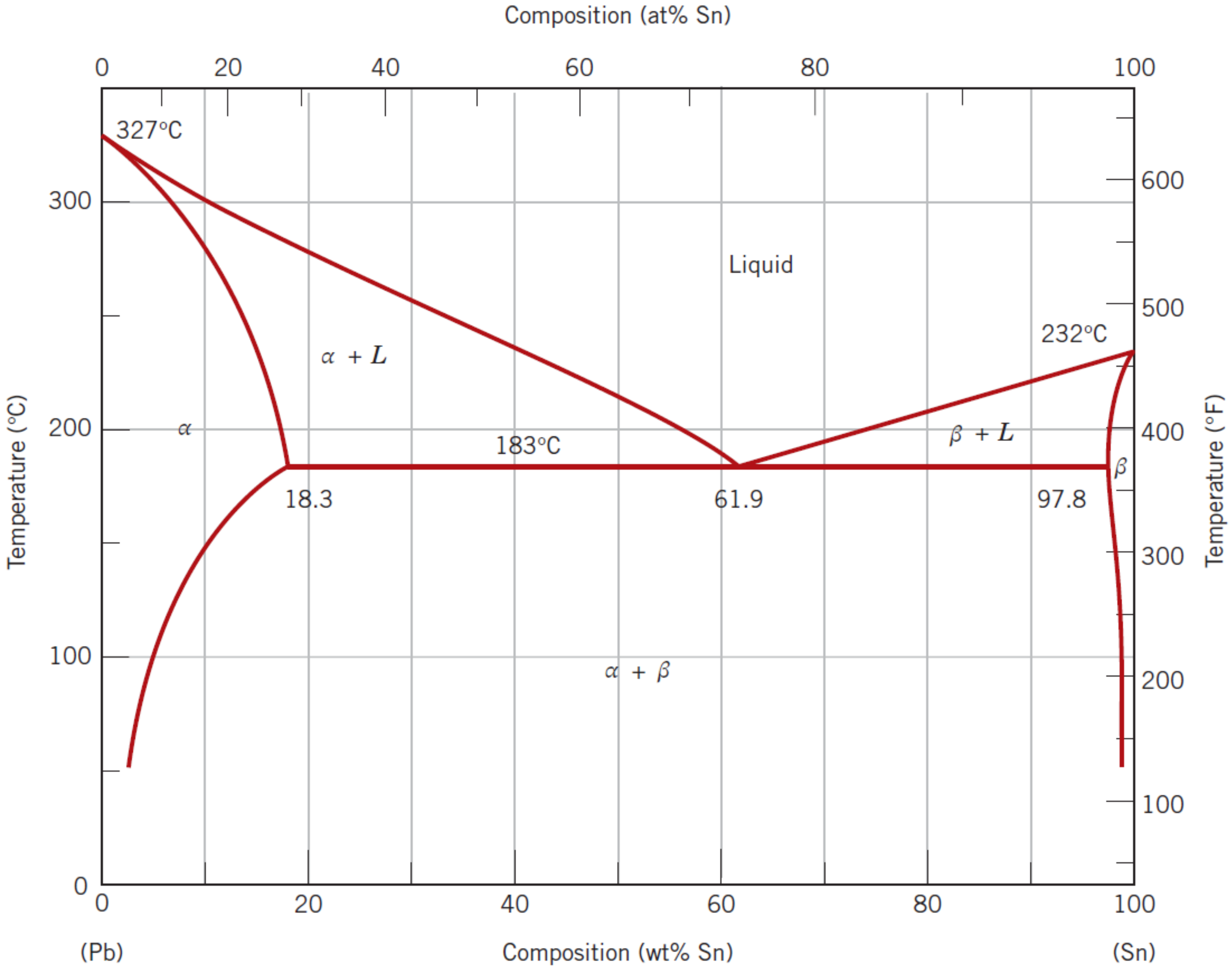
DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

Depending on composition, several different types of microstructures are possible for the slow cooling of alloys belonging to binary eutectic systems.

These possibilities will be considered in terms of the lead–tin phase diagram.

The first case is for compositions ranging between a pure component and the maximum solid solubility for that component at room temperature [20°C (70°F)].

For the lead–tin system, this includes lead-rich alloys containing between 0 and about 2 wt% Sn (for the α-phase solid solution) and also between approximately 99 wt% Sn and pure tin (for the β phase).



DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

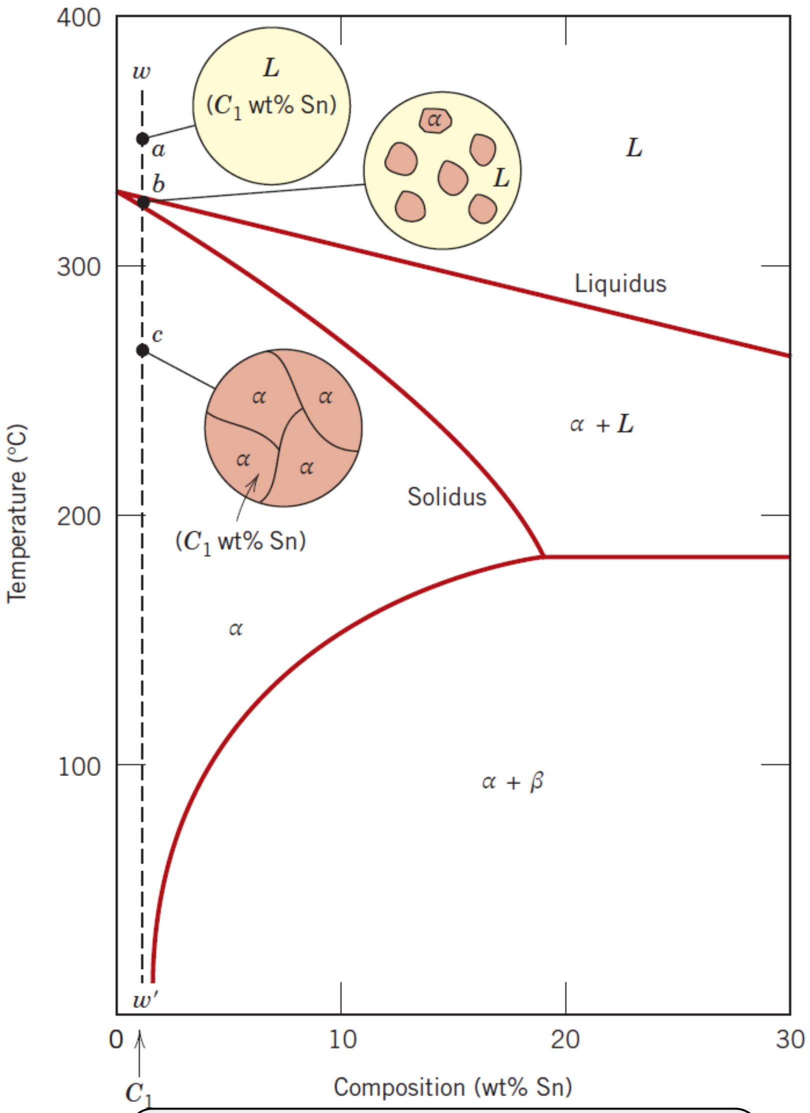
For example, consider an alloy of composition C_1 as it is slowly cooled from a temperature within the liquid-phase region, say, 350°C; this corresponds to moving down the dashed vertical line *ww′* in the figure.

The alloy remains totally liquid and of composition C_1 until we cross the liquidus line at approximately 330°C, at which time the solid α phase begins to form.

While passing through this narrow $\alpha + L$ phase region, solidification proceeds in the same manner as was described for the copper–nickel alloy in the preceding section—that is, with continued cooling, more of the solid α forms.

Furthermore, liquid- and solid-phase compositions are different, which follow along the liquidus and solidus phase boundaries, respectively.

Solidification reaches completion at the point where *ww′* crosses the solidus line.

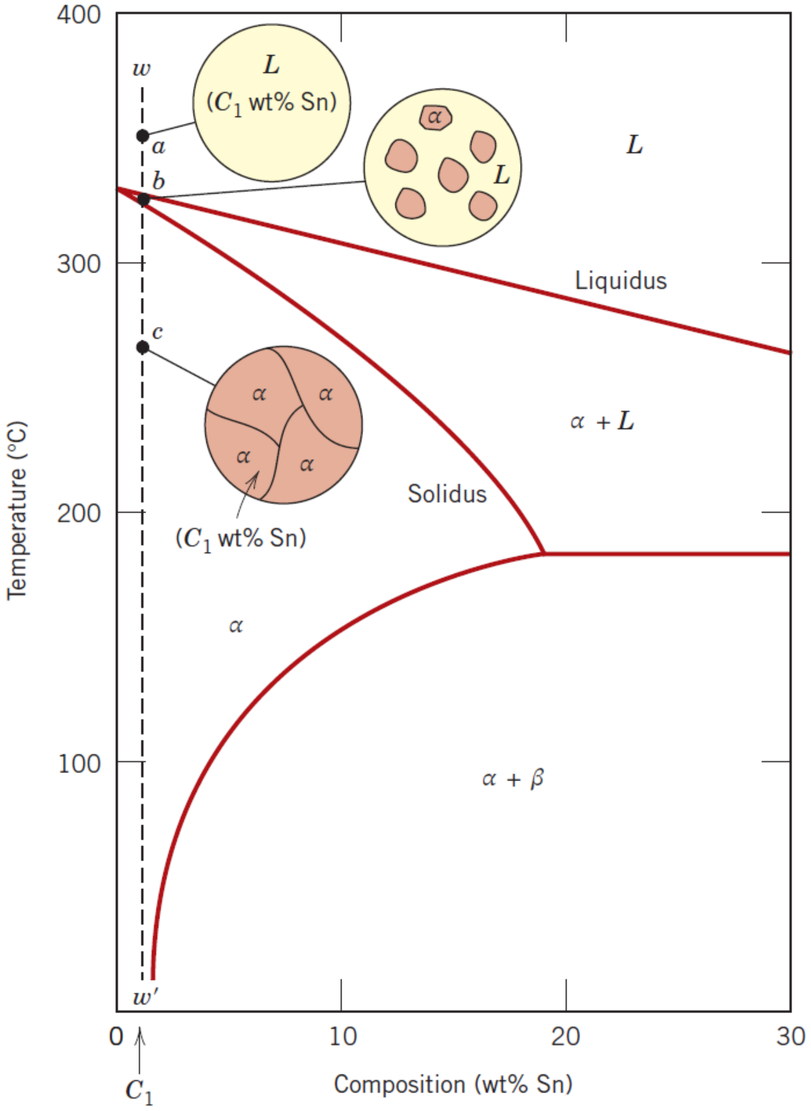


Applicable for alloys containing between 0 and about 2 wt% Sn.

DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

The resulting alloy is polycrystalline with a uniform composition of C_1, and no subsequent changes occur upon cooling to room temperature.

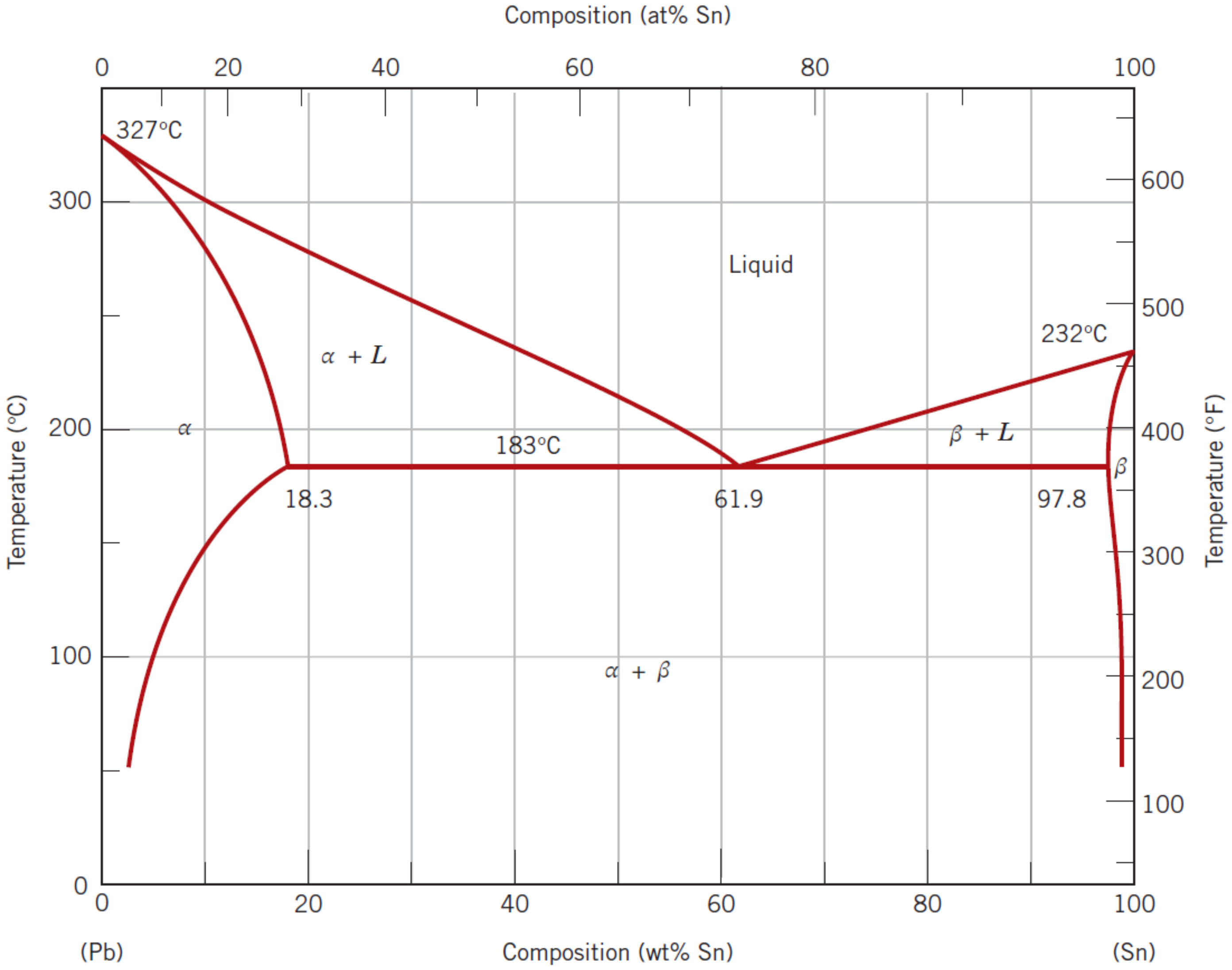
This microstructure is represented schematically by the inset at point *c*.



DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

The second case considered is for compositions that range between the room temperature solubility limit and the maximum solid solubility at the eutectic temperature.

For the lead–tin system, these compositions extend from about 2 to 18.3 wt% Sn (for lead-rich alloys) and from 97.8 to approximately 99 wt% Sn (for tin-rich alloys).



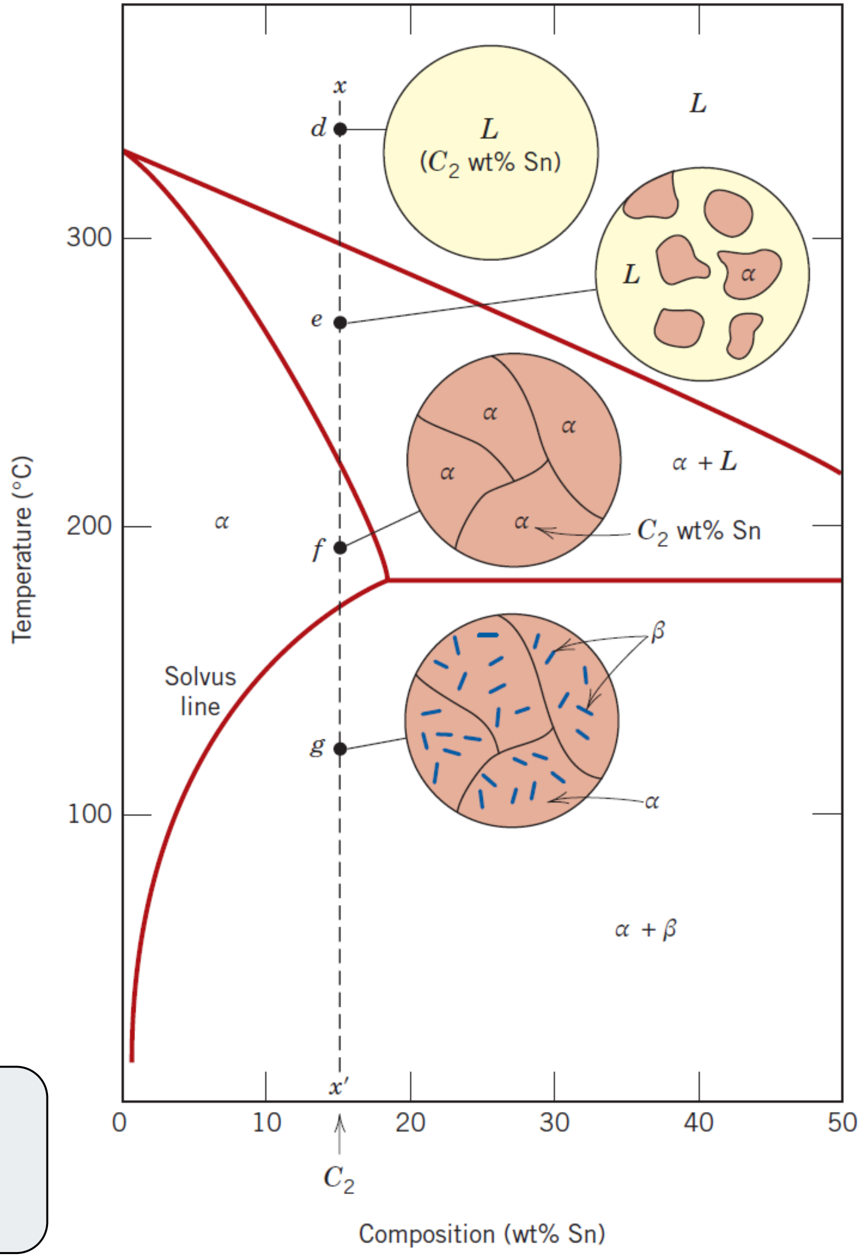
DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

Let us examine an alloy of composition C_2 as it is cooled along the vertical line *xx*′.

Down to the intersection of *xx*′ and the solvus line, changes that occur are similar to the previous case as we pass through the corresponding phase regions (as demonstrated by the insets at points *d*, *e*, and *f*). Just above the solvus intersection, point *f*, the microstructure consists of α grains of composition C_2.

Upon crossing the solvus line, the α solid solubility is exceeded, which results in the formation of small β-phase particles; these are indicated in the microstructure inset at point *g*.

With continued cooling, these particles grow in size because the mass fraction of the β phase increases slightly with decreasing temperature.



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

DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

The third case involves solidification of the eutectic composition, 61.9 wt% Sn (C_3 in The figure).

Consider an alloy having this composition that is cooled from a temperature within the liquid-phase region (e.g., 250°C) down the vertical line *yy′* .

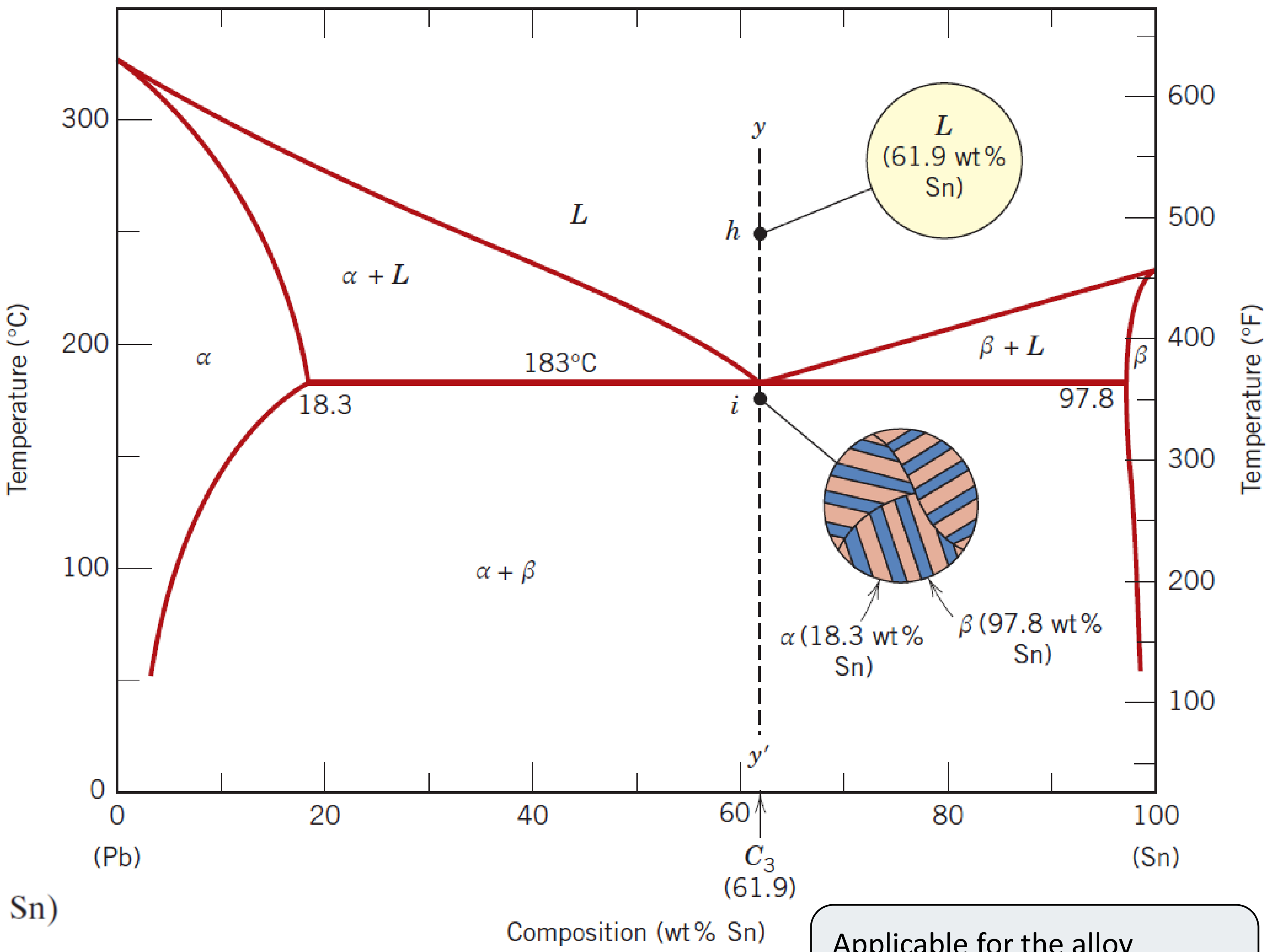
As the temperature is lowered, no changes occur until we reach the eutectic temperature, 183°C.

Upon crossing the eutectic isotherm, the liquid transforms into the two α and β phases.

This transformation may be represented by the reaction

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

in which the α- and β-phase compositions are dictated by the eutectic isotherm end points.



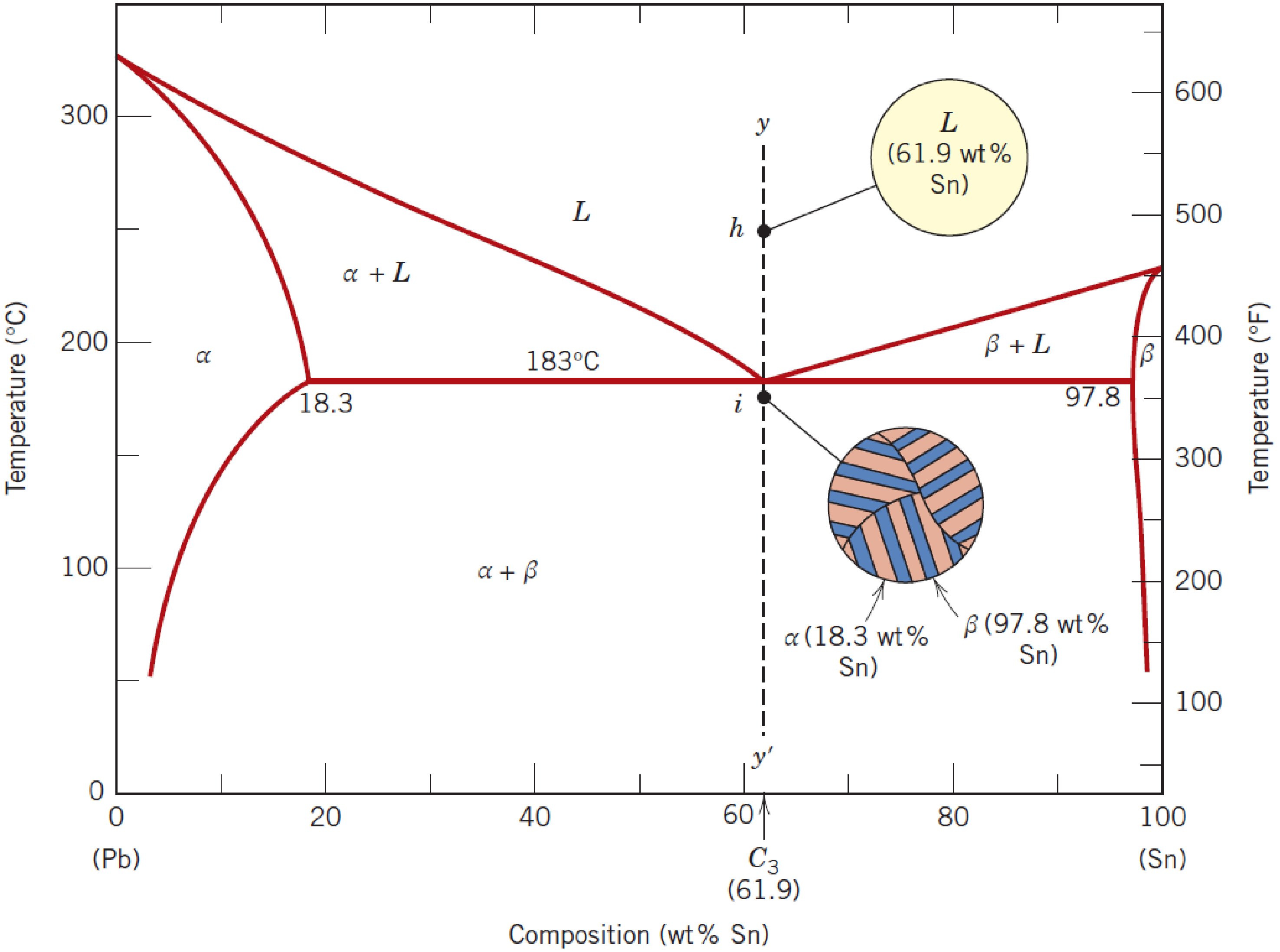
Applicable for the alloy containing 61.9 wt% Sn only.

DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

During this transformation, there must be a redistribution of the lead and tin components because the α and β phases have different compositions, neither of which is the same as that of the liquid.

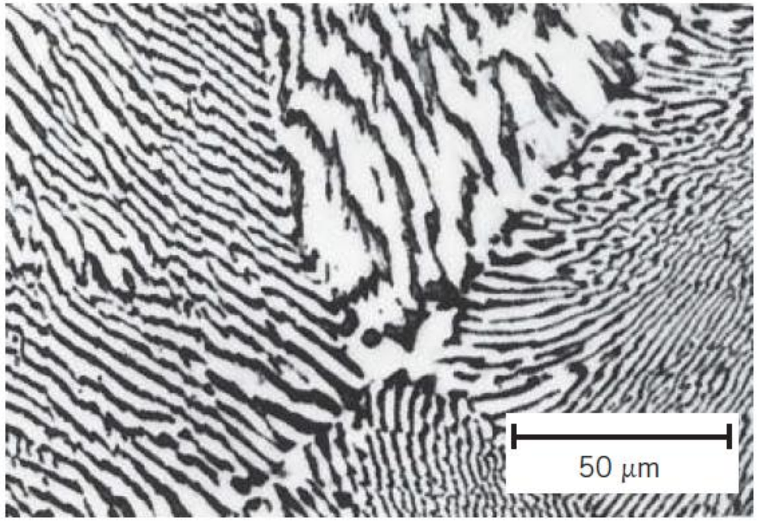
This redistribution is accomplished by atomic diffusion. The microstructure of the solid that results from this transformation consists of alternating layers (sometimes called *lamellae*) of the α and β phases that form simultaneously during the transformation.

This microstructure, represented schematically, point *i*, is called a **eutectic structure** and is characteristic of this reaction.



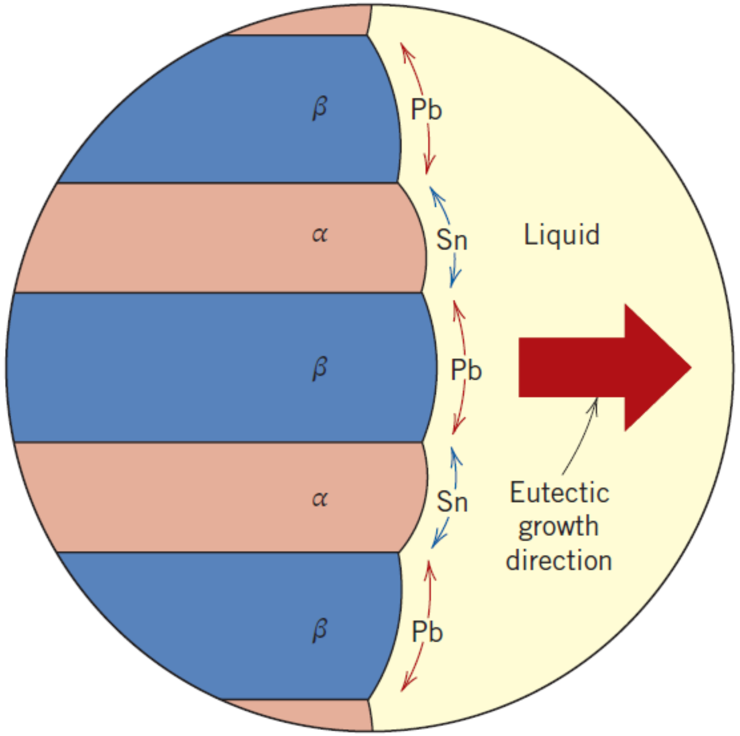
DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

A photomicrograph of this structure for the lead–tin eutectic is shown.



Subsequent cooling of the alloy from just below the eutectic to room temperature results in only minor microstructural alterations.

The microstructural change that accompanies this eutectic transformation is represented schematically below, which shows the α–β layered eutectic growing into and replacing the liquid phase.



The process of the redistribution of lead and tin occurs by diffusion in the liquid just ahead of the eutectic–liquid interface.

The arrows indicate the directions of diffusion of lead and tin atoms; 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.

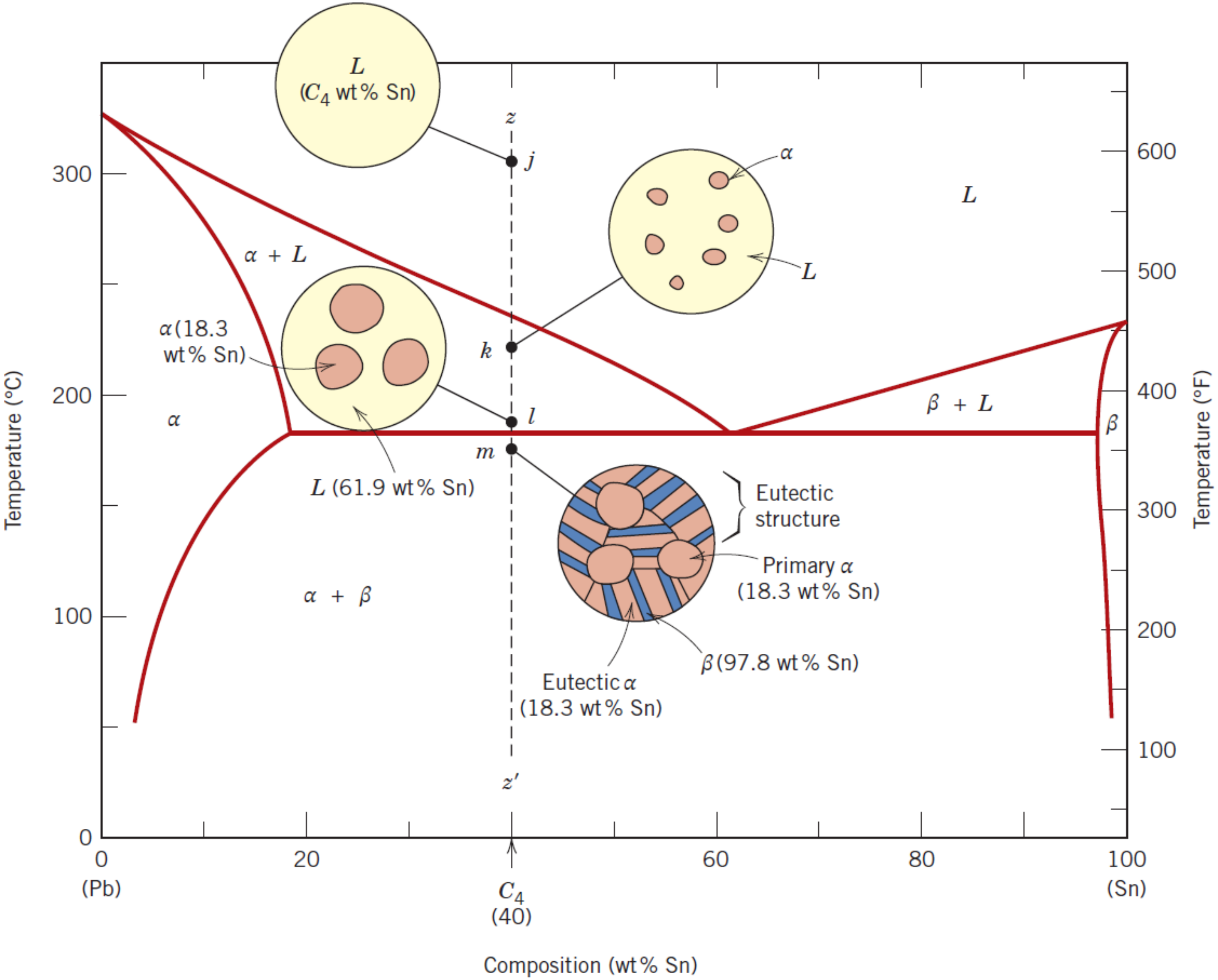
The eutectic structure forms in these alternating layers because, for this lamellar configuration, atomic diffusion of lead and tin need only occur over relatively short distance s.

DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

The fourth and final microstructural case for this system includes all compositions other than the eutectic that, when cooled, cross the eutectic isotherm.

Consider, for example, the composition C_4, which lies to the left of the eutectic; as the temperature is lowered, we move down the line zz', beginning at point j.

The microstructural development between points j and l is similar to that for the second case, such that just prior to crossing the eutectic isotherm (point l), the α and liquid phases are present with compositions of approximately 18.3 and 61.9 wt% Sn, respectively, as determined from the appropriate tie line.



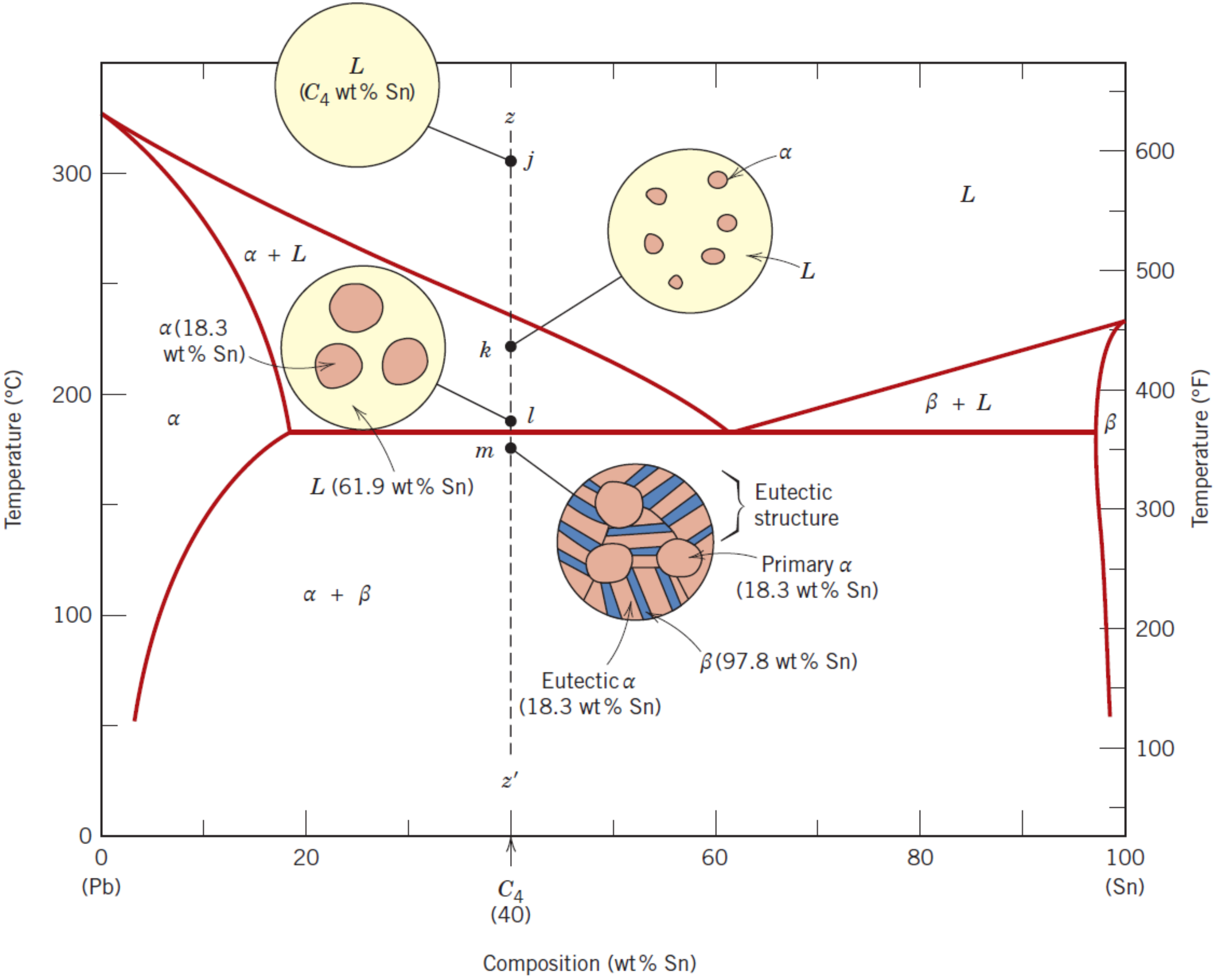
DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

As the temperature is lowered to just below the eutectic, the liquid phase, which is of the eutectic composition, transforms into the eutectic structure (i.e., alternating *α* and *β* lamellae); insignificant changes occur with the *α* phase that formed during cooling through the *α* + *L* region.

This microstructure is represented schematically by the inset at point *m*.

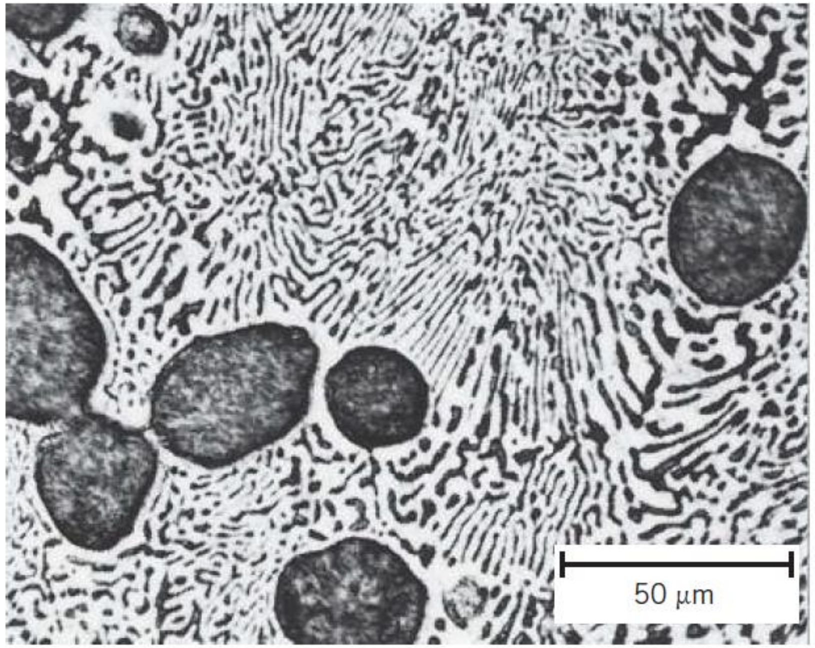
Thus, the *α* phase is present both in the eutectic structure and also as the phase that formed while cooling through the *α* + *L* phase field.

To distinguish one *α* from the other, that which resides in the eutectic structure is called **eutectic** *α*, whereas the other that formed prior to crossing the eutectic isotherm is termed **primary** *α*; both are labelled.

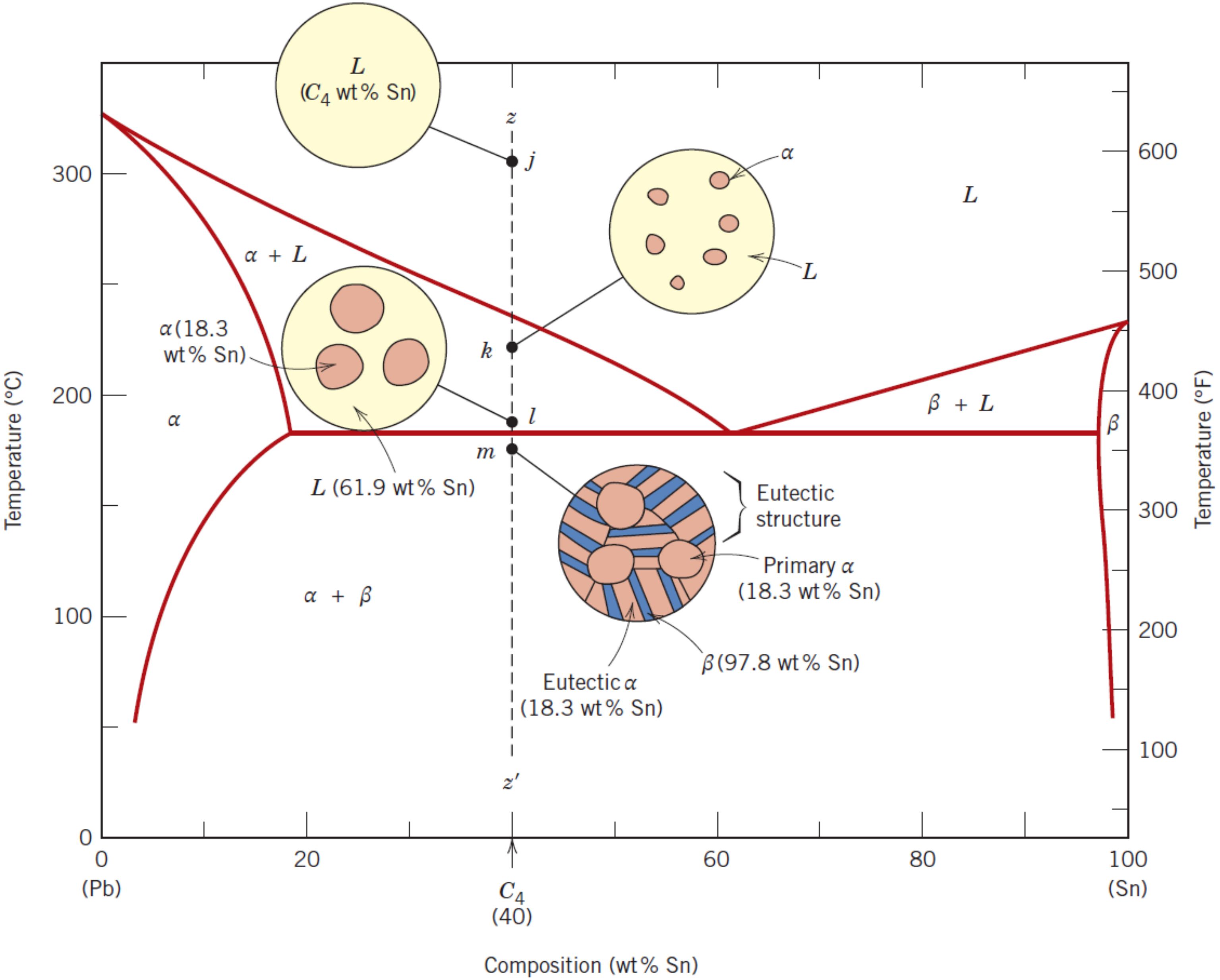


DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

The photomicrograph is of a lead–tin alloy in which both primary *α* and eutectic structures are shown.



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×.

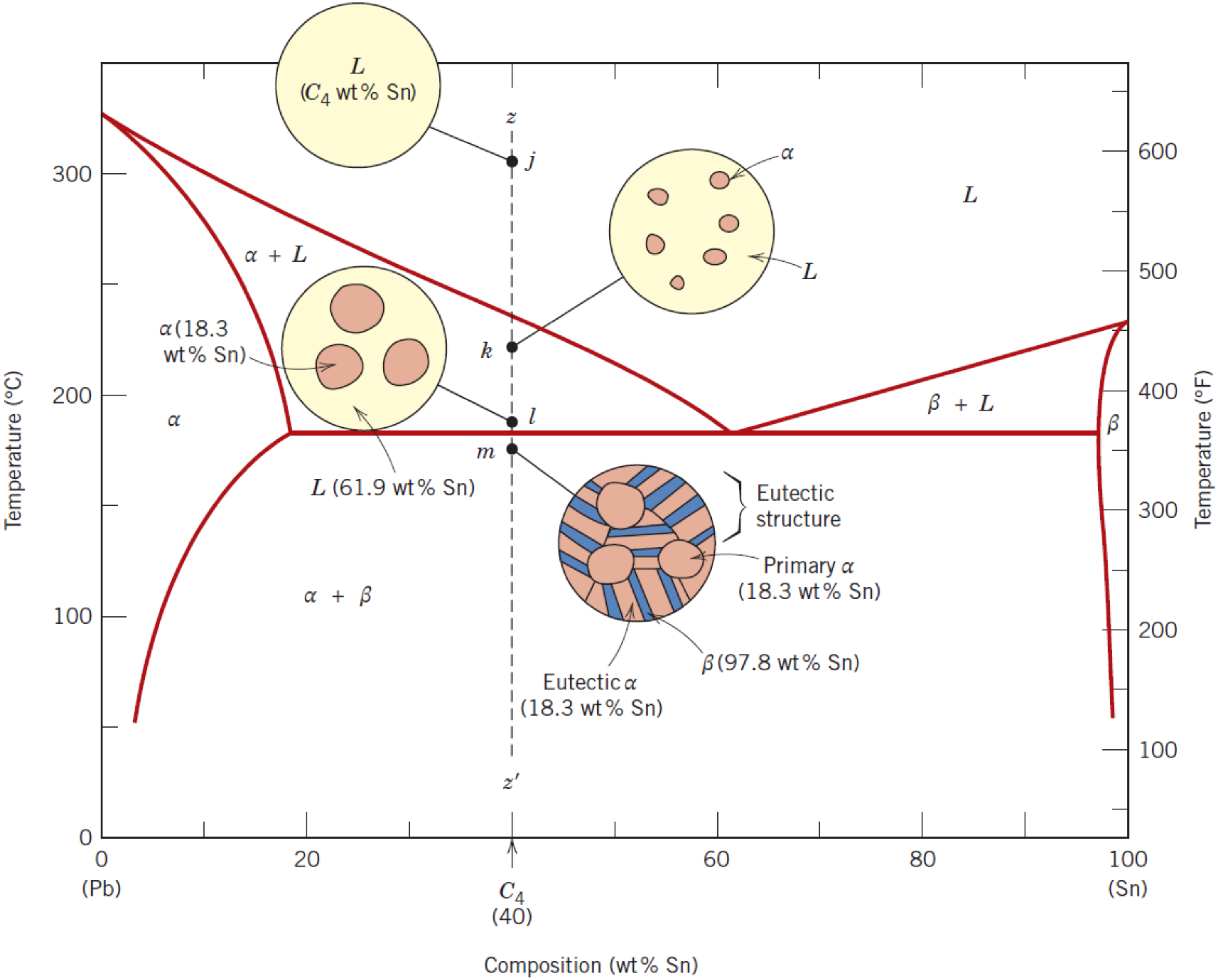


DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

In dealing with microstructures, it is sometimes convenient to use the term **microconstituent**—an element of the microstructure having an identifiable and characteristic structure.

For example, in the point *m* inset, there are two microconstituents—primary *α* and the eutectic structure.

Thus, the eutectic structure is a microconstituent even though it is a mixture of two phases because it has a distinct lamellar structure with a fixed ratio of the two phases.

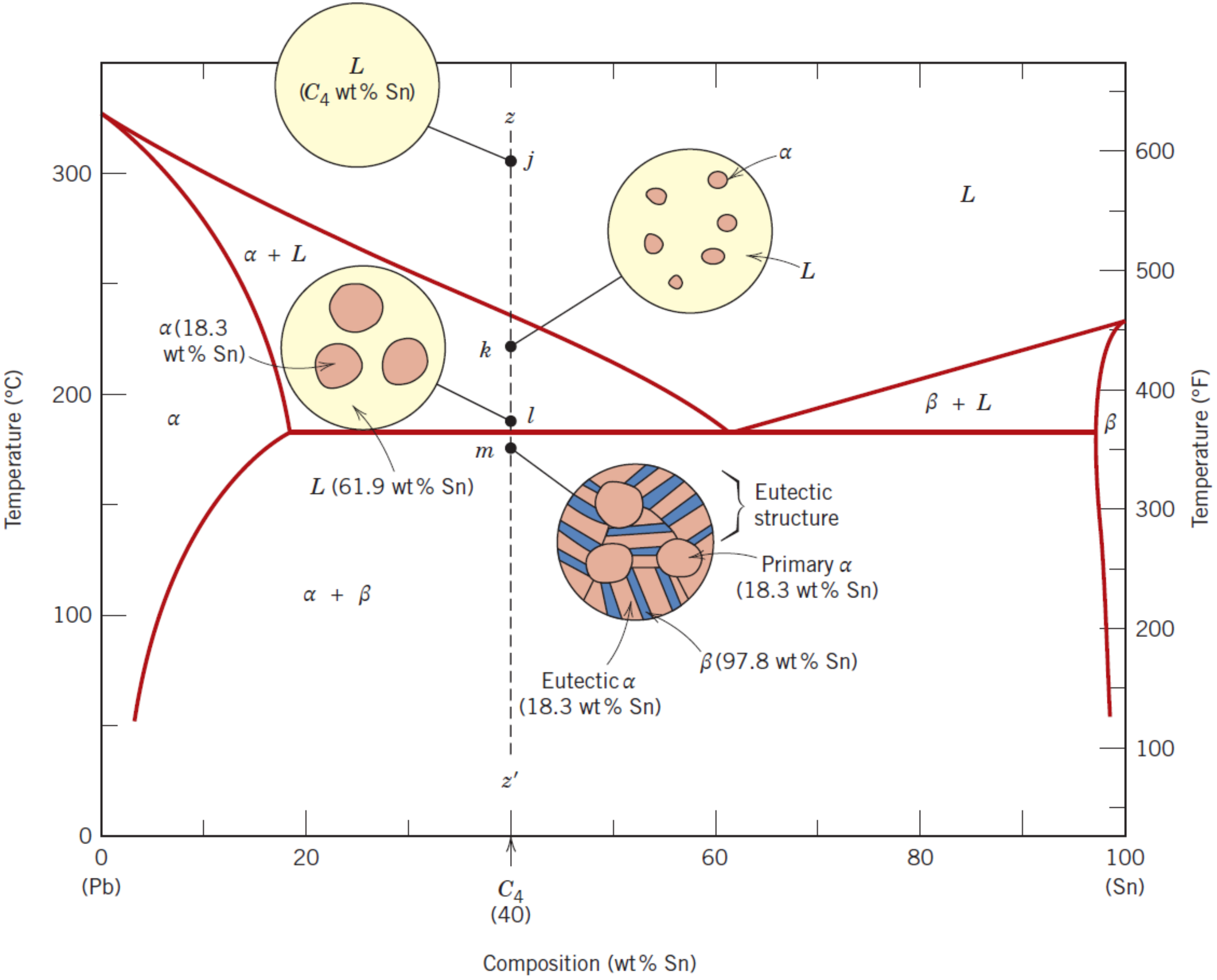


DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

It is possible to compute the relative amounts of both eutectic and primary α microconstituents.

Because the eutectic microconstituent always forms from the liquid having the eutectic composition, this microconstituent may be assumed to have a composition of 61.9 wt% Sn.

Hence, the lever rule is applied using a tie line between the α−($\alpha + \beta$) phase boundary (18.3 wt% Sn) and the eutectic composition.



DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

For example, consider the alloy of composition C_4'.

The fraction of the eutectic microconstituent W_e is just the same as the fraction of liquid W_L from which it transforms, or:

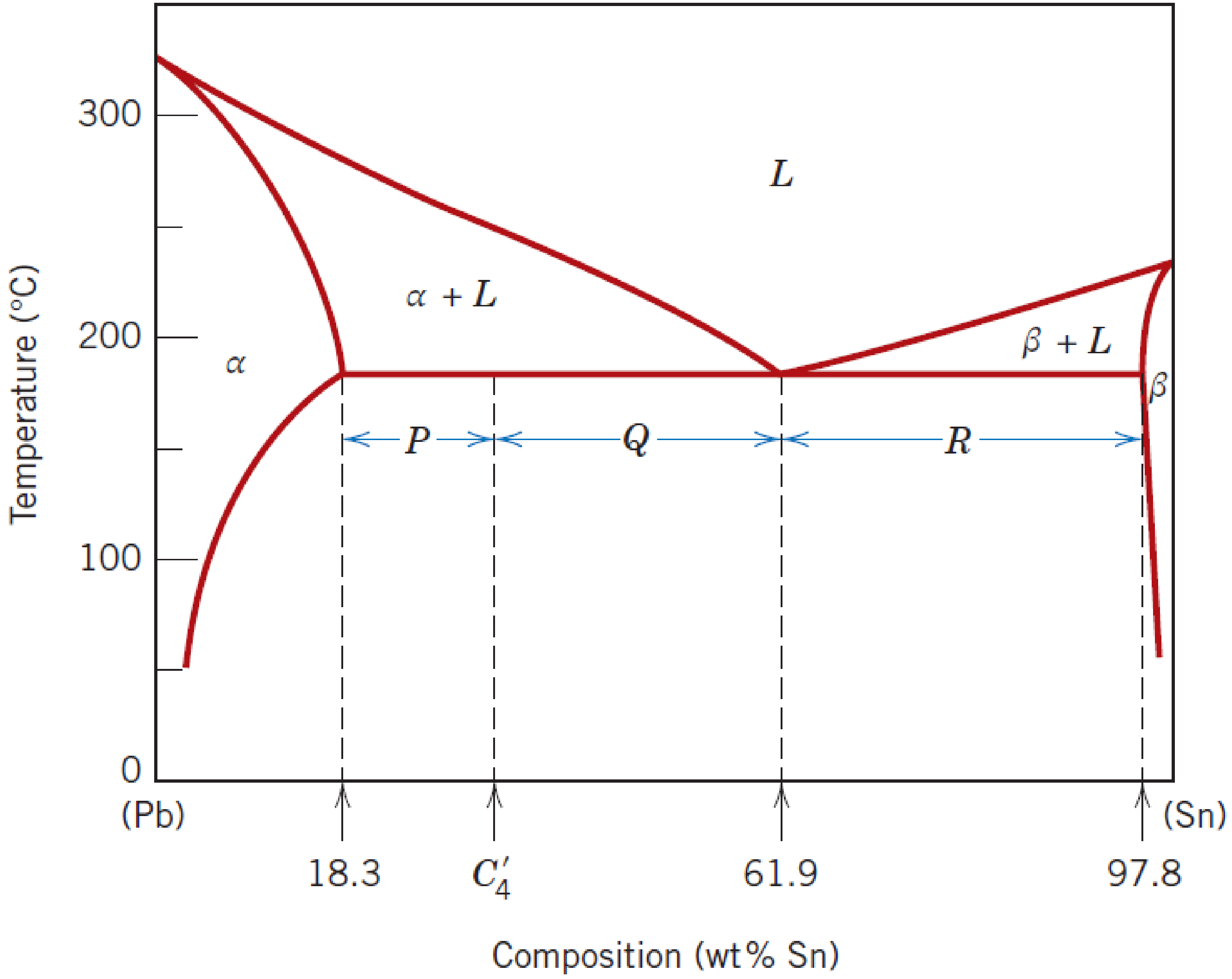
$$W_e = W_L = \frac{P}{P+Q}$$

$$= \frac{C_4' - 18.3}{61.9 - 18.3} = \frac{C_4' - 18.3}{43.6}$$

Furthermore, the fraction of primary α, $W_{\alpha'}$, is just the fraction of the α phase that existed prior to the eutectic transformation or,

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

$$= \frac{61.9 - C_4'}{61.9 - 18.3} = \frac{61.9 - C_4'}{43.6}$$



DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

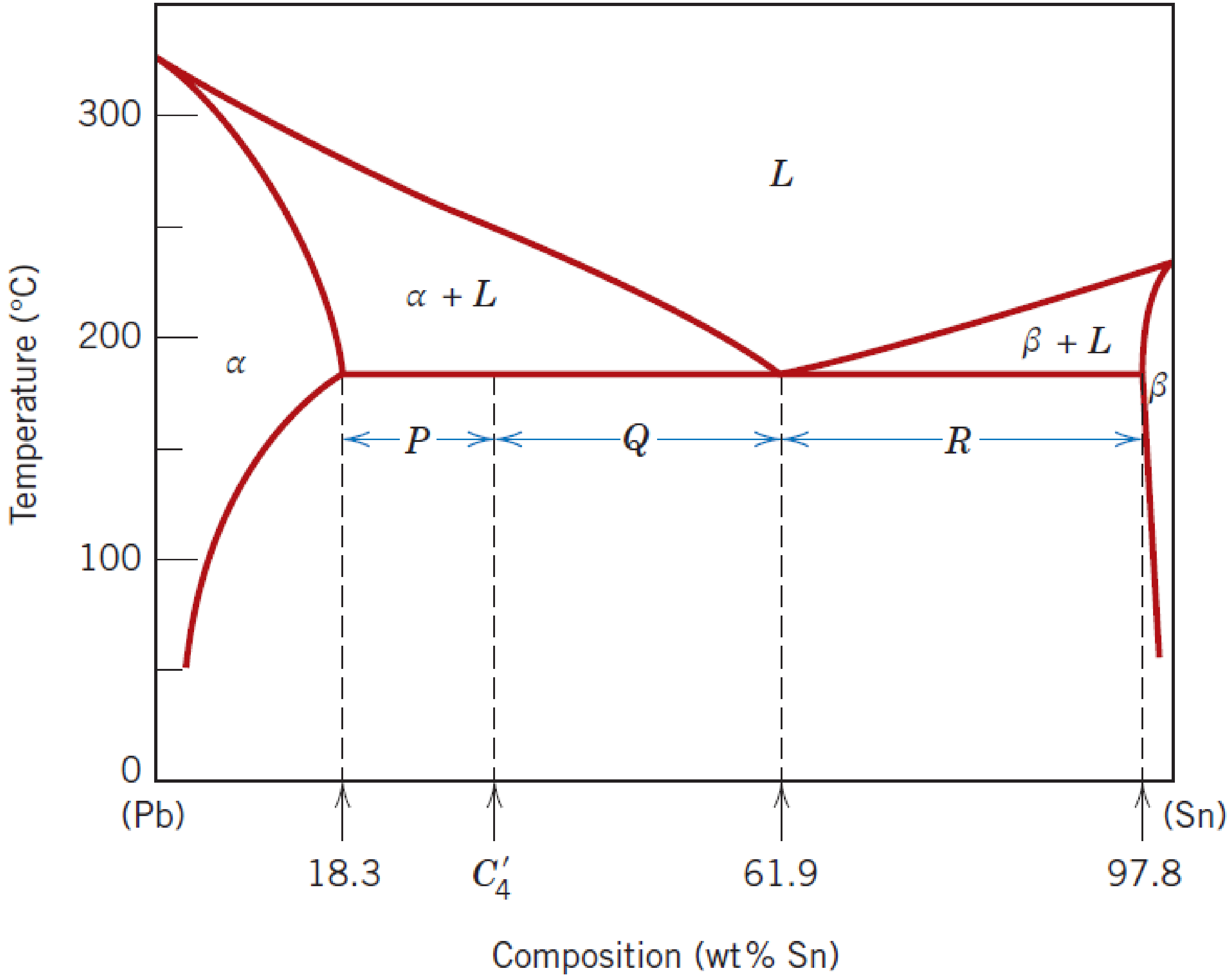
The fractions of *total* α, W_α (both eutectic and primary), and also of total β, $W\beta$, are determined by use of the lever rule and a tie line that extends *entirely across the* α + β *phase field*.

Again, for an alloy having composition $C_{4'}$,

$$W_\alpha = \frac{Q+R}{P+Q+R} = \frac{97.8 - C_4'}{97.8 - 18.3} = \frac{97.8 - C_4'}{79.5}$$

and

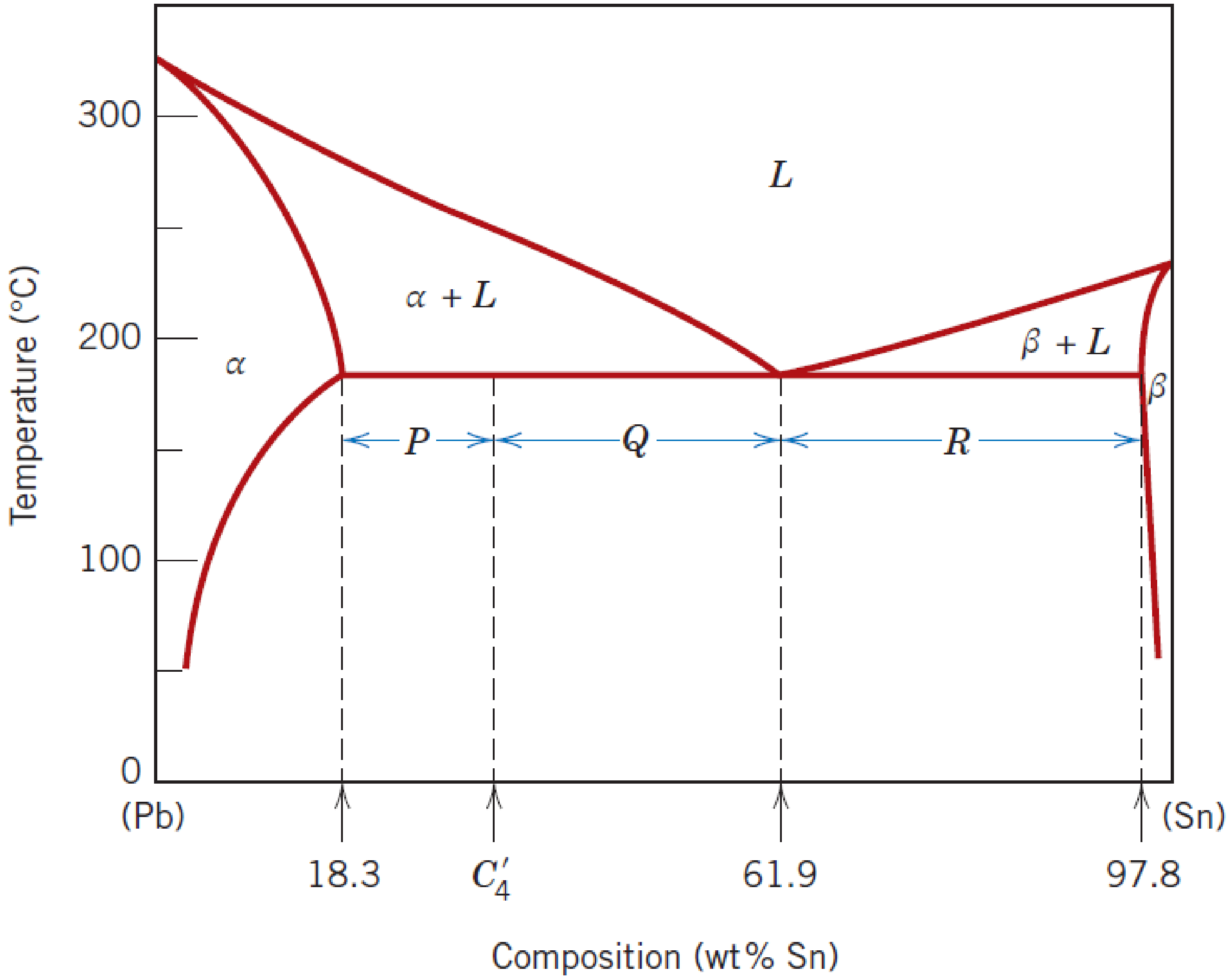
$$W_\beta = \frac{P}{P+Q+R} = \frac{C_4' - 18.3}{97.8 - 18.3} = \frac{C_4' - 18.3}{79.5}$$



DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

Analogous transformations and microstructures result for alloys having compositions to the right of the eutectic (i.e., between 61.9 and 97.8 wt% Sn).

However, below the eutectic temperature, the microstructure will consist of the eutectic and primary β microconstituents because, upon cooling from the liquid, we pass through the β + liquid phase field.

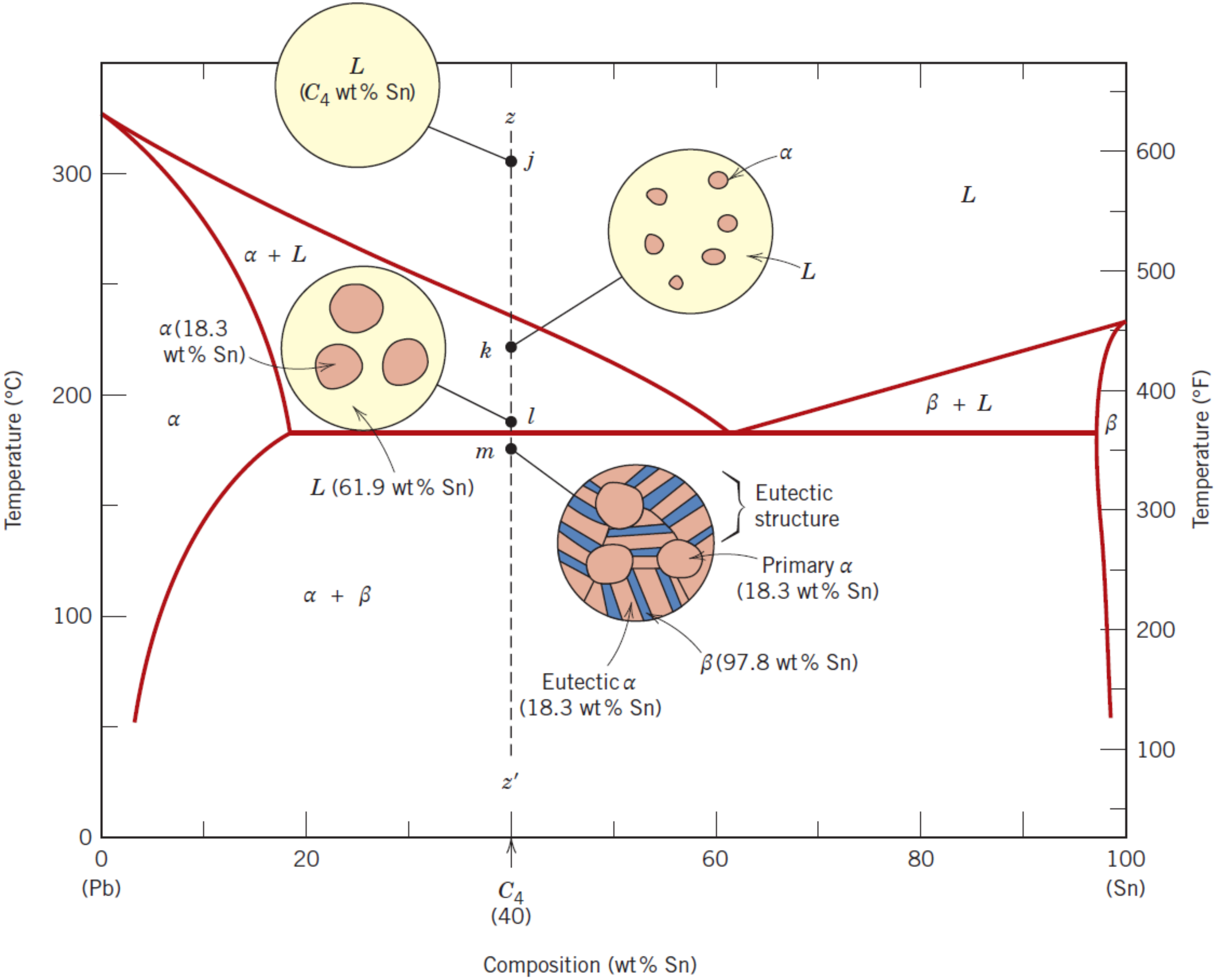


DEVELOPMENT OF MICROSTRUCTURE IN EUTECTIC ALLOYS

When, for the fourth case represented in here, conditions of equilibrium are not maintained while passing through the α (or β) + liquid phase region, the following consequences will be realized for the microstructure upon crossing the eutectic isotherm:

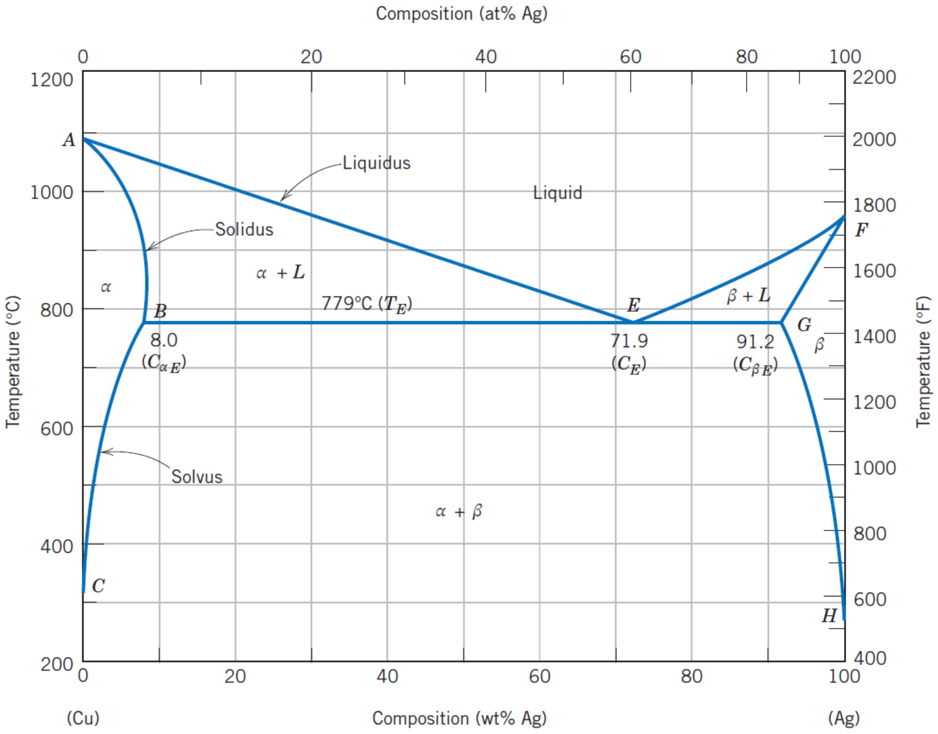
(1) grains of the primary microconstituent will be cored, that is, have a nonuniform distribution of solute across the grains; and

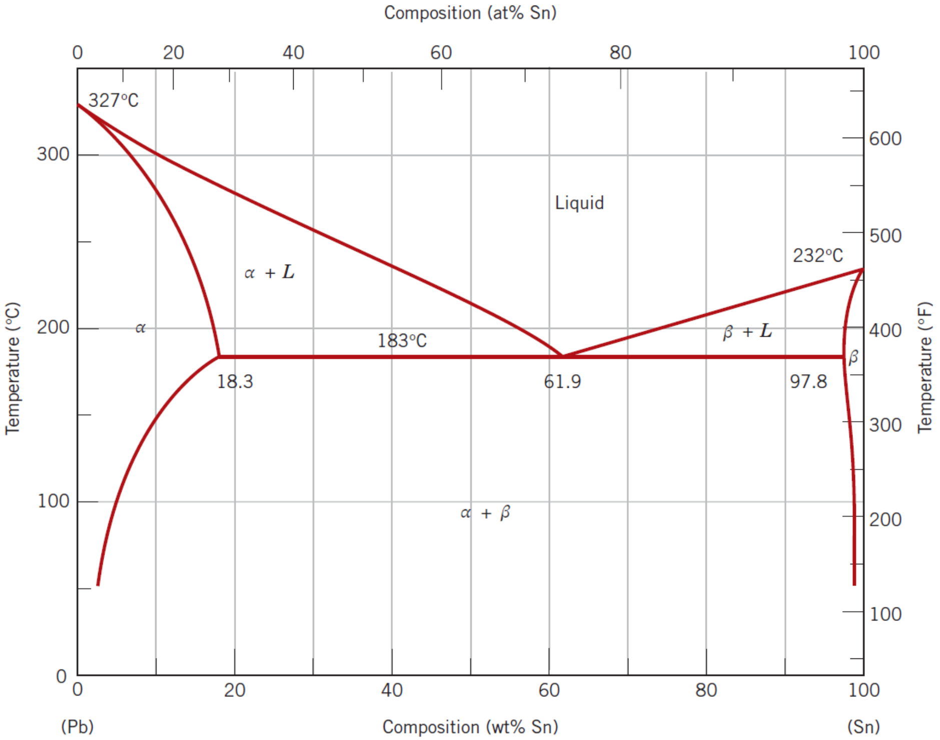
(2) the fraction of the eutectic microconstituent formed will be greater than for the equilibrium situation.



EQUILIBRIUM DIAGRAMS HAVING INTERMEDIATE PHASES OR COMPOUNDS

The isomorphous and eutectic phase diagrams discussed thus far are relatively simple, but those for many binary alloy systems are much more complex. The eutectic copper–silver and lead–tin phase diagrams have only two solid phases, α and β; these are sometimes termed **terminal solid solutions** because they exist over composition ranges near the concentration extremes of the phase diagram.

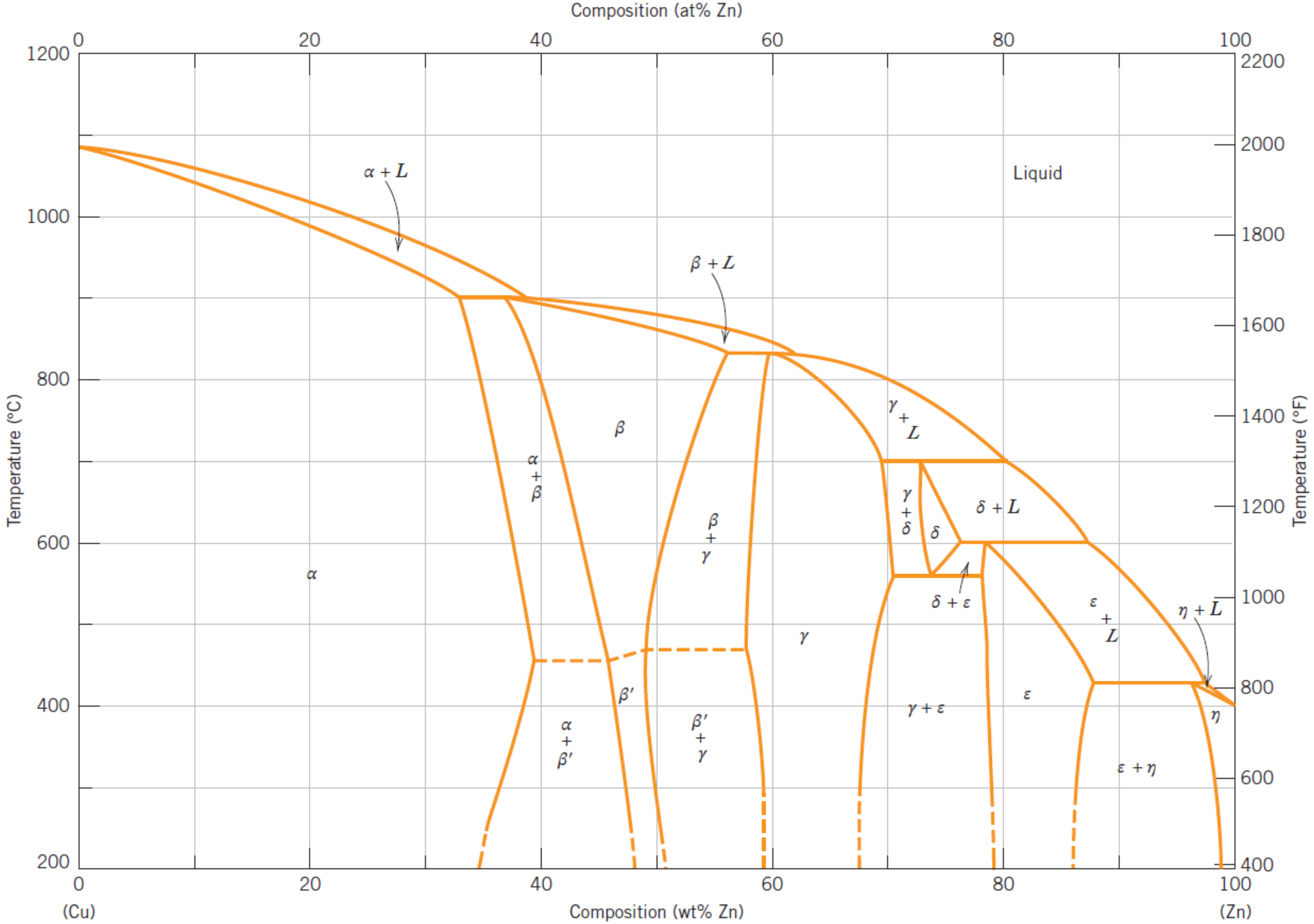




EQUILIBRIUM DIAGRAMS HAVING INTERMEDIATE PHASES OR COMPOUNDS

For other alloy systems, **intermediate solid solutions** (or *intermediate phases*) may be found at other than the two composition extremes. Such is the case for the copper–zinc system.

Its phase diagram may at first appear formidable because there are some invariant reactions similar to the eutectic that have not yet been discussed.

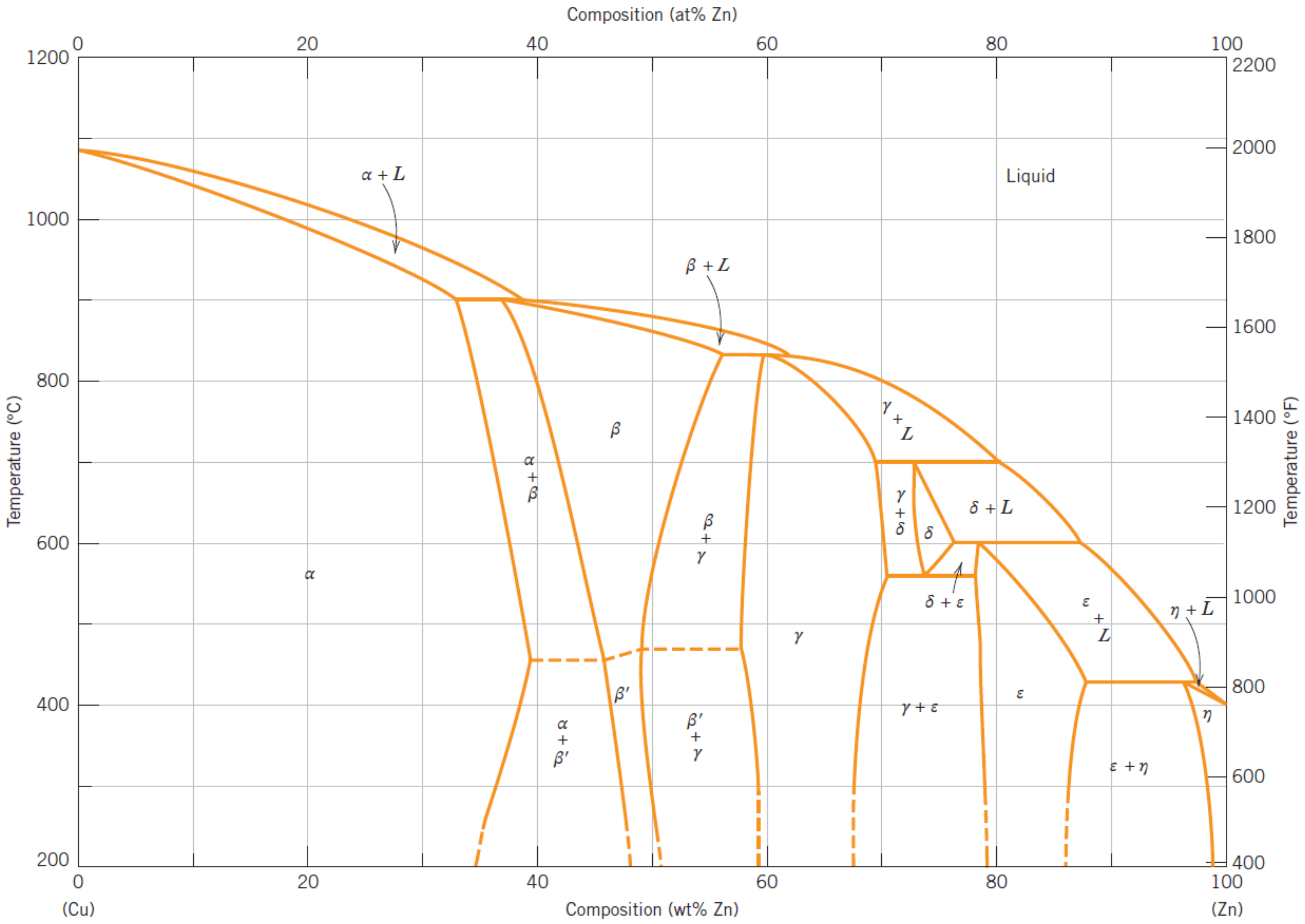


EQUILIBRIUM DIAGRAMS HAVING INTERMEDIATE PHASES OR COMPOUNDS

In addition, there are six different solid solutions—two terminal (α and η) and four intermediate (β, γ, δ, and ε). (The β' phase is termed an *ordered solid solution*, one in which the copper and zinc atoms are situated in a specific and ordered arrangement within each unit cell.)

Some phase boundary lines near the bottom of the figure are dashed to indicate that their positions have not been exactly determined.

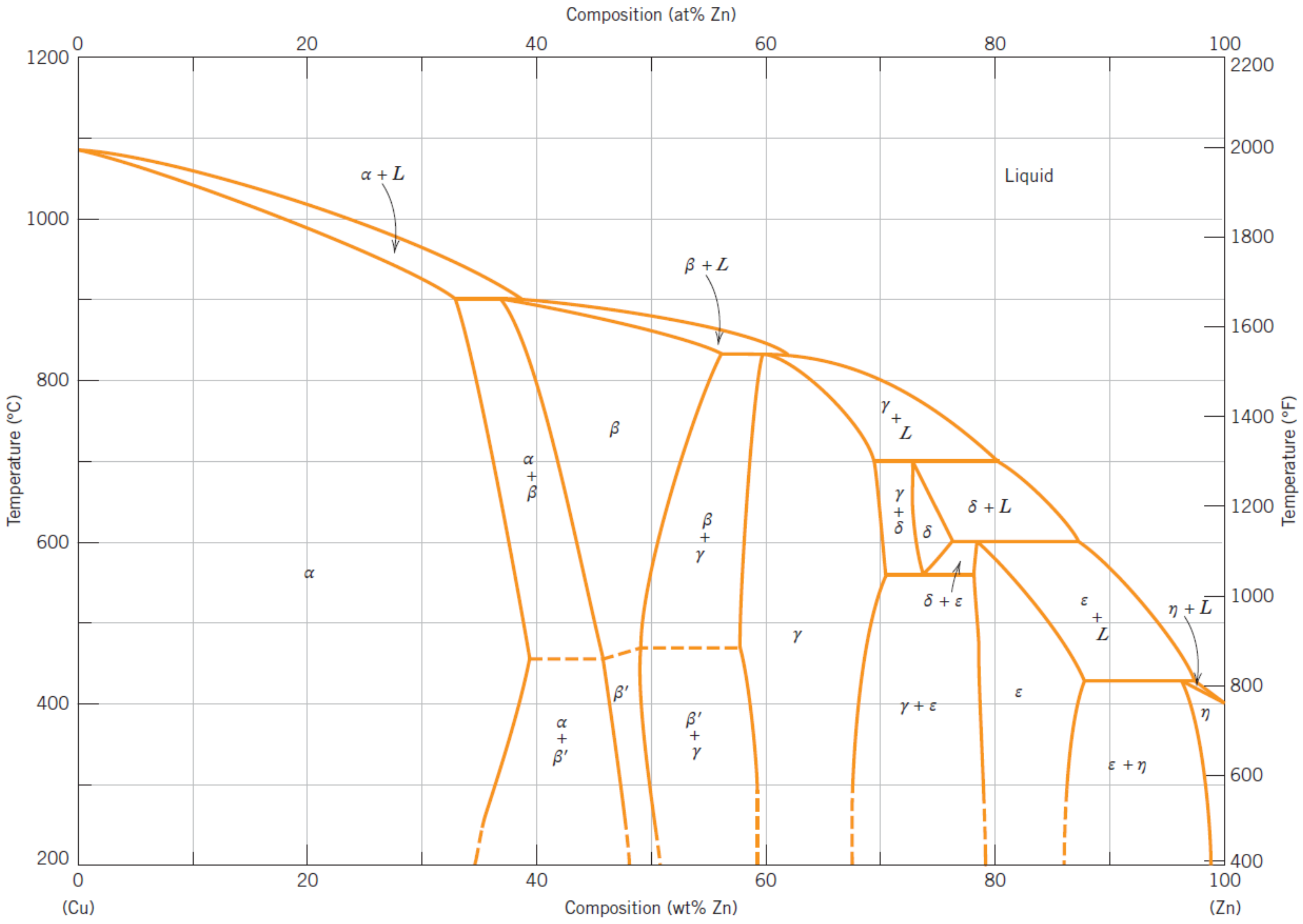
The reason for this is that at low temperatures, diffusion rates are very slow, and inordinately long times are required to attain equilibrium.



EQUILIBRIUM DIAGRAMS HAVING INTERMEDIATE PHASES OR COMPOUNDS

Again, only single- and two-phase regions are found on the diagram, and the same rules outlined earlier are used to compute phase compositions and relative amounts.

The commercial brasses are copper–rich copper–zinc alloys; for example, cartridge brass has a composition of 70 wt% Cu–30 wt% Zn and a microstructure consisting of a single α phase.

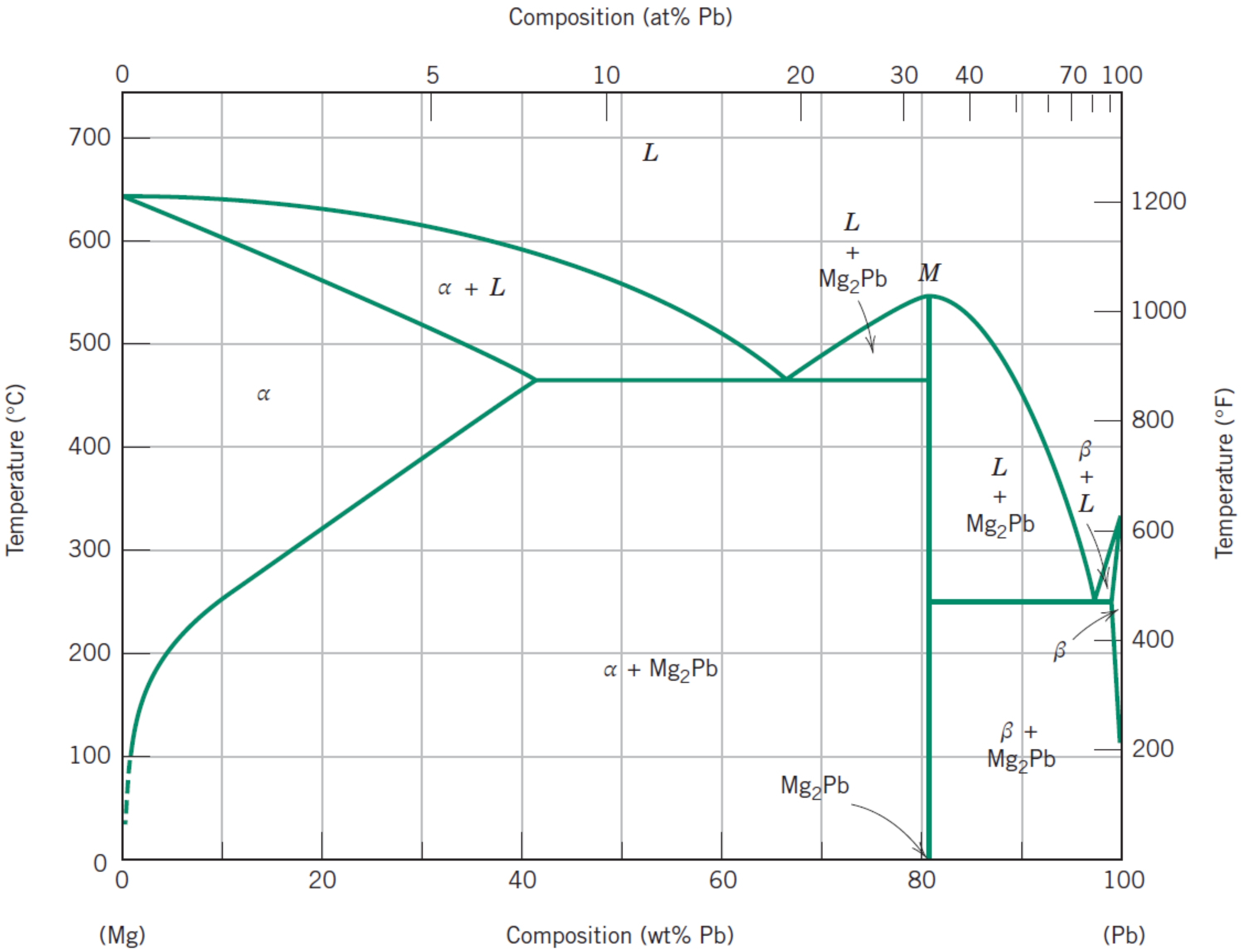


EQUILIBRIUM DIAGRAMS HAVING INTERMEDIATE PHASES OR COMPOUNDS

For some systems, discrete intermediate compounds rather than solid solutions may be found on the phase diagram, and these compounds have distinct chemical formulas; for metal–metal systems, they are called **intermetallic compounds.**

For example, consider the magnesium–lead system.

The compound Mg_2Pb has a composition of 19 wt% Mg–81 wt% Pb (33 at% Pb) and is represented as a vertical line on the diagram, rather than as a phase region of finite width; hence, Mg_2Pb can exist by itself only at this precise composition.

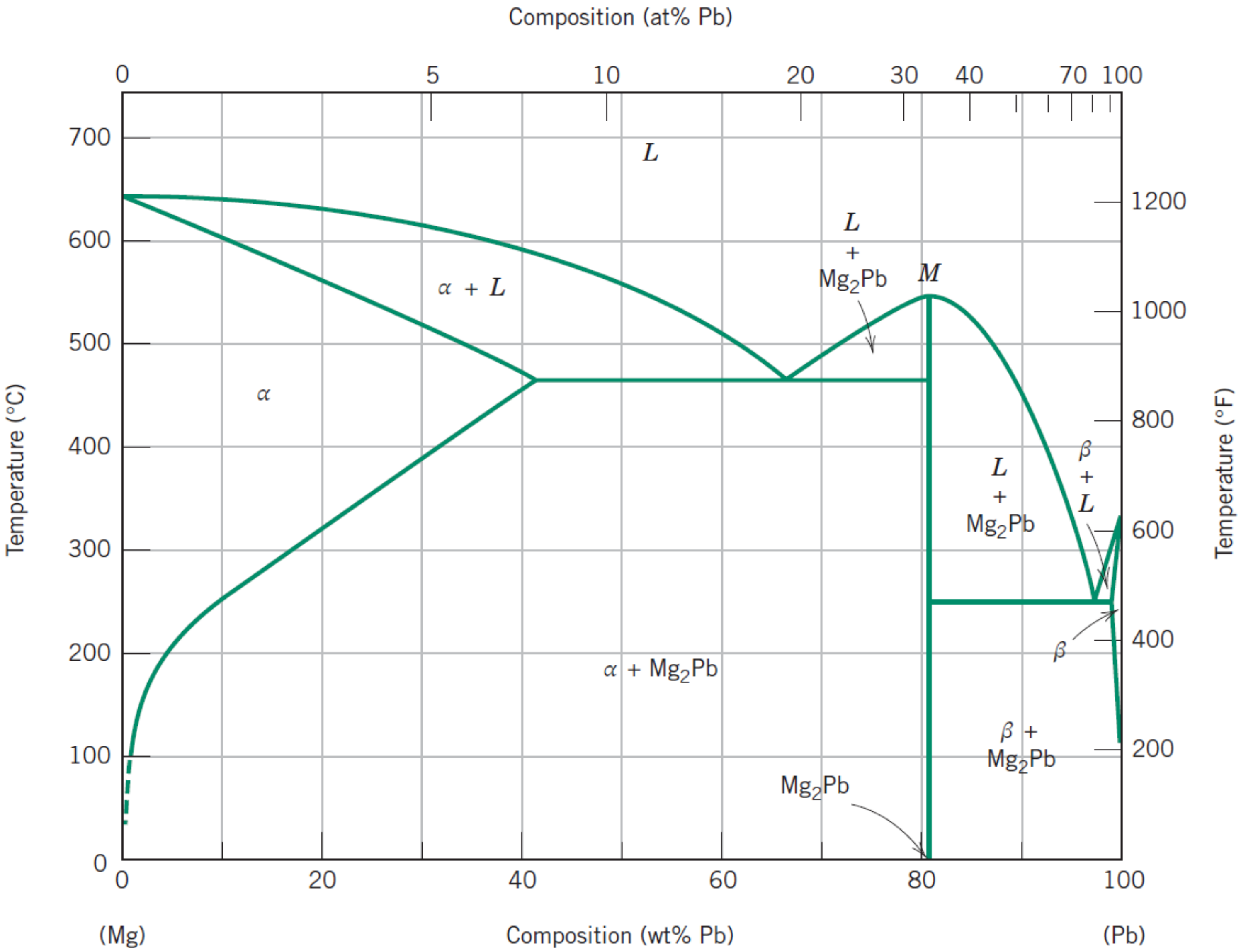


EQUILIBRIUM DIAGRAMS HAVING INTERMEDIATE PHASES OR COMPOUNDS

Several other characteristics are worth noting for this magnesium–lead system. First, the compound Mg_2Pb melts at approximately 550°C (1020°F), as indicated by point *M* in.

Also, the solubility of lead in magnesium is rather extensive, as indicated by the relatively large composition span for the α-phase field.

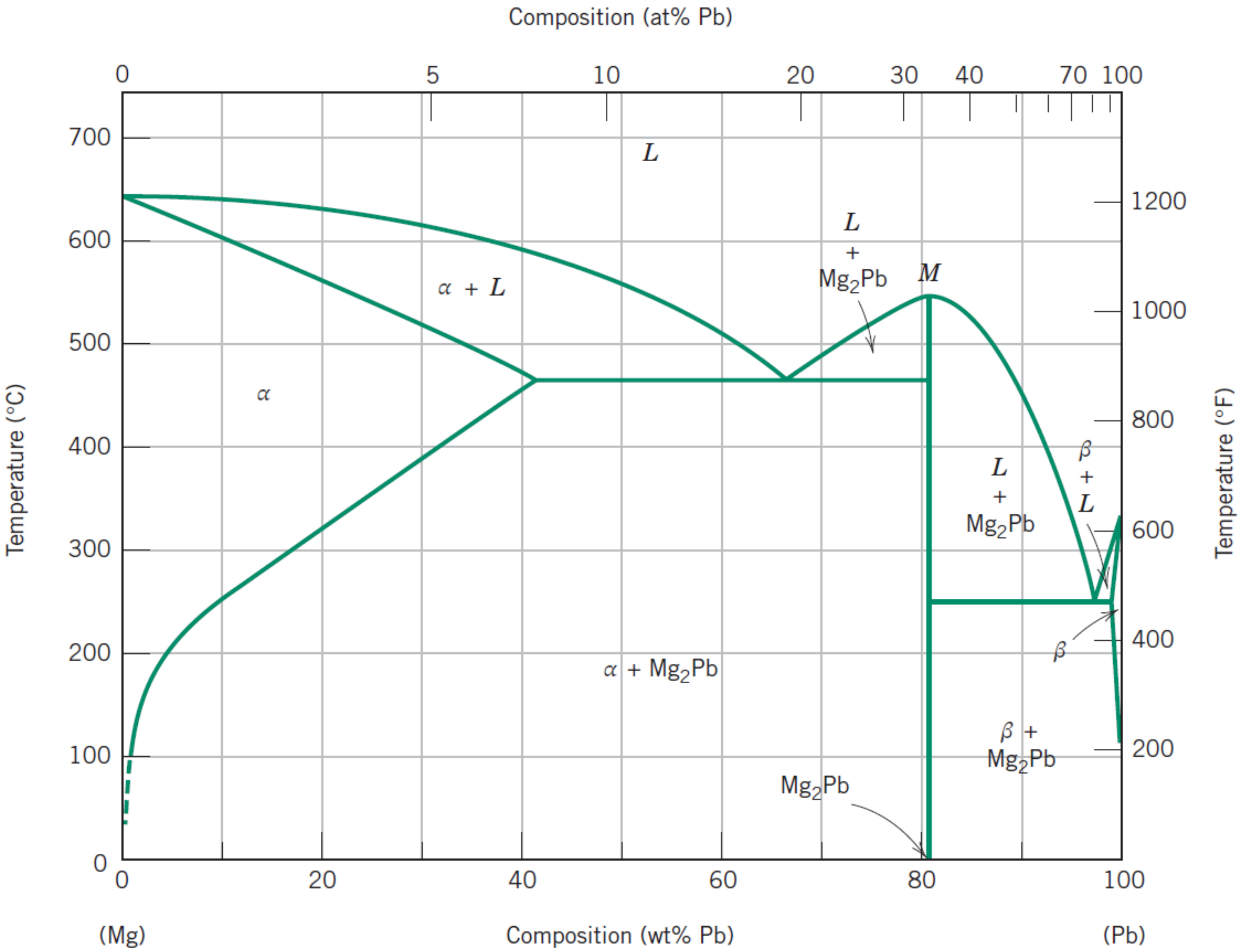
However, the solubility of magnesium in lead is extremely limited. This is evident from the very narrow β terminal solid-solution region on the right, or lead-rich, side of the diagram.



EQUILIBRIUM DIAGRAMS HAVING INTERMEDIATE PHASES OR COMPOUNDS

Finally, this phase diagram may be thought of as two simple eutectic diagrams joined back to back, one for the Mg–Mg_2Pb system and the other for Mg_2Pb–Pb; as such, the compound Mg_2Pb is really considered to be a component.

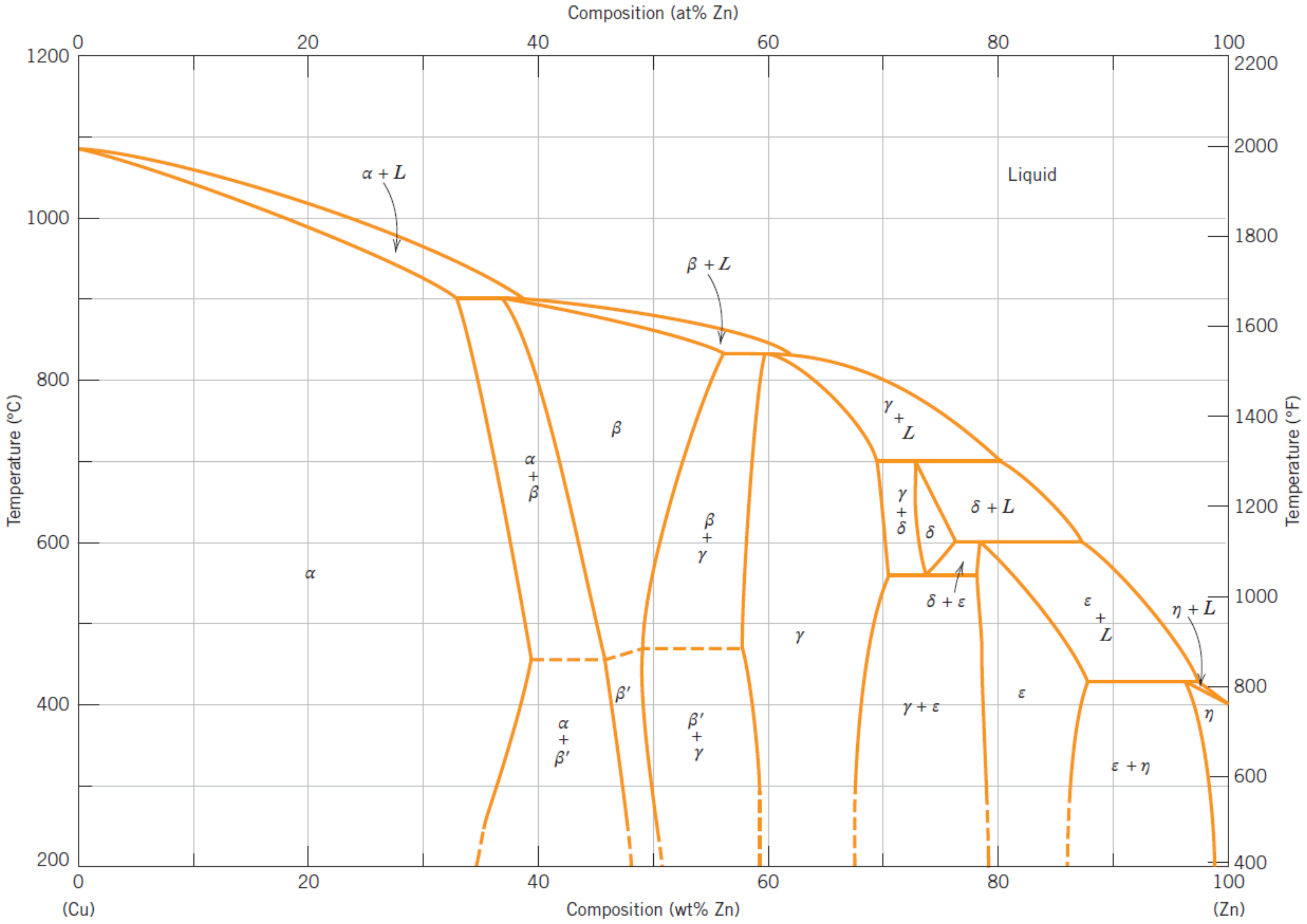
This separation of complex phase diagrams into smaller-component units may simplify them and expedite their interpretation.



EUTECTOID AND PERITECTIC REACTIONS

In addition to the eutectic, other invariant reactions involving three different phases are found for some alloy systems.

One of these occurs for the copper–zinc system at 560°C (1040°F) and 74 wt% Zn–26 wt% Cu.



EUTECTOID AND PERITECTIC REACTIONS

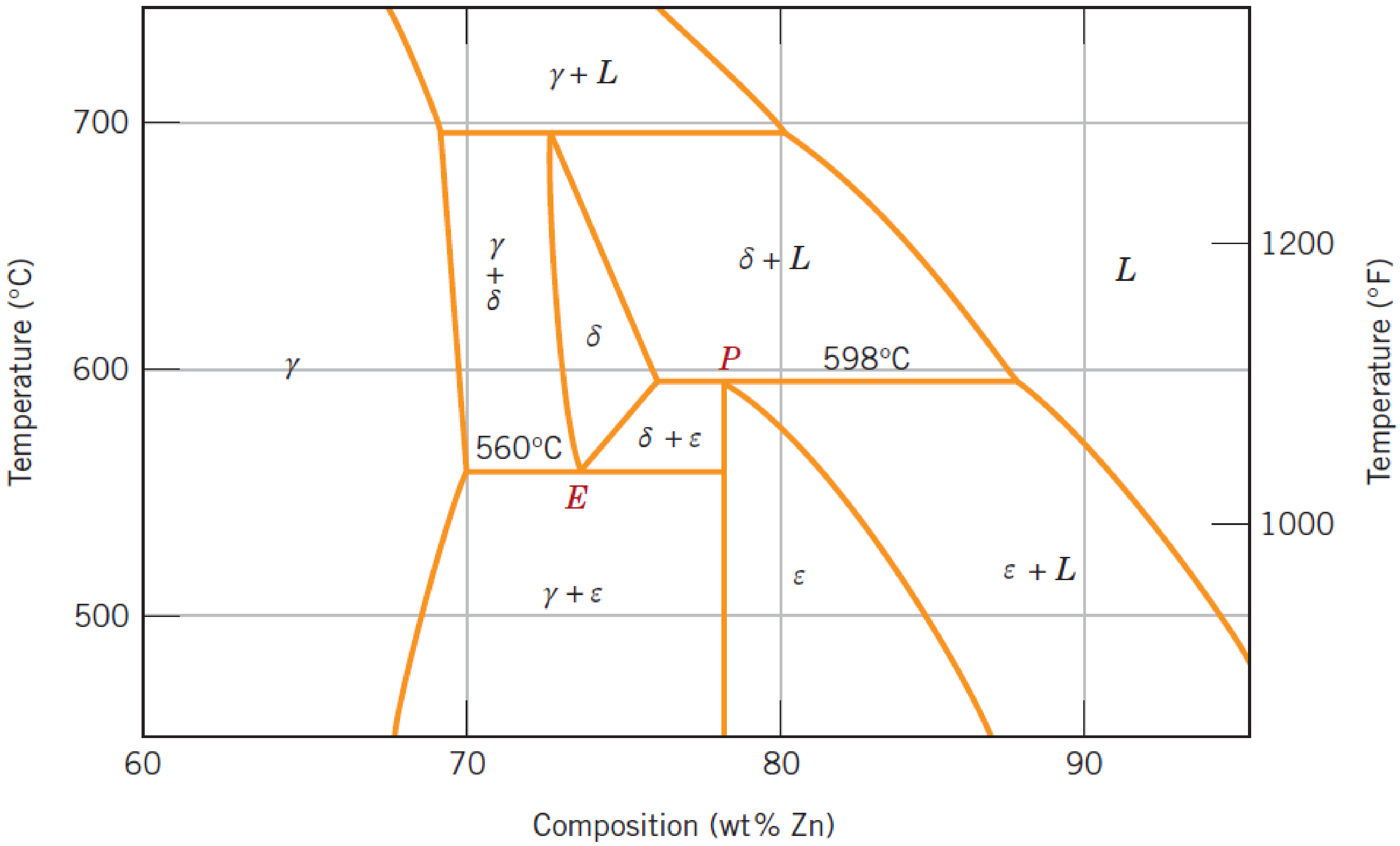
A portion of the phase diagram in this vicinity is enlarged.

Upon cooling, a solid δ phase transforms into two other solid phases (γ and ε) according to the reaction

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

The low-temperature solid phase may be an intermediate solid solution (e.g., ε in the preceding reaction), or it may be a terminal solid solution.

One of the latter peritectics exists at about 97 wt% Zn and 435°C (815°F), where the η phase, when heated, transforms into ε and liquid phases.



Three other peritectics are found for the Cu–Zn system, the reactions of which involve β, δ, and γ intermediate solid solutions as the low-temperature phases that transform upon heating.

CONGRUENT PHASE TRANSFORMATIONS

Phase transformations may be classified according to whether there is any change in composition for the phases involved.

Those for which there are no compositional alterations are said to be **congruent transformations.**

Conversely, for *incongruent transformations*, at least one of the phases experiences a change in composition.

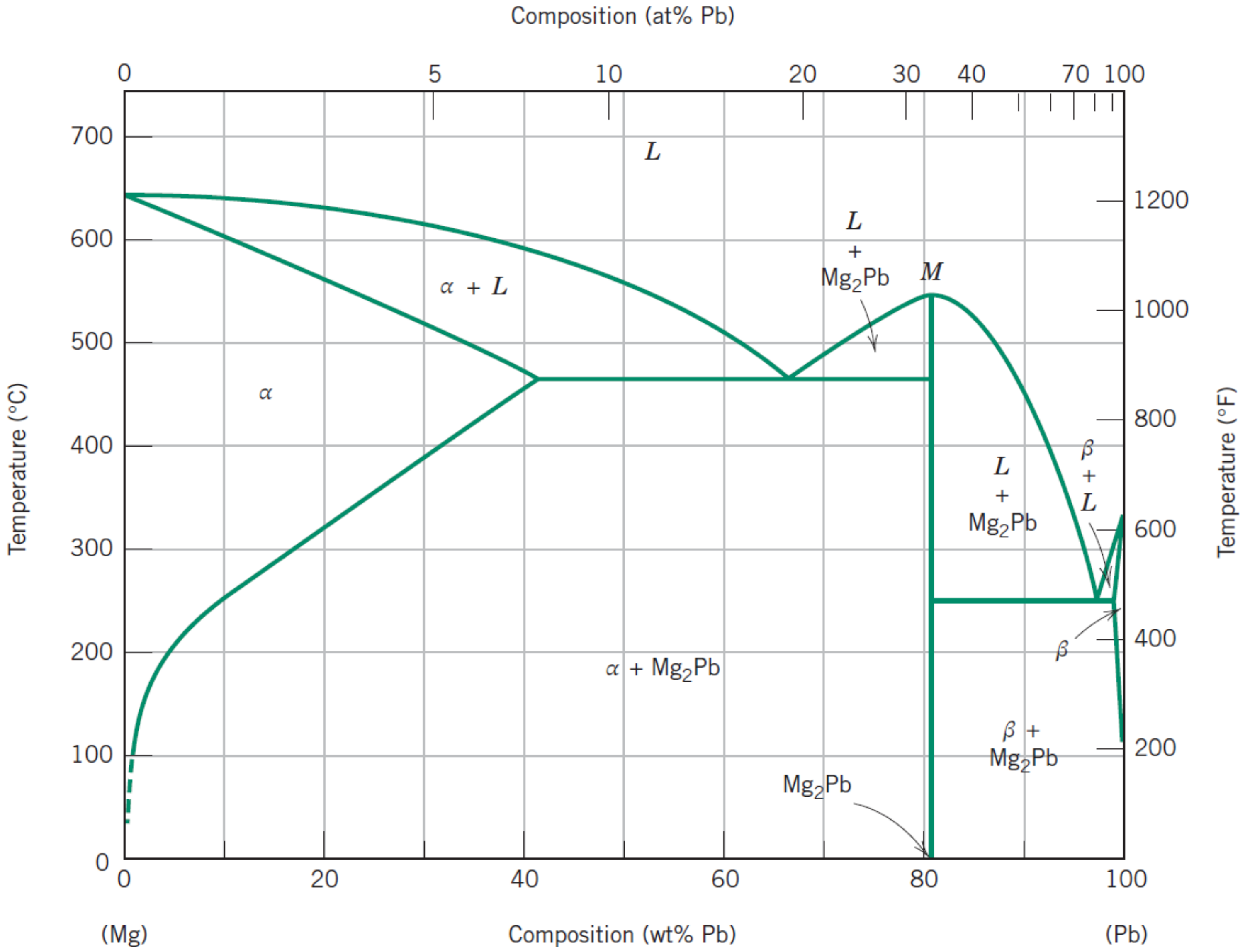
Examples of congruent transformations include allotropic transformations and melting of pure materials.

Eutectic and eutectoid reactions, as well as the melting of an alloy that belongs to an isomorphous system, all represent incongruent transformations.

Intermediate phases are sometimes classified on the basis of whether they melt congruently or incongruently.

CONGRUENT PHASE TRANSFORMATIONS

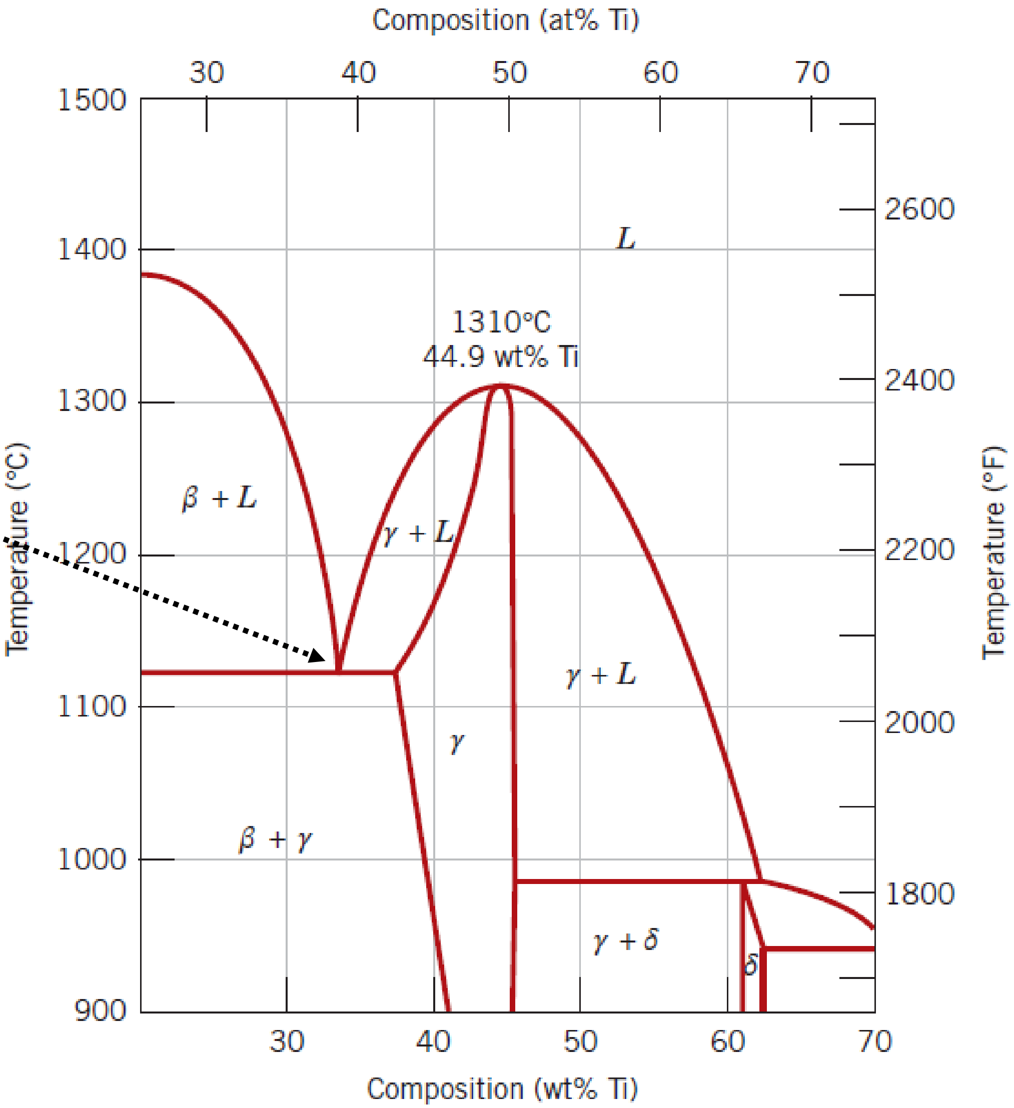
The intermetallic compound Mg_2Pb melts congruently at the point designated *M* on the magnesium–lead phase diagram.



CONGRUENT PHASE TRANSFORMATIONS

For the nickel–titanium system, there is a congruent melting point for the γ solid solution that corresponds to the point of tangency for the pairs of liquidus and solidus lines, at 1310°C and 44.9 wt% Ti.

The peritectic reaction is an example of incongruent melting for an intermediate phase.

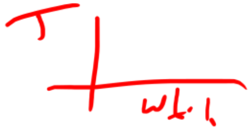


THE GIBBS PHASE RULE

The construction of phase diagrams—as well as some of the principles governing the conditions for phase equilibria—are dictated by laws of thermodynamics.

One of these is the **Gibbs phase rule,** proposed by the nineteenth-century physicist J. Willard Gibbs.

This rule represents a criterion for the number of phases that coexist within a system at equilibrium and is expressed by the simple equation: $P + F = C + N$



- P is the number of phases present.
- The parameter 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. Expressed another way, F is the number of these variables that can be changed independently without altering the number of phases that coexist at equilibrium.
- The parameter C represents the number of components in the system.
- N is the number of noncompositional variables (e.g., temperature and pressure).

Components are normally elements or stable compounds and, in the case of phase diagrams, are the materials at the two extremes of the horizontal compositional axis (e.g., H_2O and $C_{12}H_{22}O_{11}$, and Cu and Ni for the phase diagrams.

THE GIBBS PHASE RULE

Because pressure is constant (1 atm), the parameter N is 1—temperature is the only noncompositional variable:

$$P + F = C + 1$$

The number of components C is 2 (namely, Cu and Ag), and

$$P + F = 2 + 1 = 3$$

or

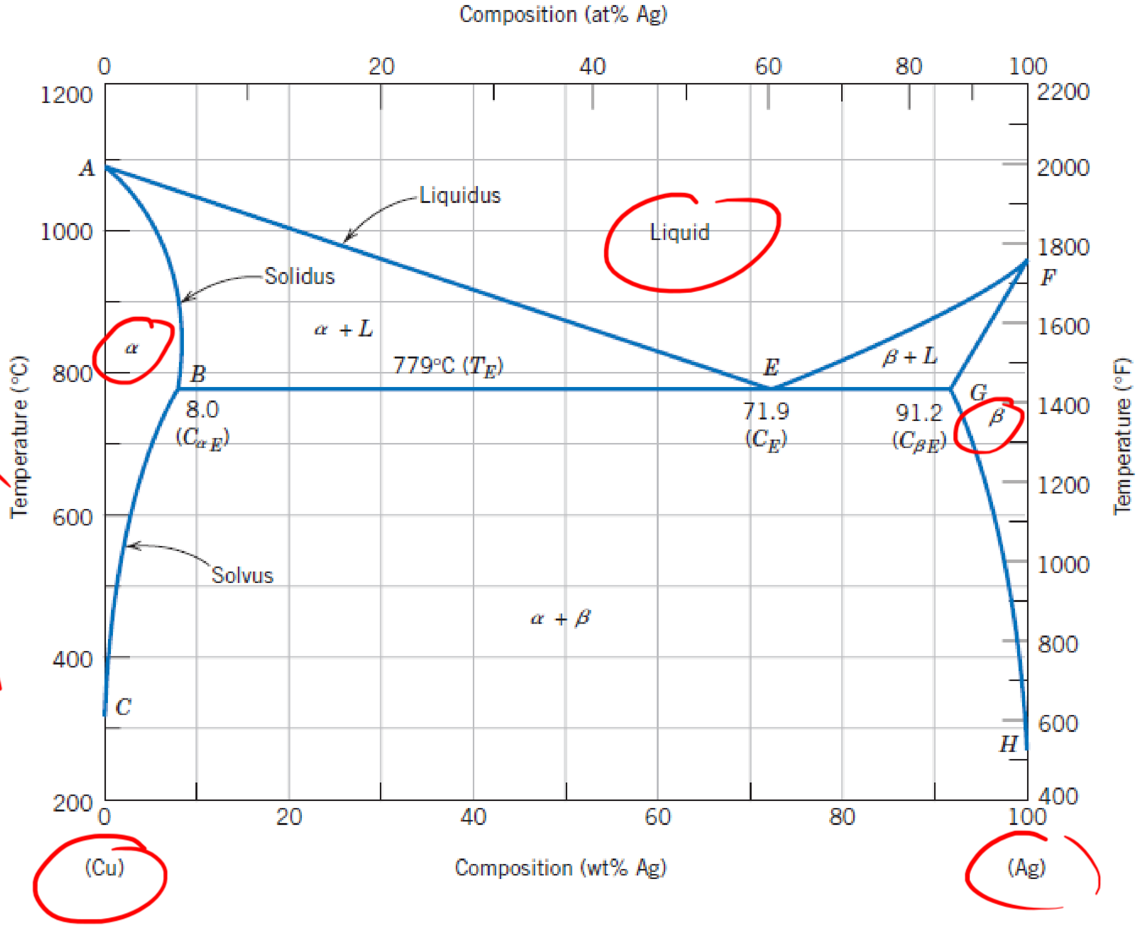
$$F = 3 - P$$

Consider the case of single-phase fields on the phase diagram (e.g., α, β, and liquid regions).

Because only one phase is present, $P = 1$ and

$$F = 3 - P = 3 - 1 = 2$$

This means that to completely describe the characteristics of any alloy that exists within one of these phase fields, we must specify two parameters—composition and temperature, which locate, respectively, the horizontal and vertical positions of the alloy on the phase diagram.

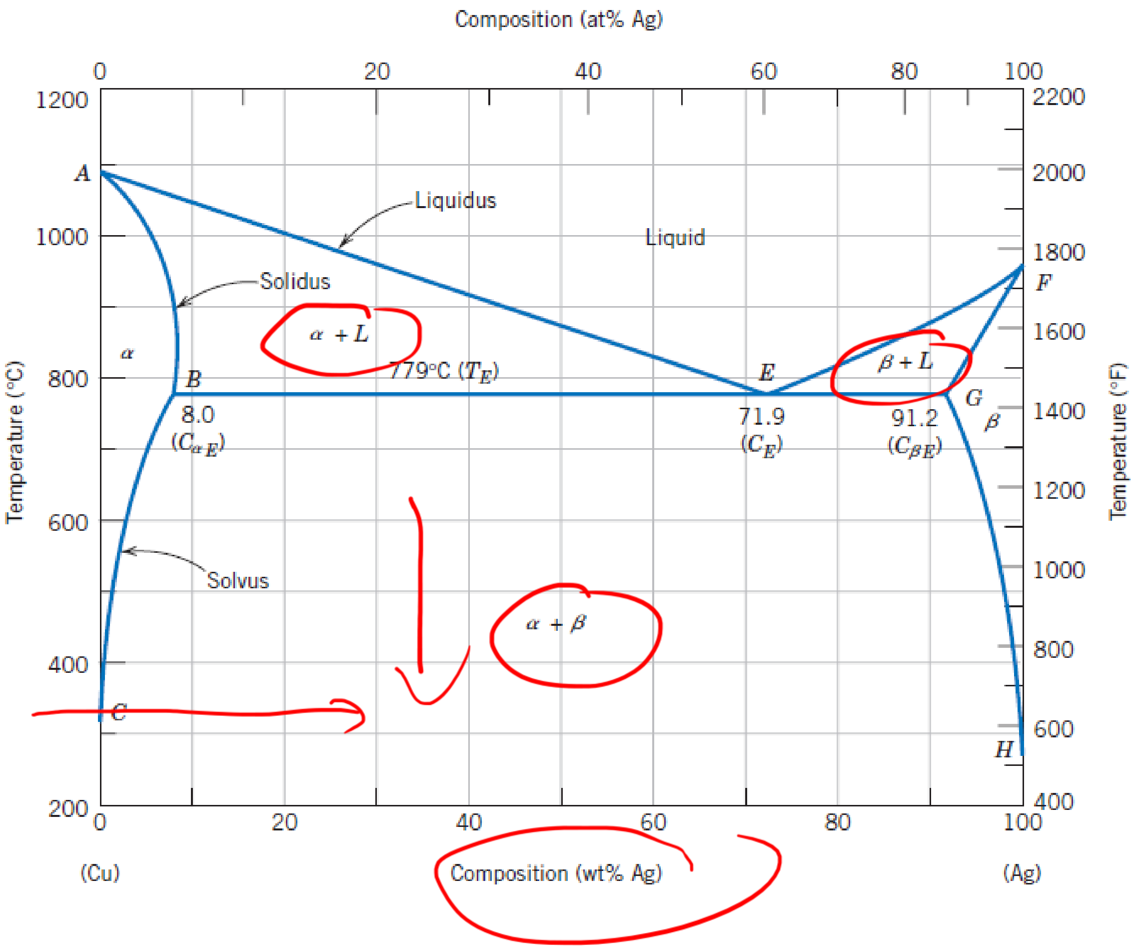


THE GIBBS PHASE RULE

For the situation in which two phases coexist—for example, $\alpha + L$, $\beta + L$, and $\alpha + \beta$ phase regions—the phase rule stipulates that we have but one degree of freedom because:

$$F = 3 - P = 3 - 2 = 1$$

Thus, it is necessary to specify either temperature or the composition of one of the phases to completely define the system.



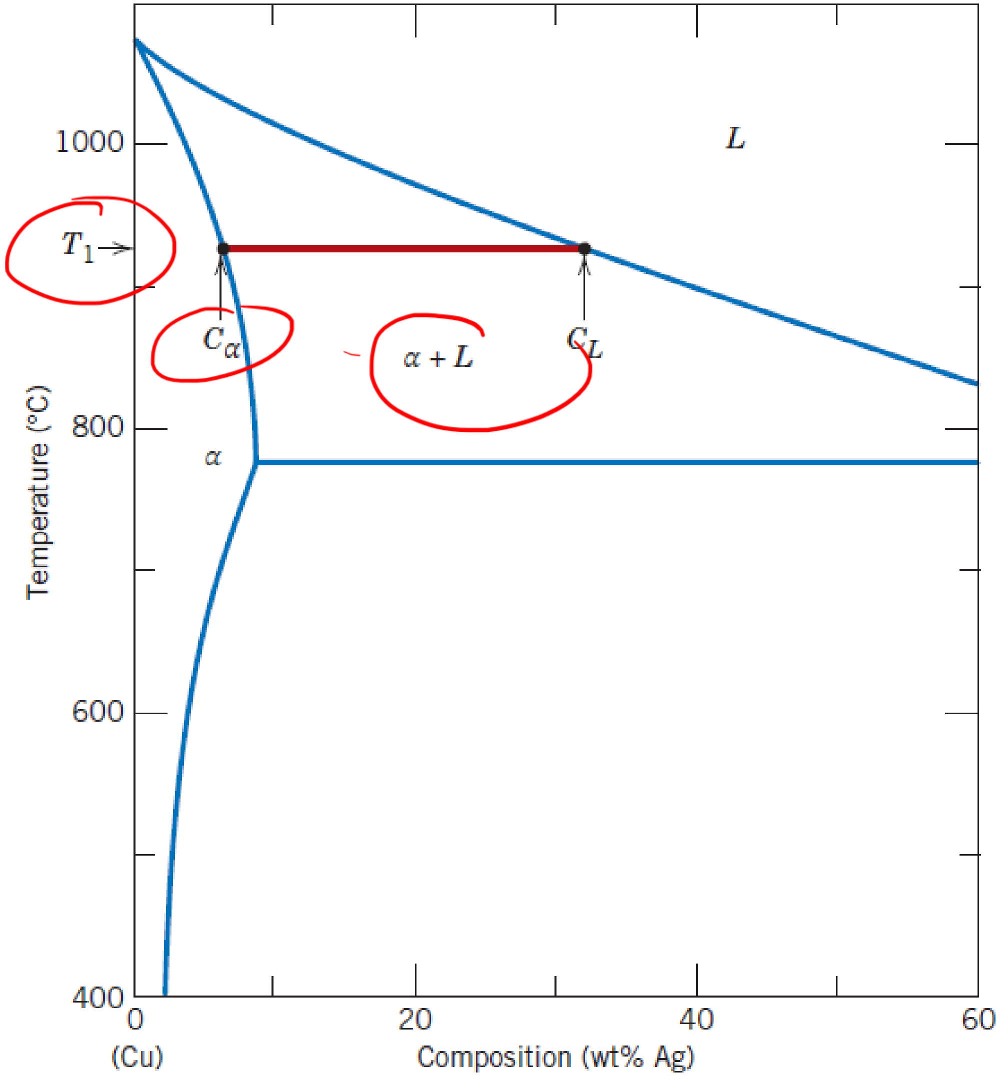
THE GIBBS PHASE RULE

For example, suppose that we decide to specify temperature for the $\alpha + L$ phase region, say, T_1 in the shown figure.

The compositions of the α and liquid phases (C_α and C_L) are thus dictated by the extremes of the tie line constructed at T_1 across the $\alpha + L$ field.

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

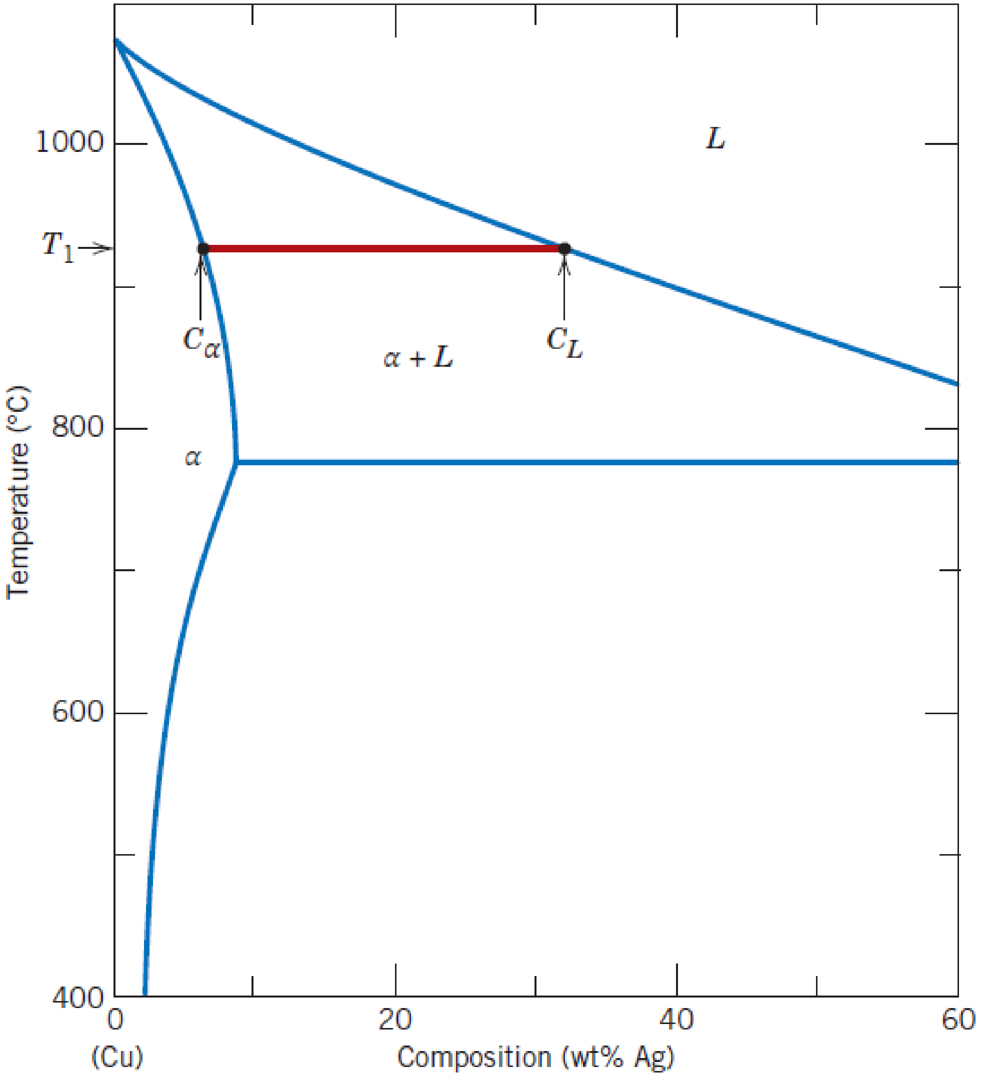
This is to say that the overall alloy composition could lie anywhere along this tie line constructed at temperature T_1 and still give C_α and C_L compositions for the respective α and liquid phases.



THE GIBBS PHASE RULE

The second alternative is to stipulate the composition of one of the phases for this two-phase situation, which thereby fixes completely the state of the system.

For example, if we specified C_α as the composition of the α phase that is in equilibrium with the liquid, then both the temperature of the alloy (T_1) and the composition of the liquid phase (C_L) are established, again by the tie line drawn across the $\alpha + L$ phase field so as to give this C_α composition.



THE GIBBS PHASE RULE

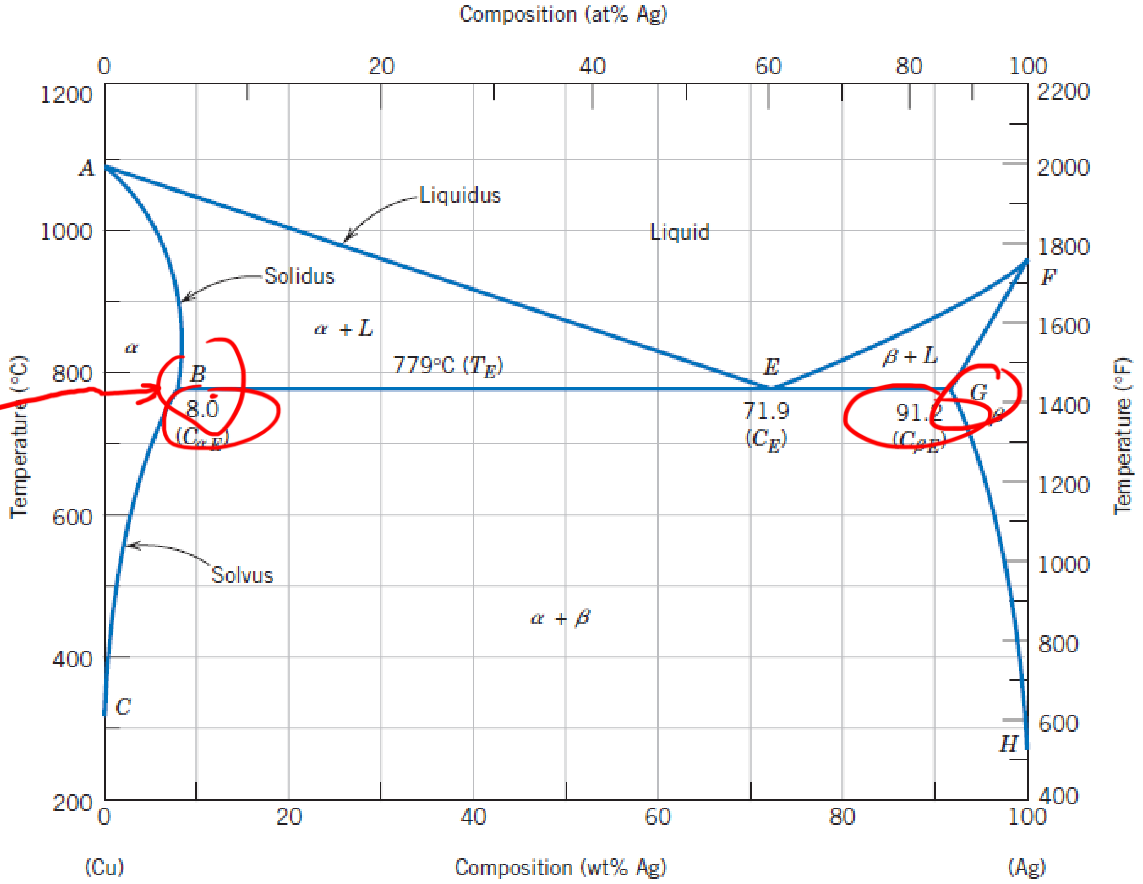
For binary systems, when three phases are present, there are no degrees of freedom because:

$$F = 3 - P = 3 - 3 = 0$$

This means that the compositions of all three phases—as well as the temperature—are fixed.

This condition is met for a eutectic system by the eutectic isotherm; for the Cu–Ag system, it is the horizontal line that extends between points *B* and *G*.

At this temperature, 779°C, the points at which each of the α, L, and β phase fields touch the isotherm line correspond to the respective phase compositions; namely, the composition of the α phase is fixed at 8.0 wt% Ag, that of the liquid at 71.9 wt% Ag, and that of the β phase at 91.2 wt% Ag.



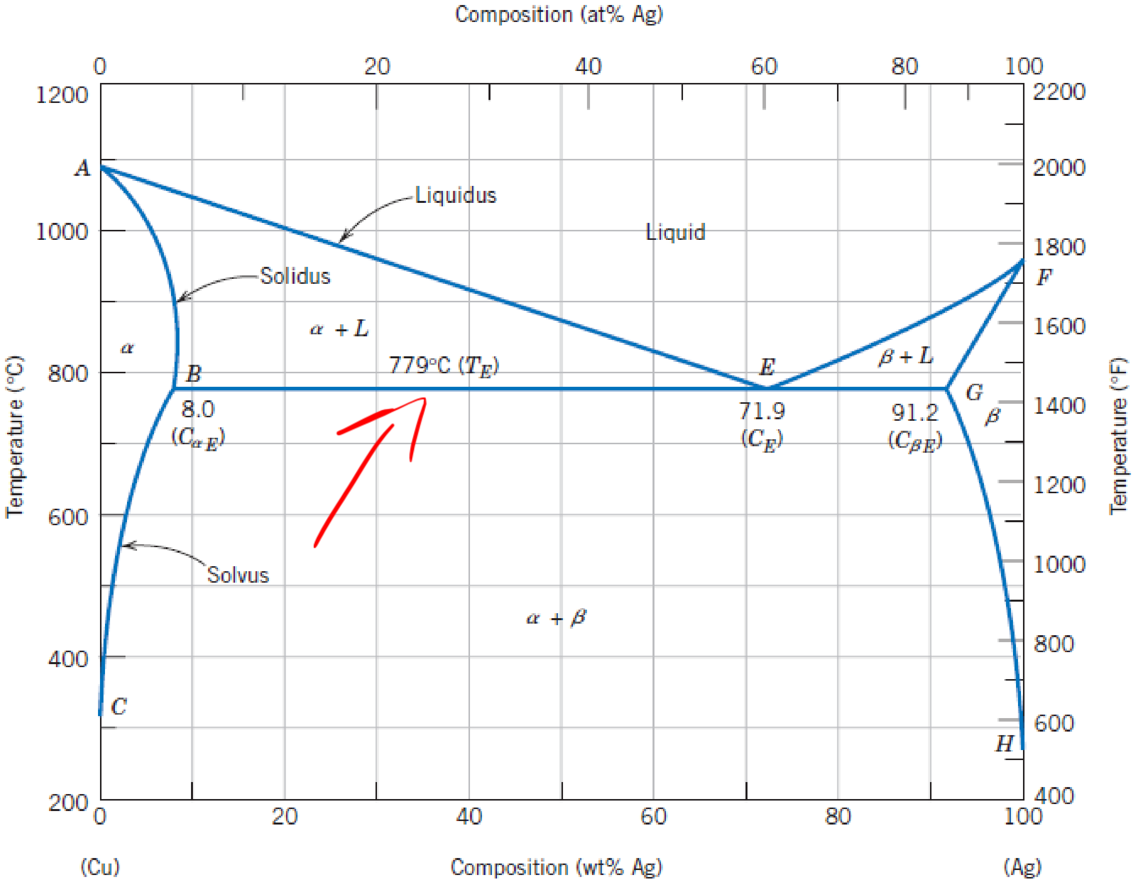
THE GIBBS PHASE RULE

Thus, three-phase equilibrium is not represented by a phase field, but rather by the unique horizontal isotherm line.

Furthermore, all three phases are in equilibrium for any alloy composition that lies along the length of the eutectic isotherm (e.g., for the Cu–Ag system at 779°C and compositions between 8.0 and 91.2 wt% Ag).

One use of the Gibbs phase rule is in analysing for nonequilibrium conditions.

For example, a microstructure for a binary alloy that developed over a range of temperatures and consists of three phases is a nonequilibrium one; under these circumstances, three phases exist only at a single temperature.



THE IRON–CARBON SYSTEM

Of all binary alloy systems, the one that is possibly the most important is that for iron and carbon.

Both steels and cast irons, primary structural materials in every technologically advanced culture, are essentially iron–carbon alloys.

This section is devoted to a study of the phase diagram for this system and the development of several of the possible microstructures.

THE IRON–IRON CARBIDE PHASE DIAGRAM

A portion of the iron–carbon phase diagram is shown.

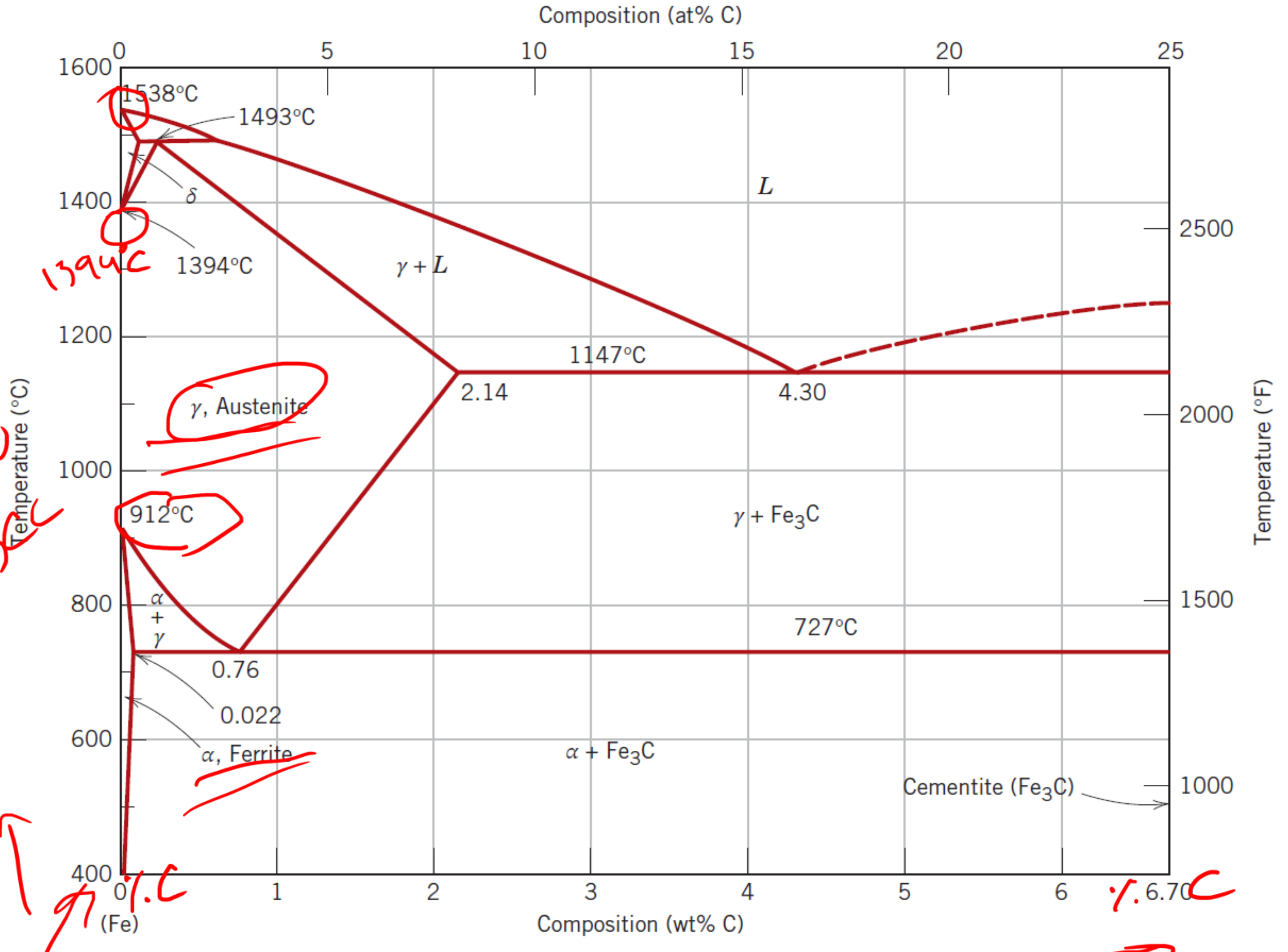
Pure iron, upon heating, experiences two changes in crystal structure before it melts.

At room temperature, the stable form, called **ferrite**, or α-iron, has a BCC crystal structure.

Fe ↓ review BCC

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.



%.6.70

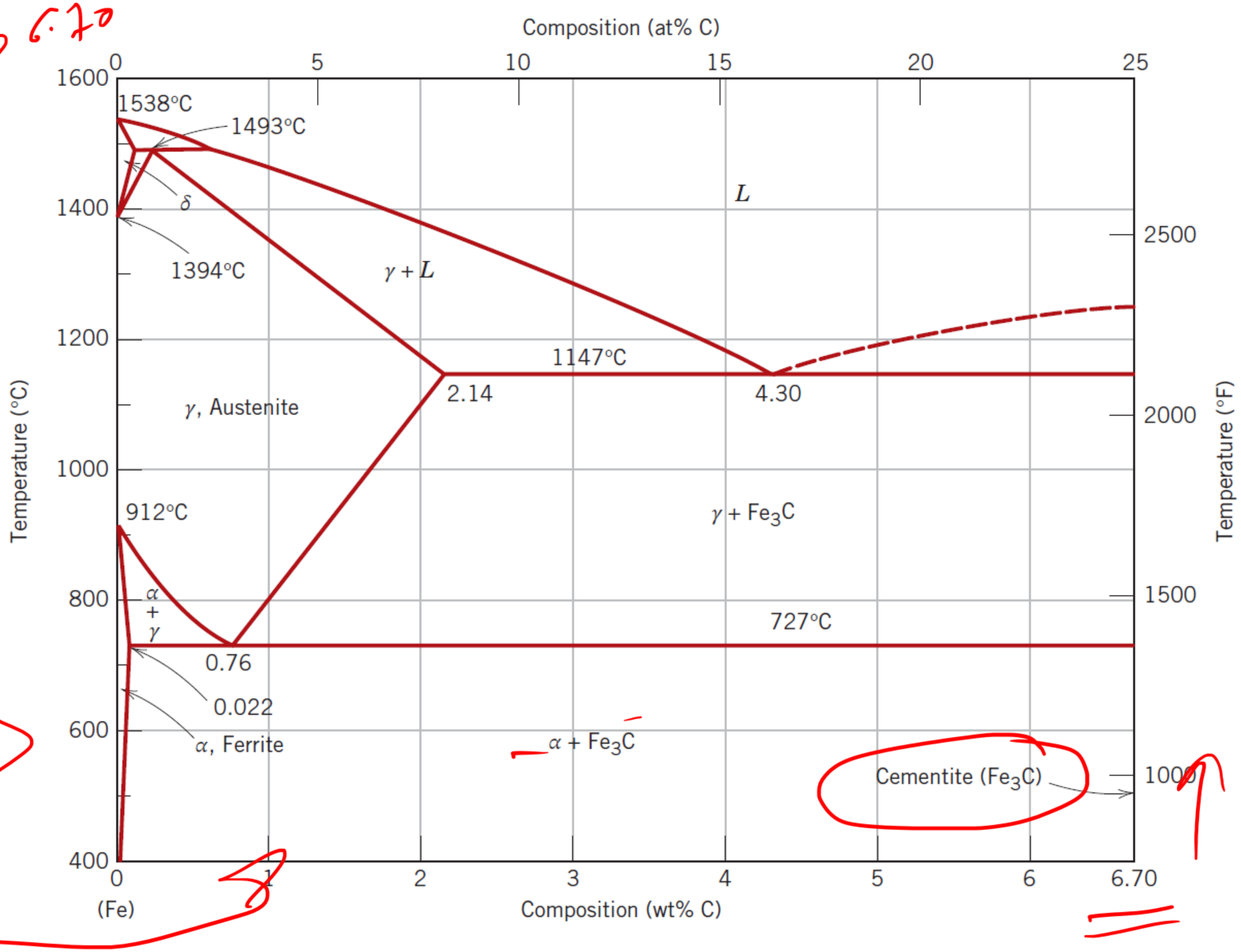
THE IRON–IRON CARBIDE PHASE DIAGRAM

The composition axis 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.

6.70

Thus, the iron–carbon system may be divided into two parts: an iron-rich portion, as shown, 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.



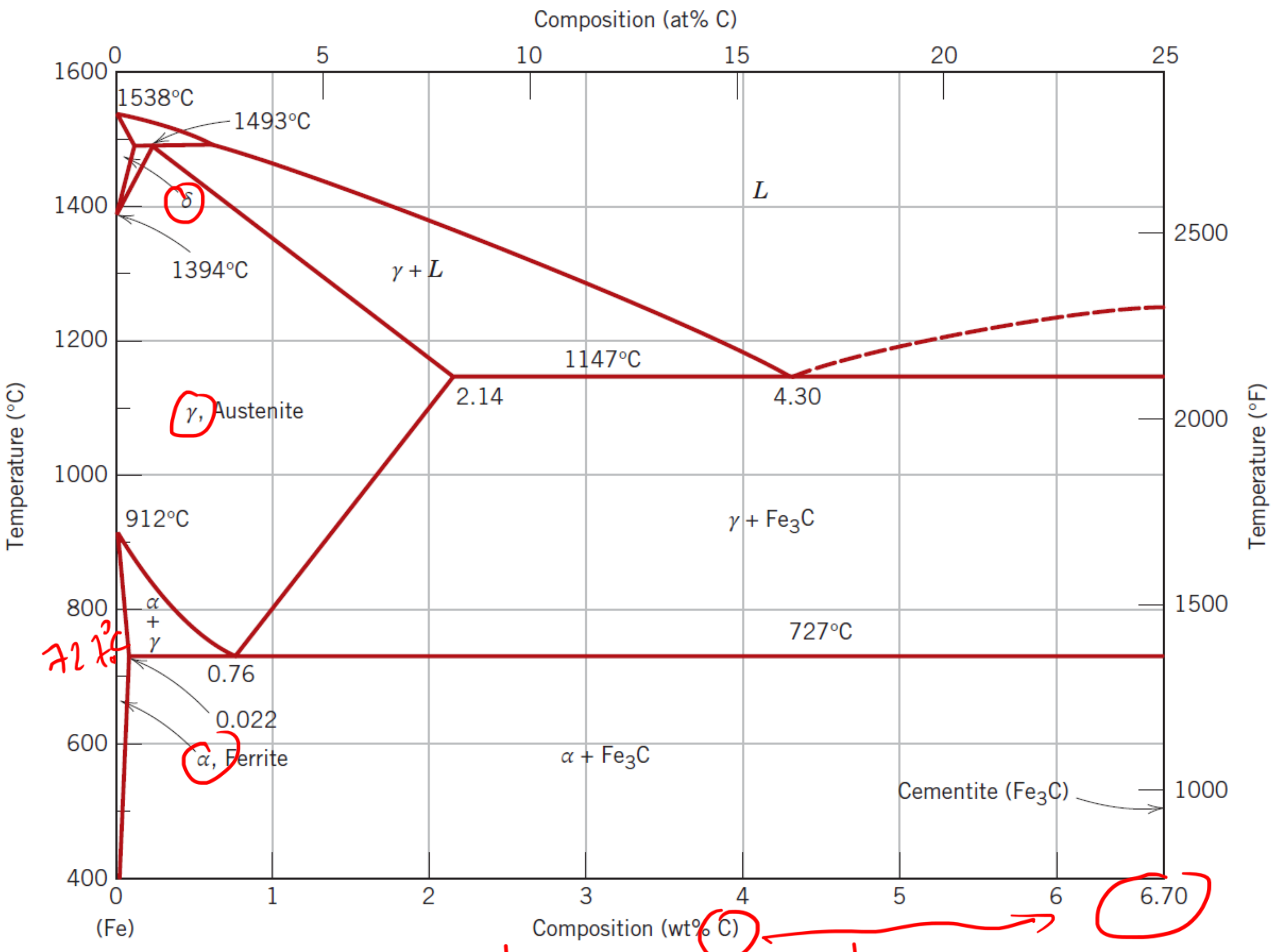
THE IRON–IRON CARBIDE PHASE DIAGRAM

The figure would be more appropriately labelled the Fe–Fe_3C phase diagram because 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 the BCC α-ferrite, only small concentrations of carbon are soluble; the maximum solubility is 0.022 wt% at 727°C (1341°F).



Ferrite → Cementite

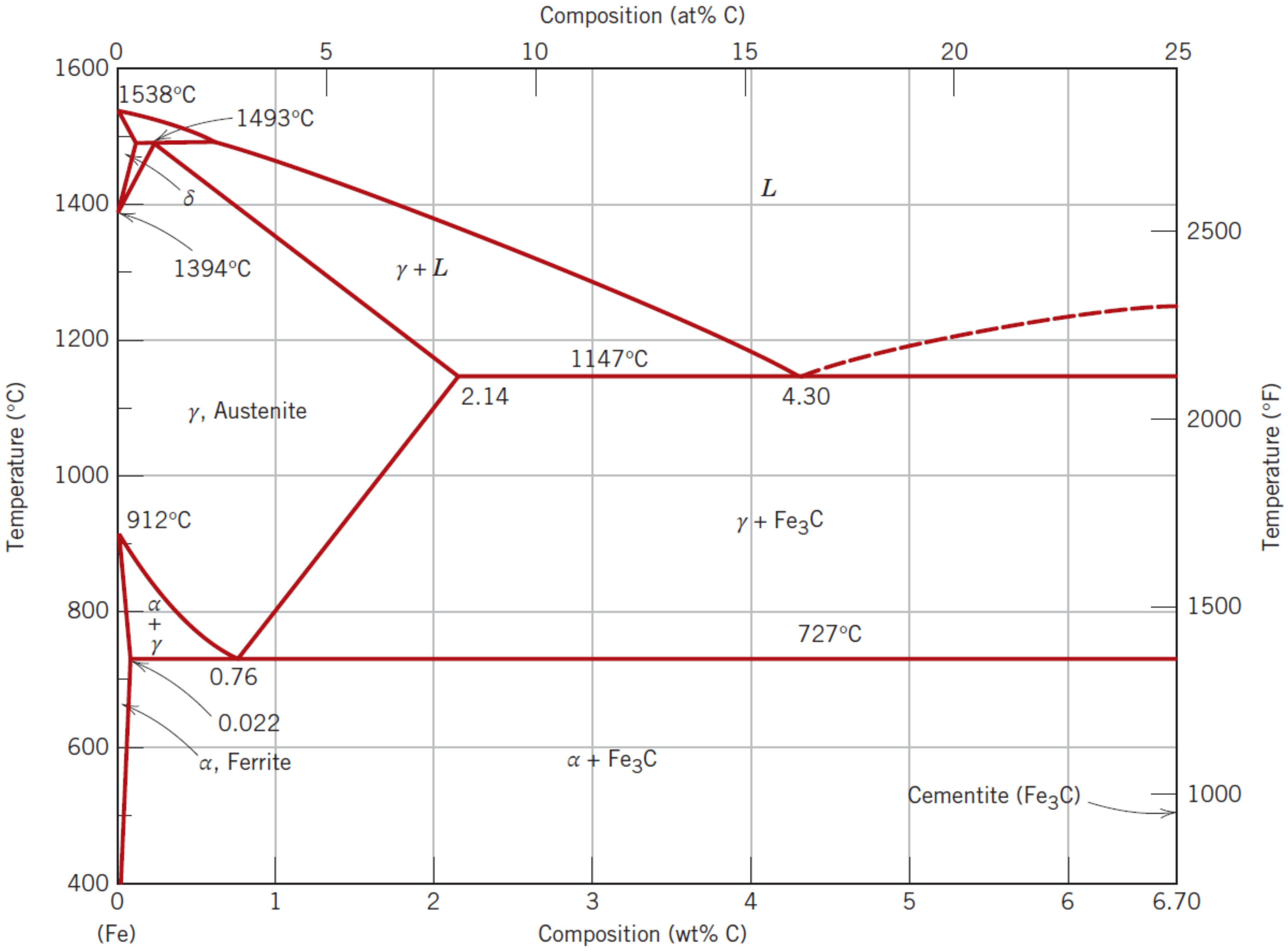
6.7% C
= 100% Cementite

THE IRON–IRON CARBIDE PHASE DIAGRAM

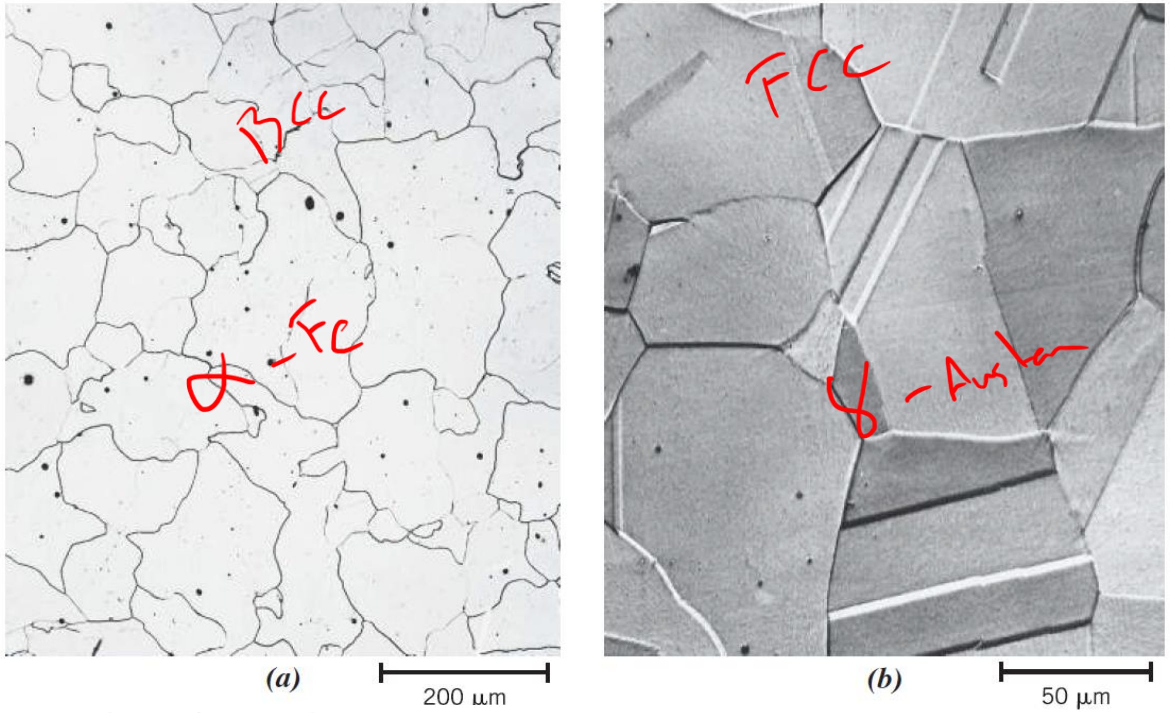
The limited solubility is explained by the shape and size of the BCC interstitial positions, which make it difficult to accommodate the carbon atoms.

Even though present in relatively low concentrations, carbon significantly influences the mechanical properties of ferrite.

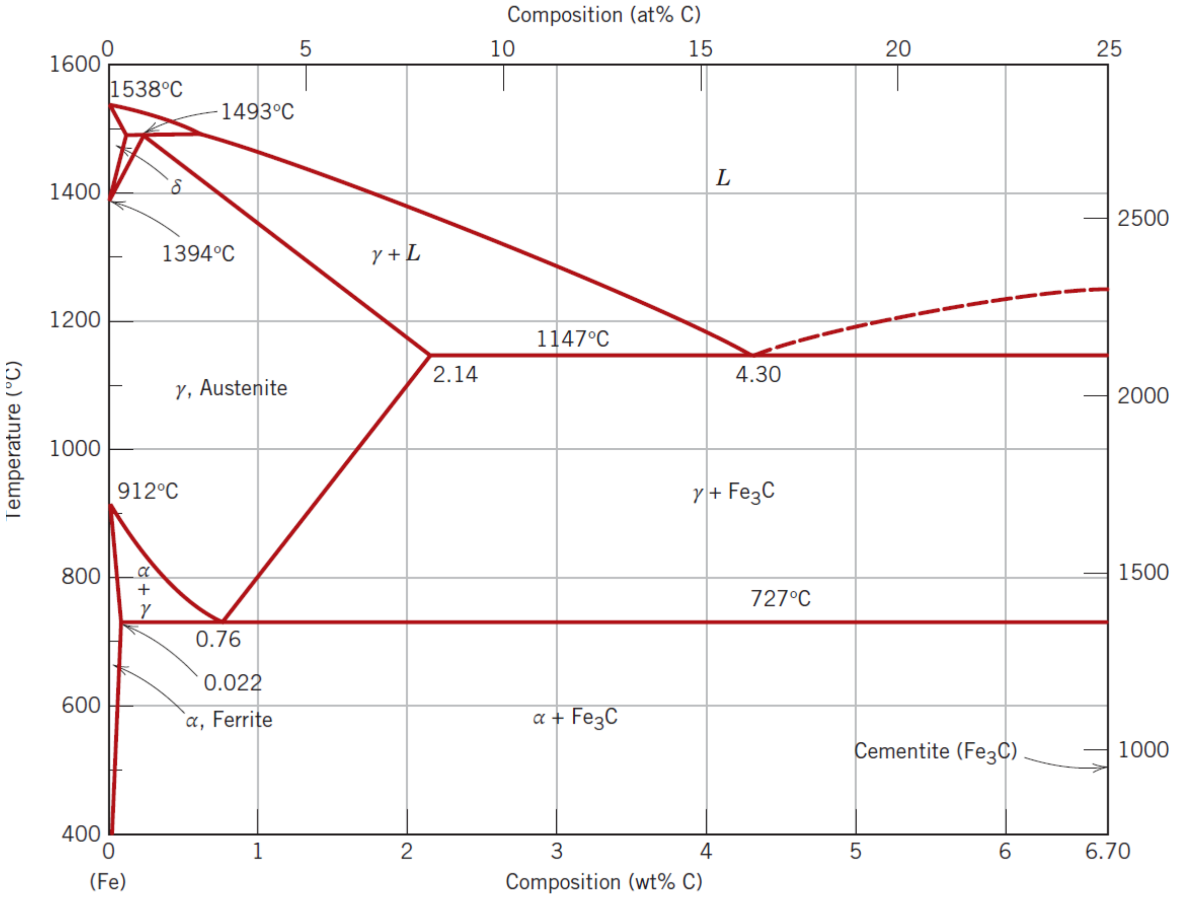
This particular iron–carbon phase is relatively soft, may be made magnetic at temperatures below 768°C (1414°F), and has a density of 7.88 g/cm^3.



THE IRON–IRON CARBIDE PHASE DIAGRAM



Photomicrographs of (*a*) α-ferrite (90×) and (*b*) austenite (325×).



THE IRON–IRON CARBIDE PHASE DIAGRAM

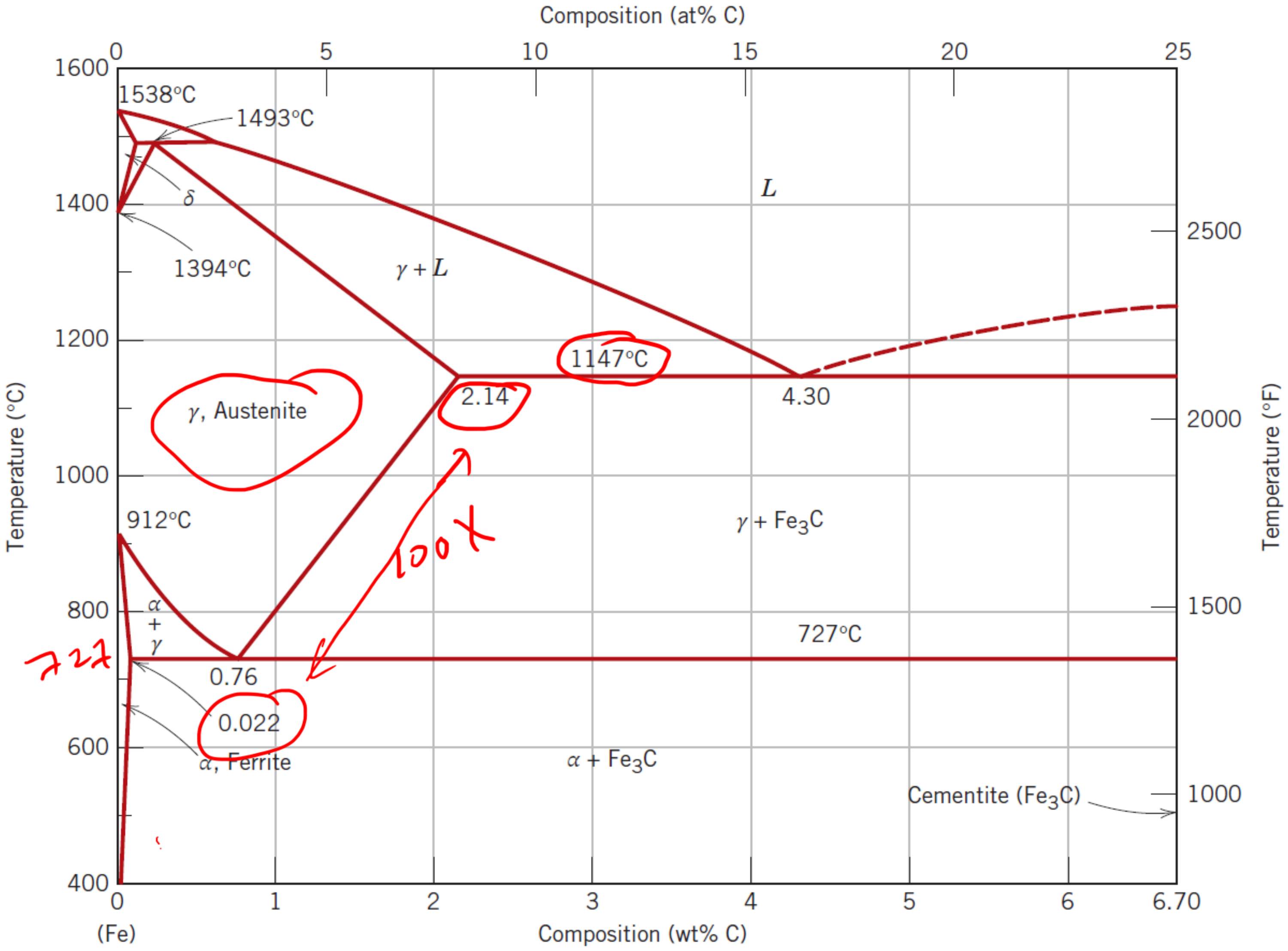
The austenite, or γ phase, of iron, when alloyed with carbon alone, is not stable below 727°C (1341°F), as indicated.

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 because the FCC octahedral sites are larger than the BCC tetrahedral sites. ??

Therefore, the strains imposed on the surrounding iron atoms are much lower.

Phase transformations involving austenite are very important in the heat treating of steels. In passing, it should be mentioned that austenite is nonmagnetic.



THE IRON–IRON CARBIDE PHASE DIAGRAM

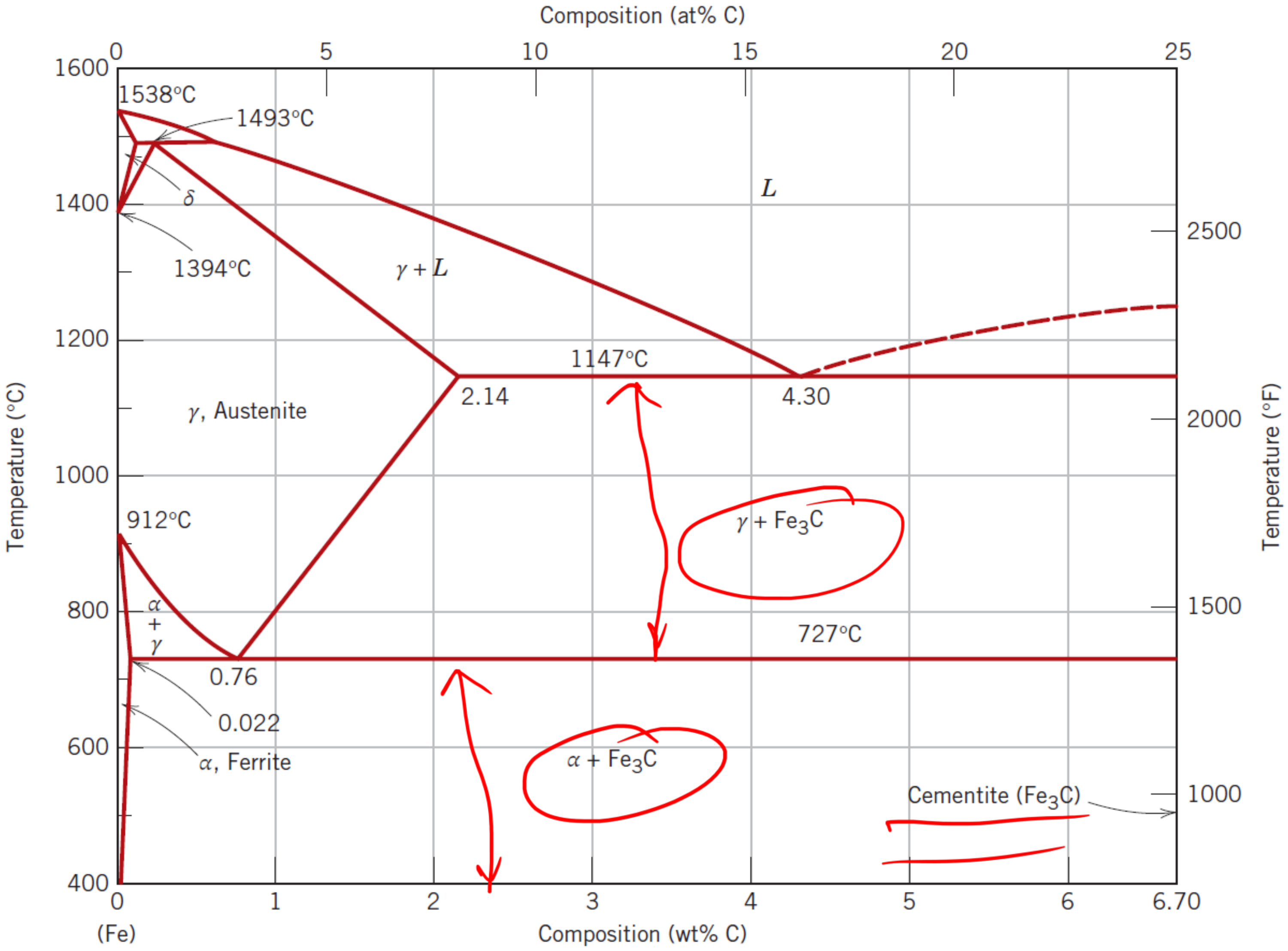
The δ-ferrite is virtually the same as α-ferrite, except for the range of temperatures over which each exists.

Because 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 $\alpha + Fe_3C$ phase region).

As indicated, Fe_3C also coexists with the γ phase between 727°C and 1147°C (1341°F and 2097°F).

Mechanically, cementite is very hard and brittle; the strength of some steels is greatly enhanced by its presence.



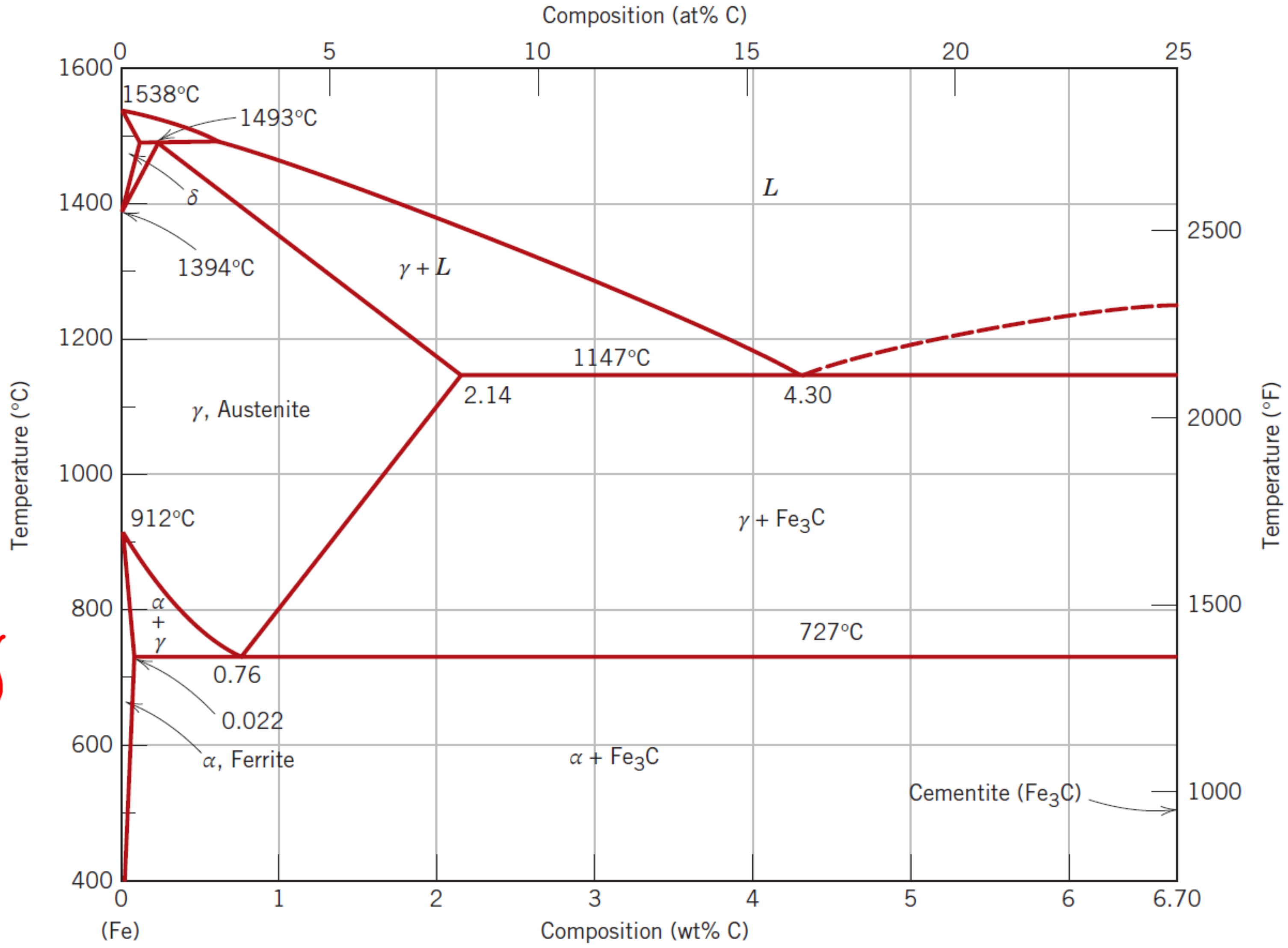
THE IRON–IRON CARBIDE PHASE DIAGRAM

Strictly speaking, cementite is only metastable; that is, it remains as a compound indefinitely at room temperature.

However, if heated to between 650°C and 700°C (1200°F and 1300°F) for several years, it gradually changes or transforms into α-iron and carbon, in the form of graphite, which remains upon subsequent cooling to room temperature.

Thus, the phase diagram is not a true equilibrium one because cementite is not an equilibrium compound.

However, because the decomposition rate of cementite is extremely sluggish, virtually all the carbon in steel is as Fe_3C instead of graphite, and the iron–iron carbide phase diagram is, for all practical purposes, valid.



THE IRON–IRON CARBIDE PHASE DIAGRAM

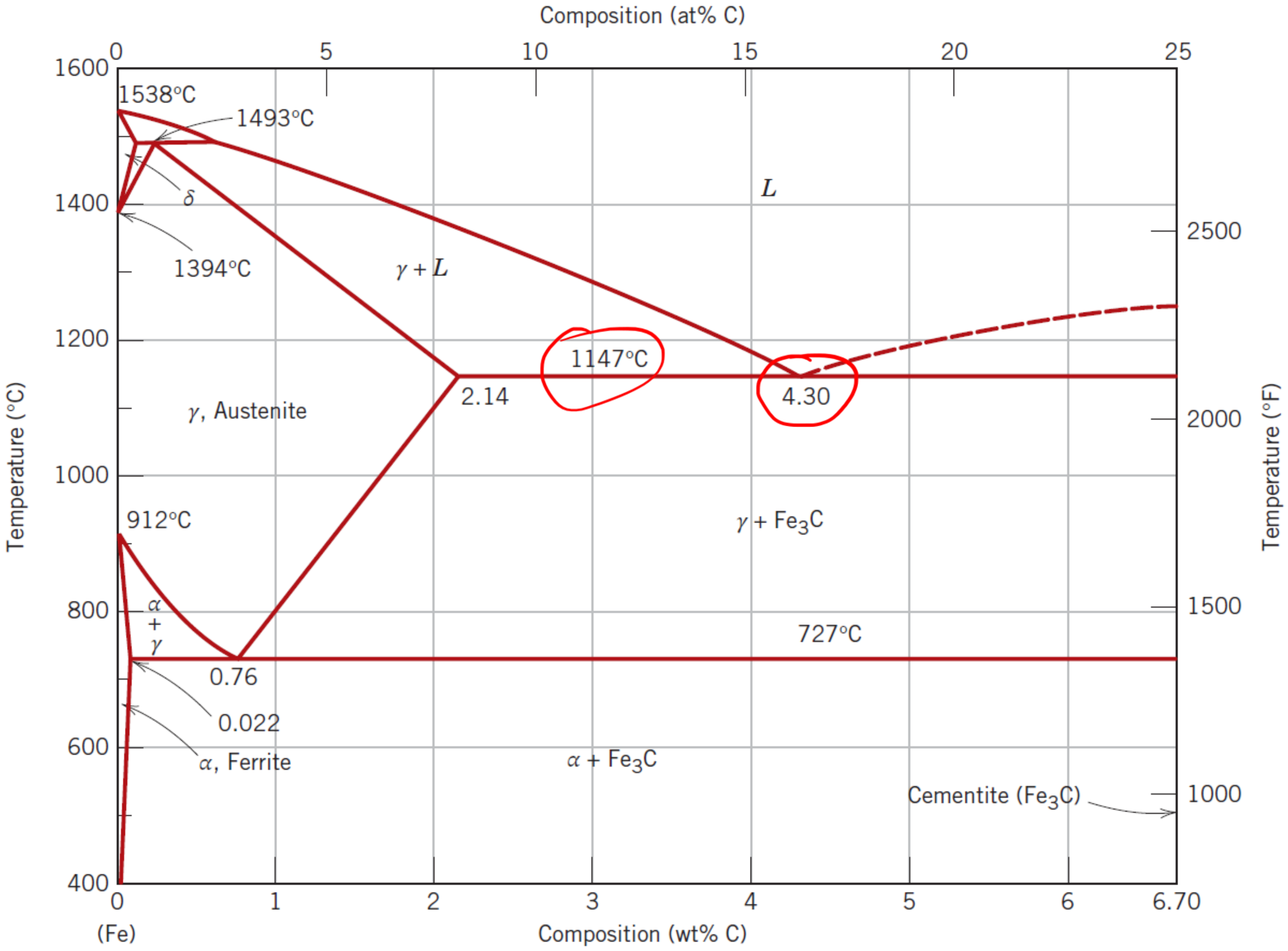
Addition of silicon to cast irons greatly accelerates this cementite decomposition reaction to form graphite.

The two-phase regions are labelled. 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:

$$L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma + Fe_3C$$

the liquid solidifies to form austenite and cementite phases.

Subsequent cooling to room temperature promotes additional phase changes.



THE IRON–IRON CARBIDE PHASE DIAGRAM

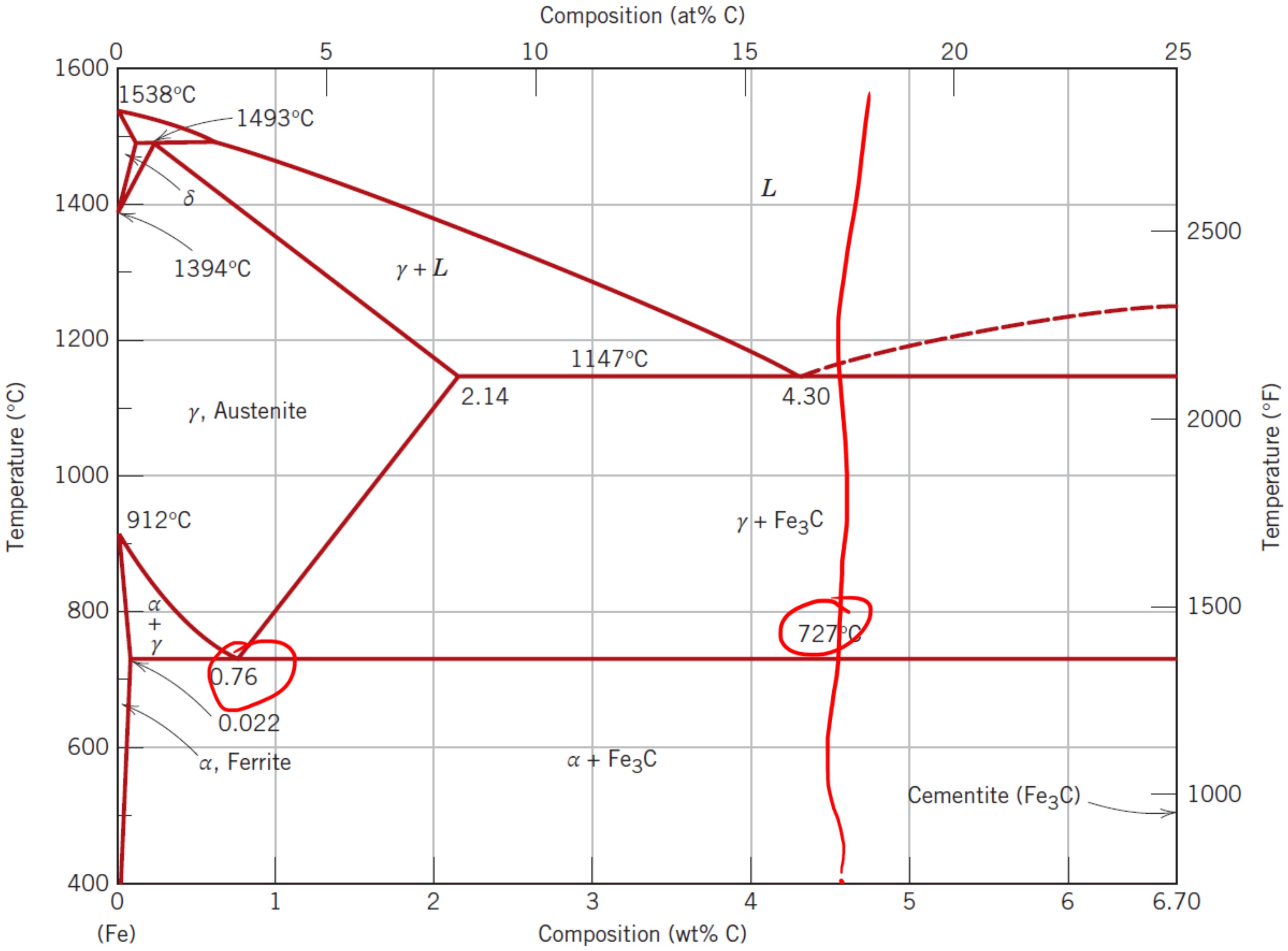
It may be noted that a **eutectoid** invariant point exists at a composition of 0.76 wt% C and a temperature of 727°C (1341°F).

This eutectoid reaction may be represented by:

$$\gamma(0.76\text{ wt\% C}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(0.022\text{ wt\% C}) + \mathrm{Fe_3C}(6.7\text{ wt\% C})$$

or, upon cooling, the solid γ phase is transformed into α-iron and cementite.

The eutectoid phase changes described above are very important, being fundamental to the heat treatment of steels.



THE IRON–IRON CARBIDE PHASE DIAGRAM

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.

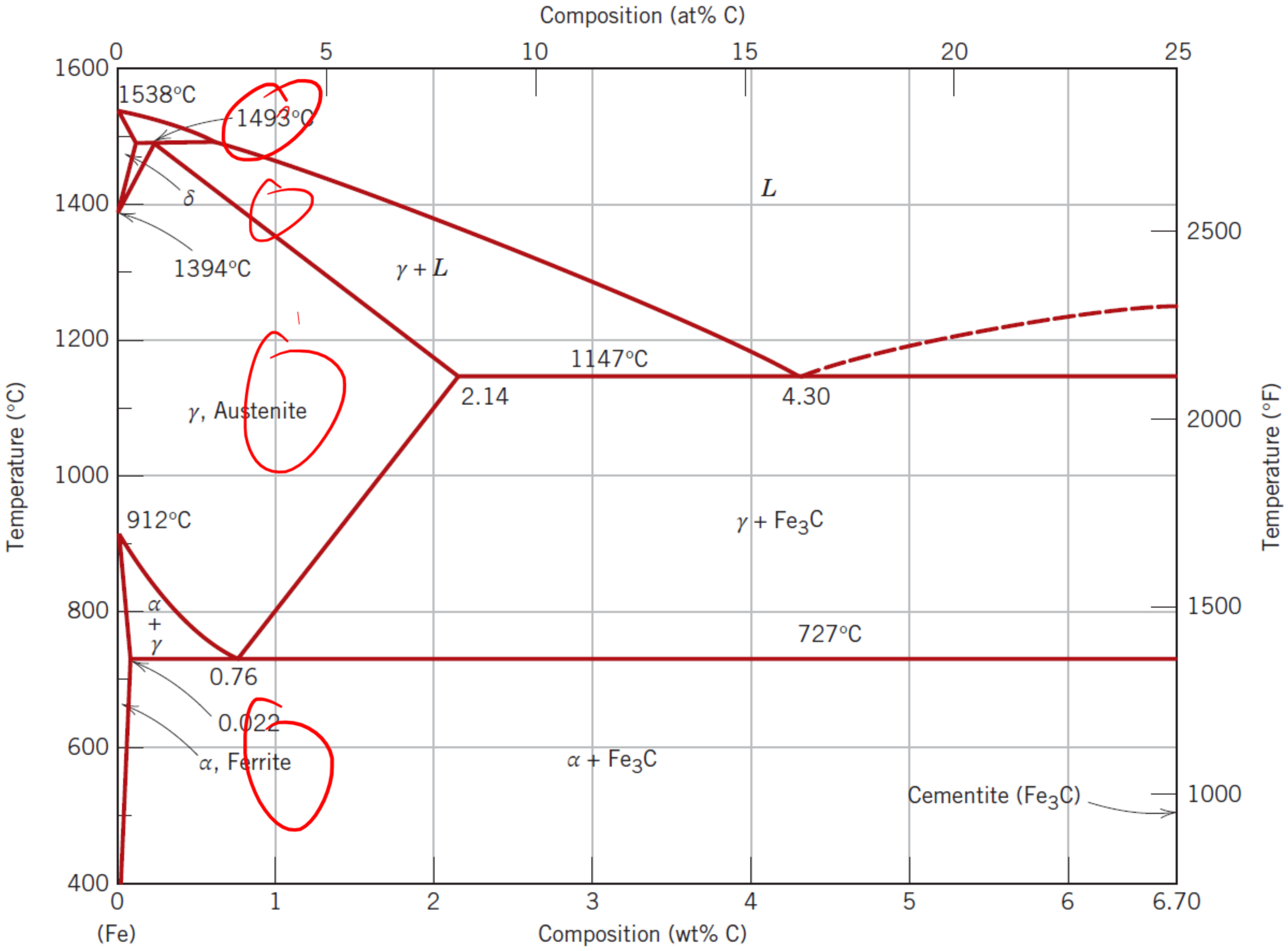
In most steels, the microstructure consists of both α and Fe_3C phases. Upon cooling to room temperature, an alloy within this composition range must pass through at least a portion of the γ-phase field; distinctive microstructures are subsequently produced.

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.

DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

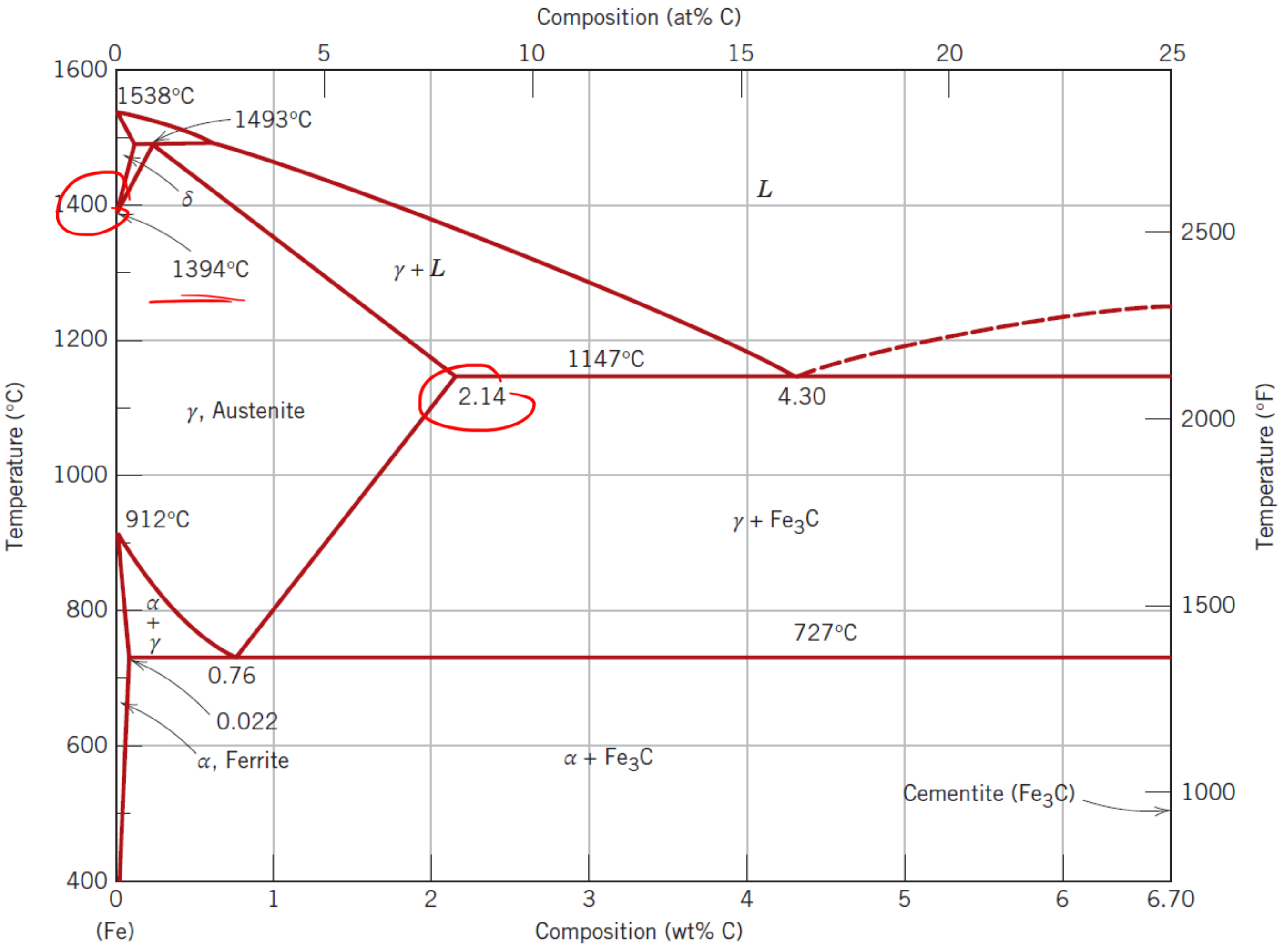
The microstructure that develops depends on both the carbon content and heat treatment.

Phase changes that occur upon passing from the γ region into the $\alpha + Fe_3C$ phase field are relatively complex.



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

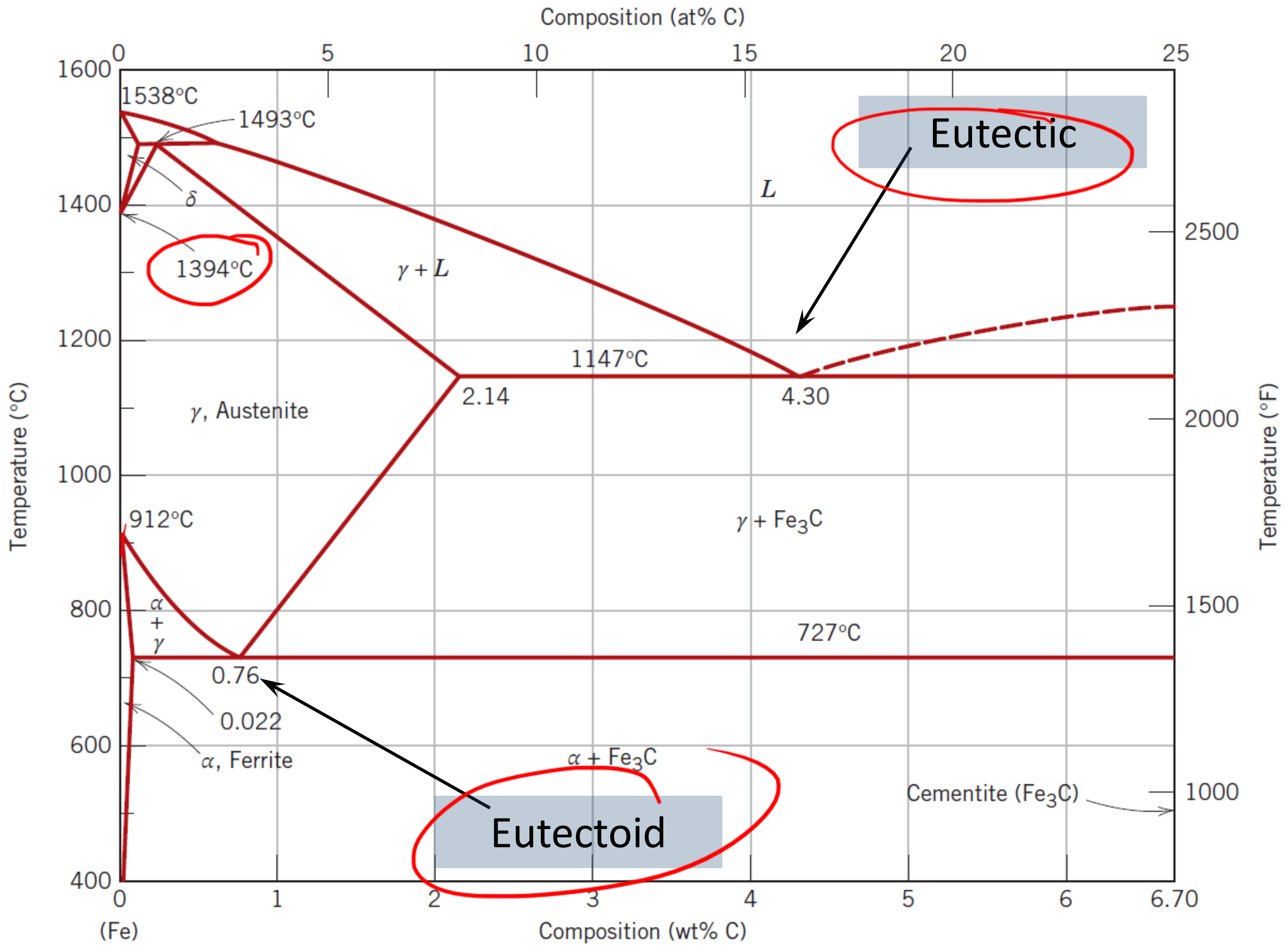
- **α-Fe (ferrite) - solid solution of C in BCC Fe**
  - ☑ Stable up to ~910 °C.
  - ☑ The maximum solubility of C in α-Fe is ~0.022 wt%
  - ☑ Transforms to FCC γ-Fe at ~910 °C.
  - ☑ When subjected to quenching, C can remain in the α solid solution, but soon precipitation of phases commences, by an 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.



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

- **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. → ??



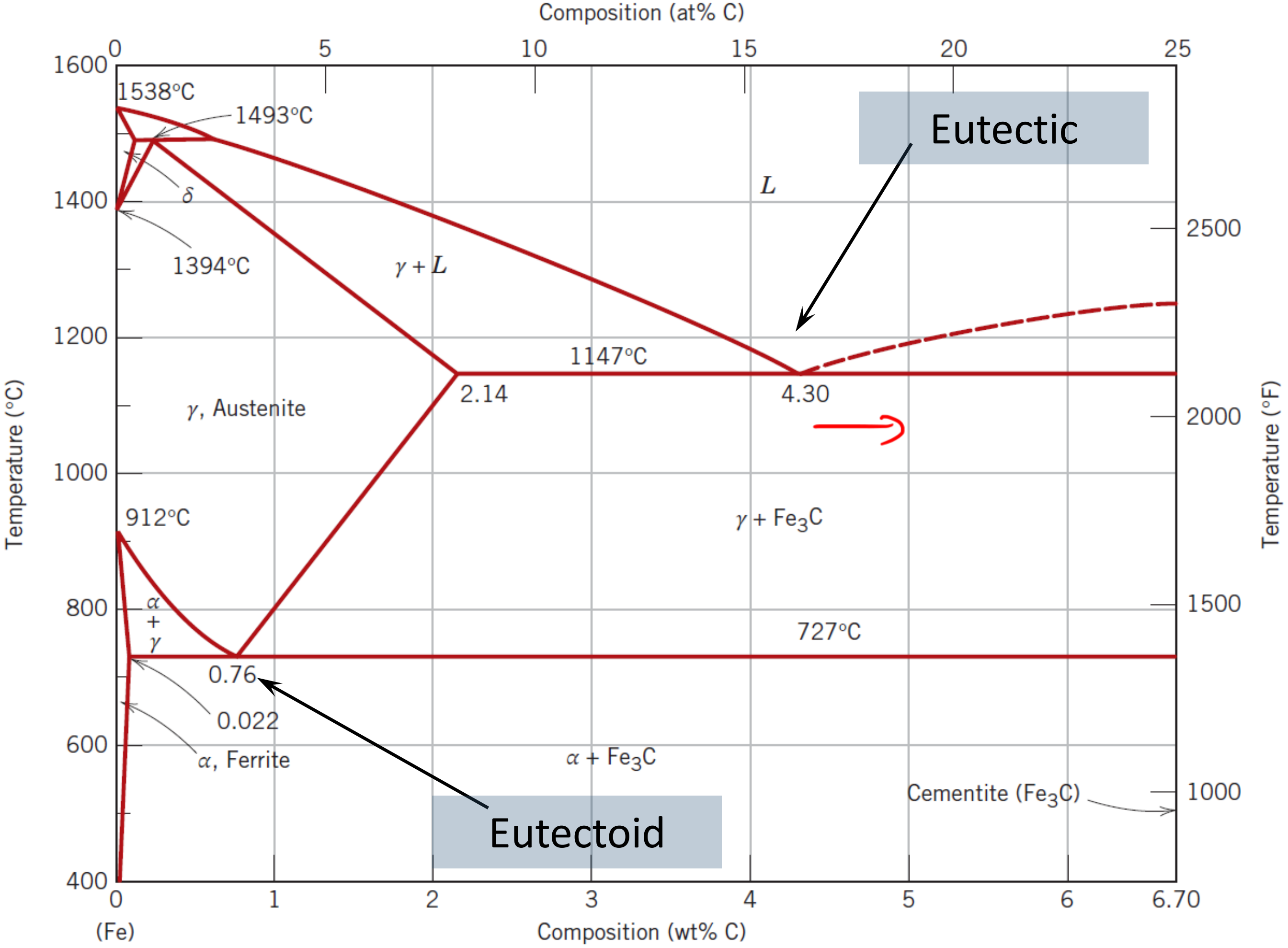
DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

- 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 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 ºC and 0.76 wt. %C

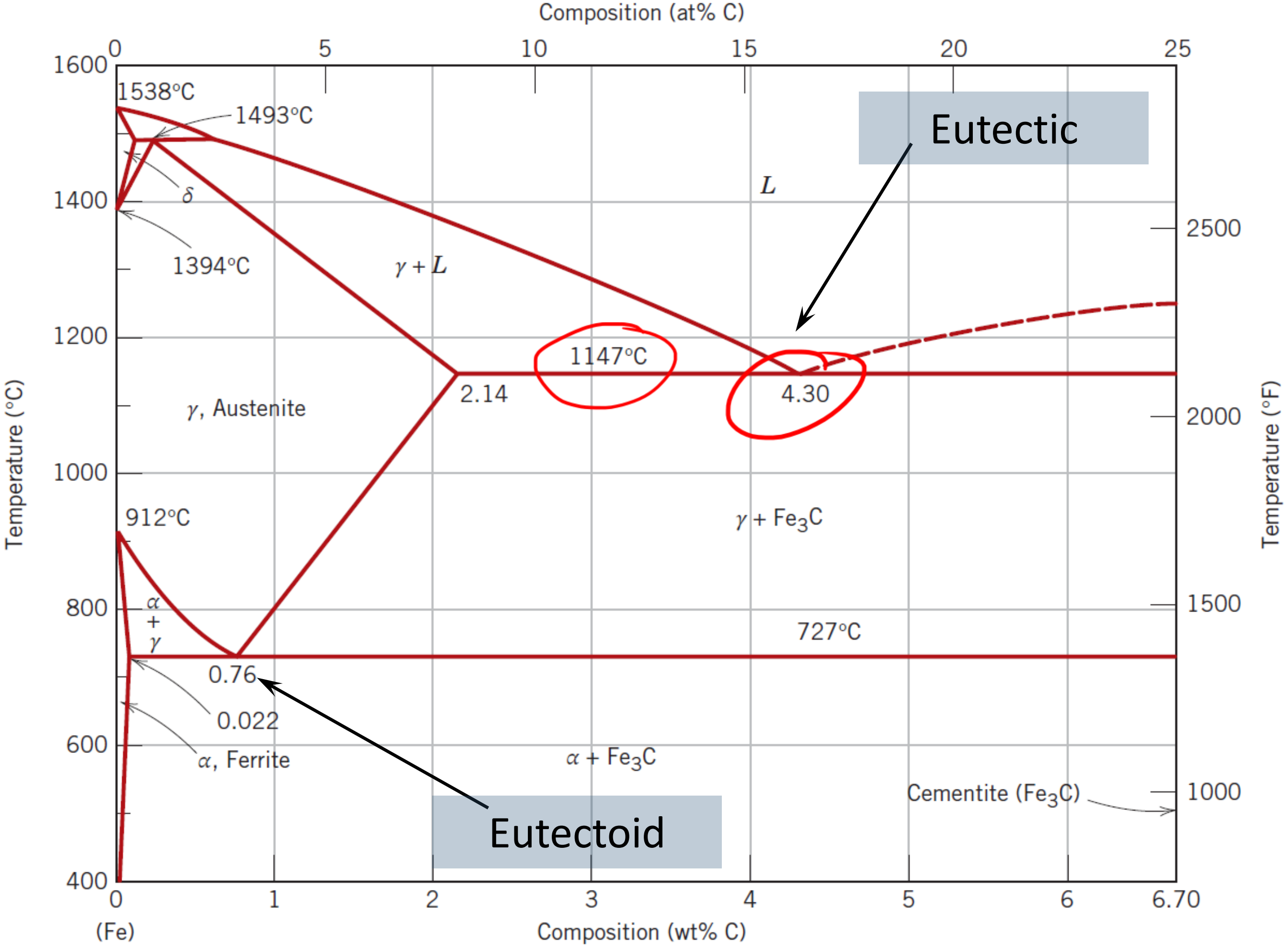
γ(0.76 wt% C) → α (0.022 wt% C) + Fe_3C



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

- 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 ºC and 4.3 wt. %C.

Liq. $\rightarrow \gamma + Fe_3C$



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

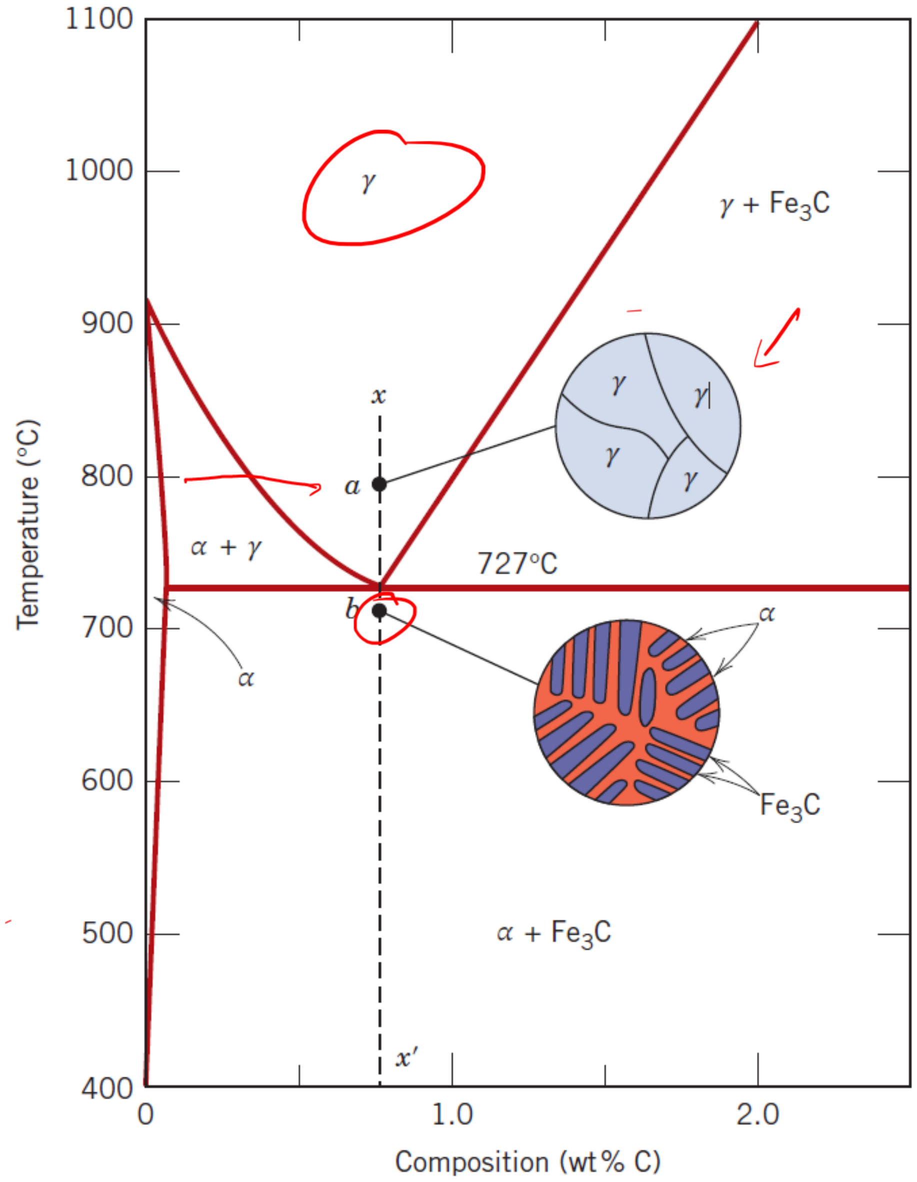
Consider, for example, an alloy of eutectoid composition (0.76 wt% C) as it is cooled from a temperature within the γ-phase region, say, 800°C—that is, beginning at point *a* and moving down the vertical line *xx*′.

Initially, the alloy is composed entirely of the austenite phase having a composition of 0.76 wt% C and corresponding microstructure, also indicated.

As the alloy is cooled, no changes occur until the eutectoid temperature (727°C) is reached. Upon crossing this temperature to point *b*, the austenite transforms according to:

$$\gamma(0.76\text{ wt\% C}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(0.022\text{ wt\% C}) + \text{Fe}_3\text{C}(6.7\text{ wt\% C})$$

The microstructure for this eutectoid steel that is slowly cooled through the eutectoid temperature consists of alternating layers or **lamellae** of the two phases (α and Fe_3C) that form simultaneously during the transformation. In this case, the relative layer thickness is approximately 8 to 1.



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

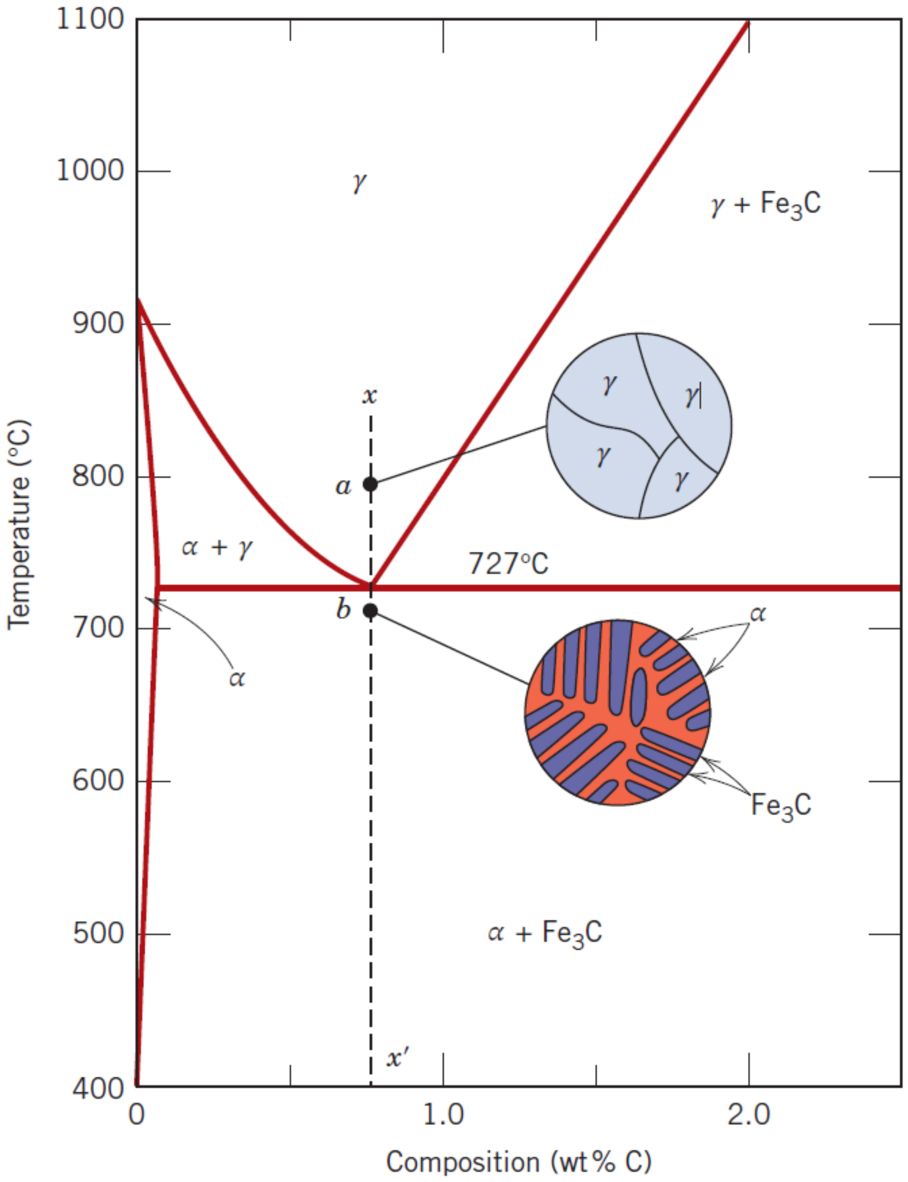
This microstructure, represented schematically, point *b*, is called **pearlite** because it has the appearance of mother-of pearl when viewed under the microscope at low magnifications.

The pearlite exists as grains, often termed colonies; within each colony the layers are oriented in essentially the same direction, which varies from one colony to another.

The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae, most of which appear dark.

Many cementite layers are so thin that adjacent phase boundaries are so close together that they are indistinguishable at this magnification and, therefore, appear dark.

Mechanically, pearlite has properties intermediate between those of the soft, ductile ferrite and the hard, brittle cementite.



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

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.

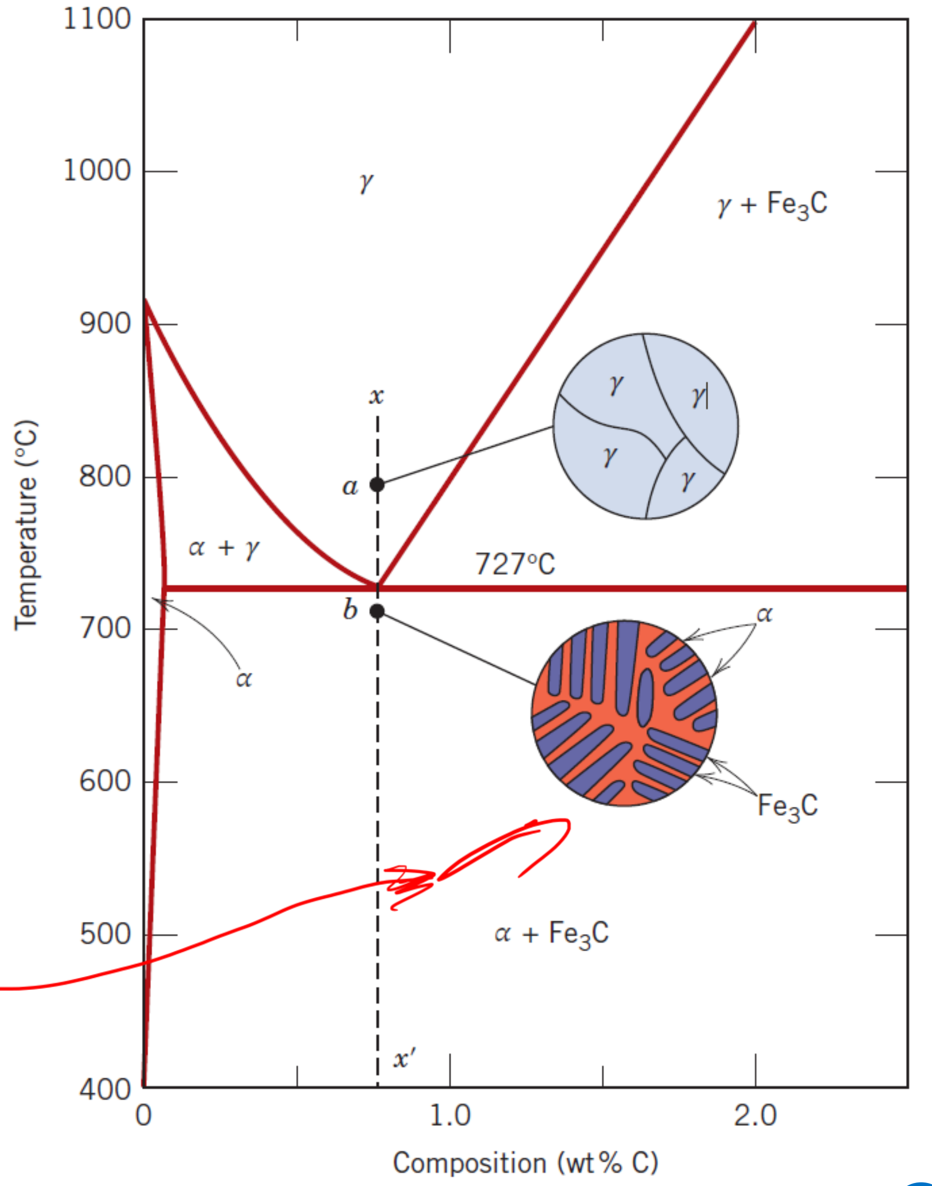
[1] γ → α

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

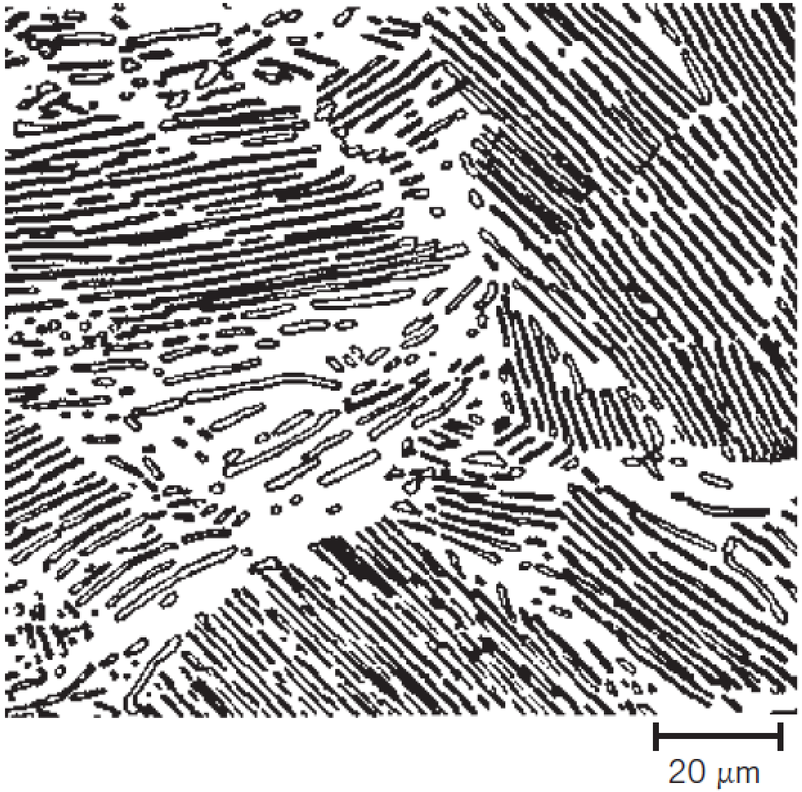
[3] Coagulation of the carbides.

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.



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS



Photomicrograph of a eutectoid steel showing the pearlite microstructure consisting of alternating layers of α-ferrite (the light phase) and Fe_3C (thin layers most of which appear dark). 470×. (From *Metals Handbook*, Vol. 9, 9th edition, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

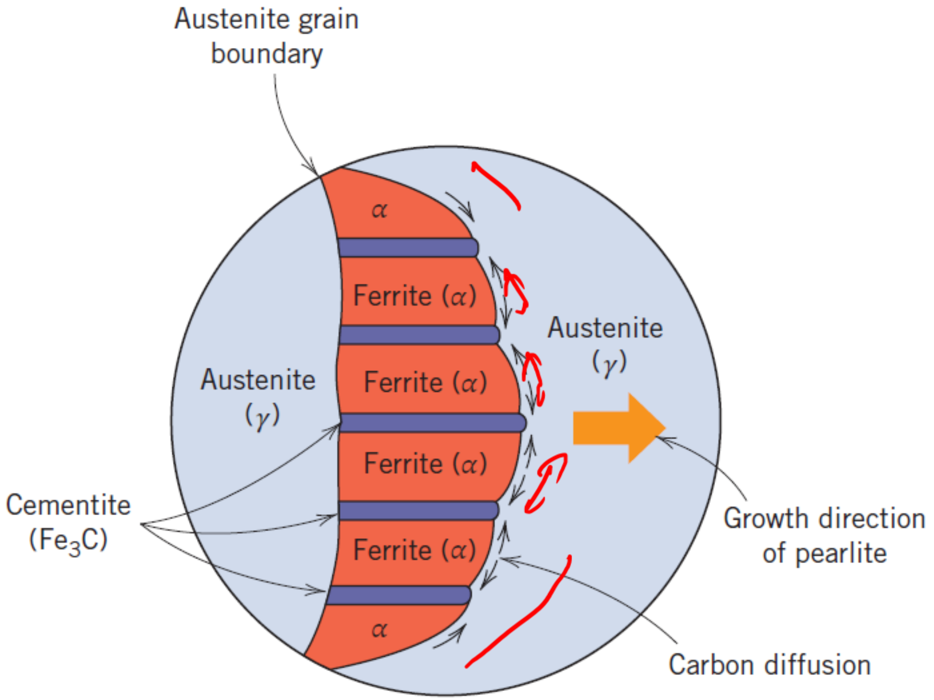
Pearlite: is a layered structure of ferrite and cementite. It forms if steel in the austenite region were allowed to cool slowly. (Simultaneous mixture of α and Fe_3C)

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).

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

DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

The alternating α and Fe_3C layers in pearlite form for the same reason that the eutectic structure forms—because the composition of the parent phase [in this case, austenite (0.76 wt% C)] is different from that of either of the product phases [ferrite (0.022 wt% C) and cementite (6.70 wt% C)], and the phase transformation requires that there be a redistribution of the carbon by diffusion.

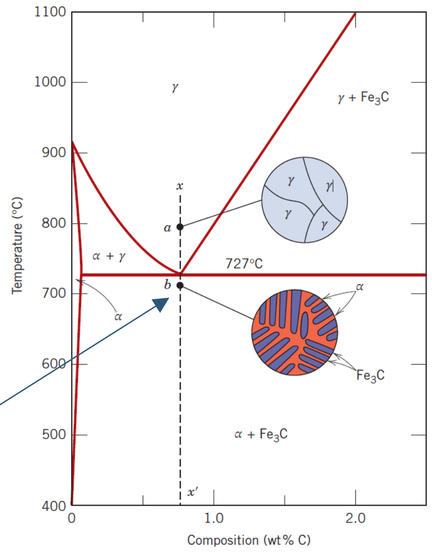


The shown figure illustrates microstructural changes that accompany this eutectoid reaction; here, the directions of carbon diffusion are indicated by arrows.

Carbon atoms diffuse away from the 0.022-wt% ferrite regions and to the 6.70-wt% cementite layers, as the pearlite extends from the grain boundary into the unreacted austenite grain.

The layered pearlite forms because carbon atoms need diffuse only minimal distances with the formation of this structure.

Subsequent cooling of the pearlite from point *b* produces relatively insignificant microstructural changes.



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

Hypoeutectoid Alloys

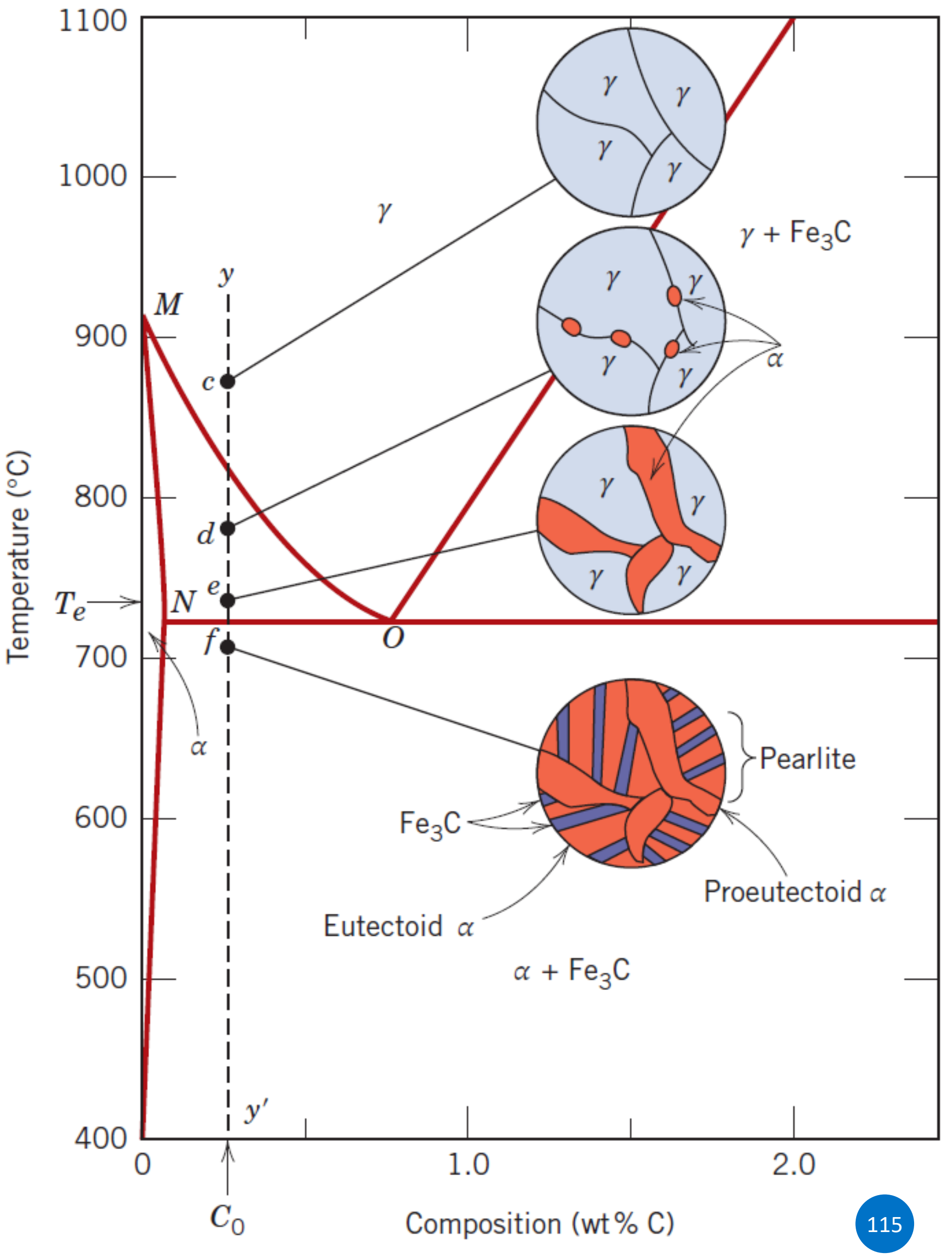
Microstructures for iron–iron carbide alloys having other than the eutectoid composition are now explored.

Consider a composition C_0 to the left of the eutectoid, between 0.022 and 0.76 wt% C; this is termed a **hypoeutectoid** ("less than eutectoid") **alloy.** Cooling an alloy of this composition is represented by moving down the vertical line *yy*′.

At about 875°C, point *c*, the microstructure consists entirely of grains of the γ phase, as shown schematically in the figure. In cooling to point *d*, about 775°C, which is within the $\alpha + \gamma$ phase region, both these phases coexist as in the schematic microstructure.

Most of the small α particles form along the original γ grain boundaries.

The compositions of both α and γ phases may be determined using the appropriate tie line; these compositions correspond, respectively, to about 0.020 and 0.40 wt% C.



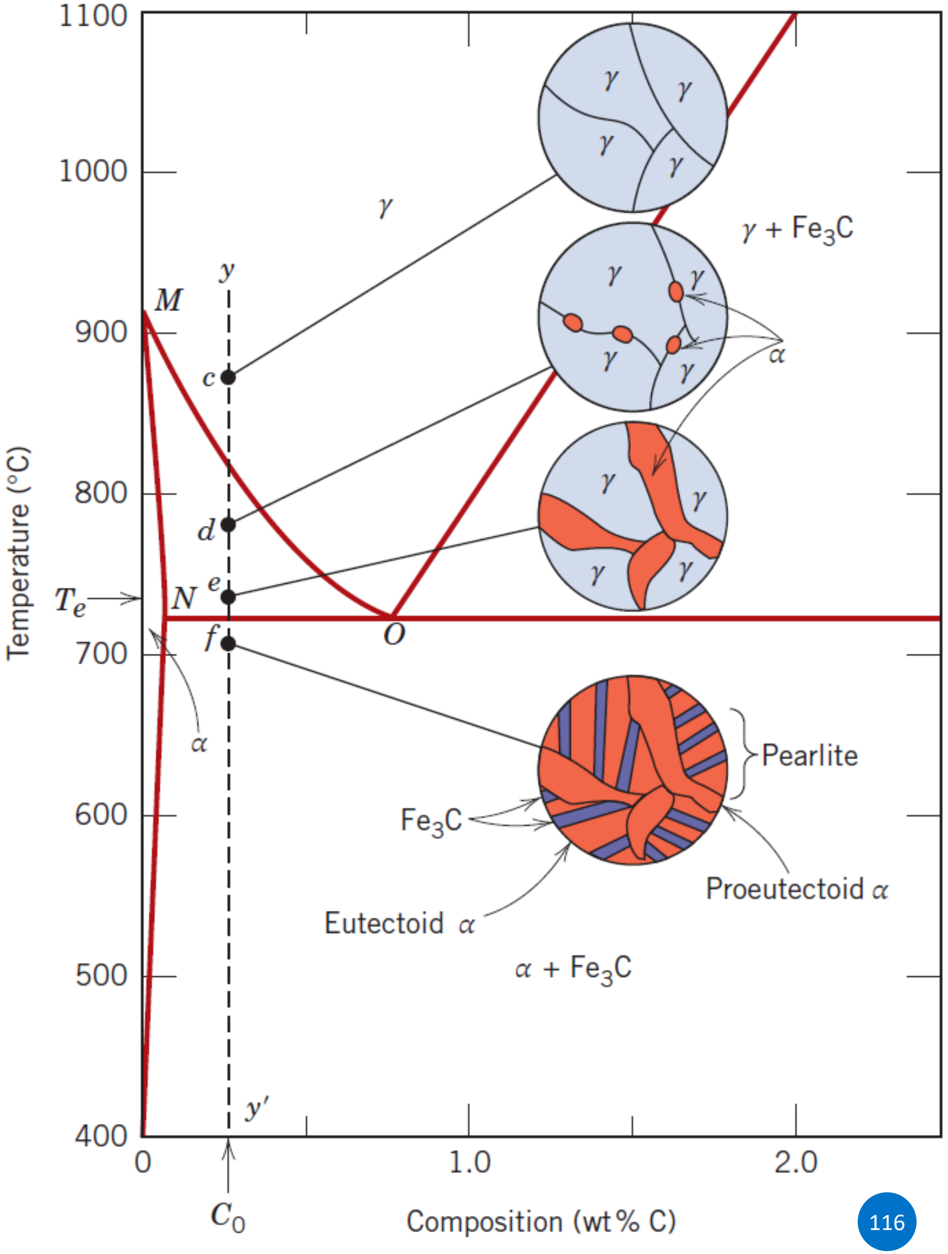
DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

While cooling an alloy through the $\alpha + \gamma$ phase region, the composition of the ferrite phase changes with temperature along the α–($\alpha + \gamma$) phase boundary, line *MN*, becoming slightly richer in carbon.

However, the change in composition of the austenite is more dramatic, proceeding along the ($\alpha + \gamma$)–γ boundary, line *MO*, as the temperature is reduced.

Cooling from point *d* to *e*, just above the eutectoid but still in the $\alpha + \gamma$ region, produces an increased fraction of the α phase and a microstructure similar to that also shown: the α particles will have grown larger.

At this point, the compositions of the α and γ phases are determined by constructing a tie line at the temperature T_e; the α phase contains 0.022 wt% C, whereas the γ phase is of the eutectoid composition, 0.76 wt% C.



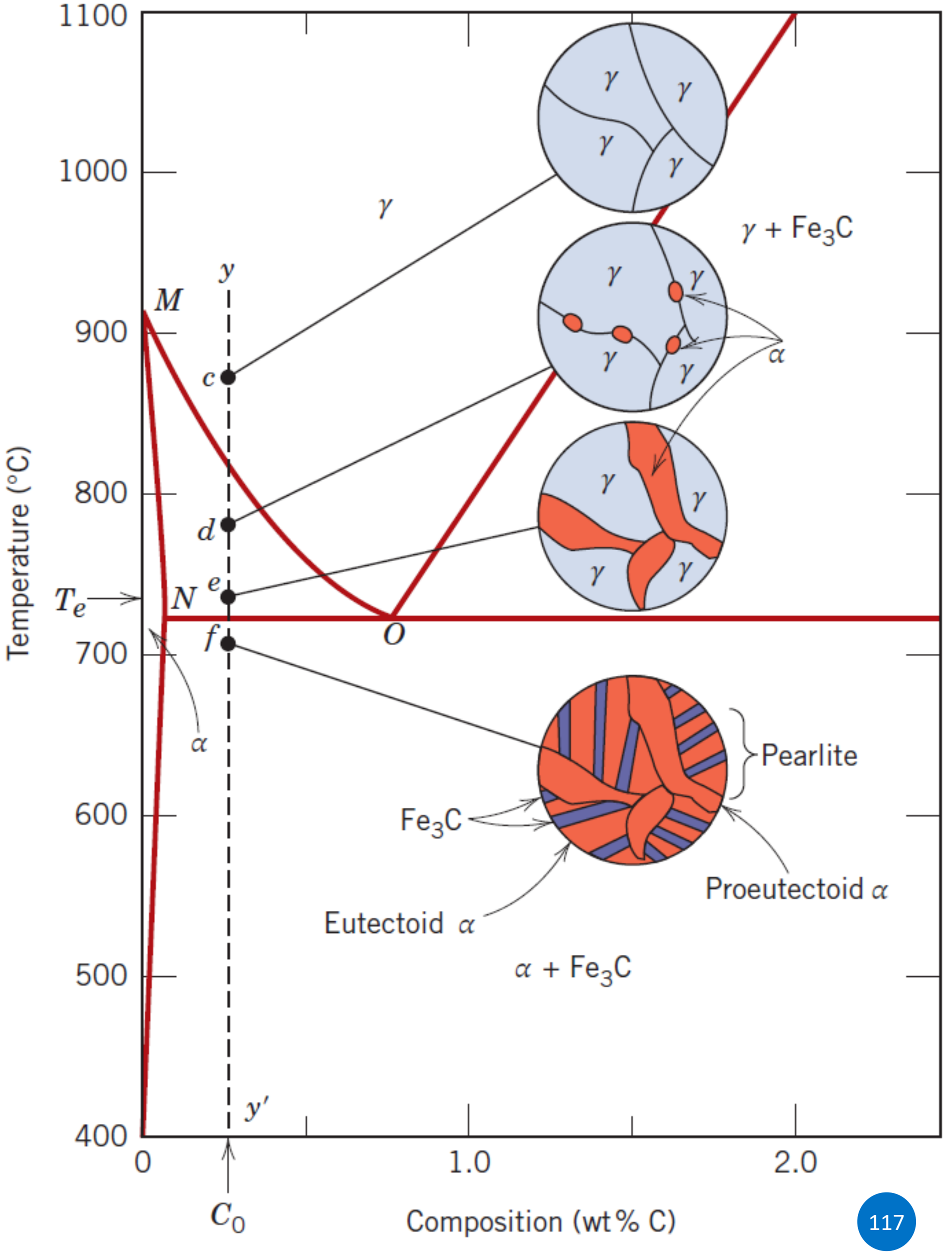
DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

As the temperature is lowered just below the eutectoid, to point f, all of the γ phase that was present at temperature T_e (and having the eutectoid composition) transforms into pearlite.

There is virtually no change in the α phase that existed at point e in crossing the eutectoid temperature—it is normally present as a continuous matrix phase surrounding the isolated pearlite colonies.

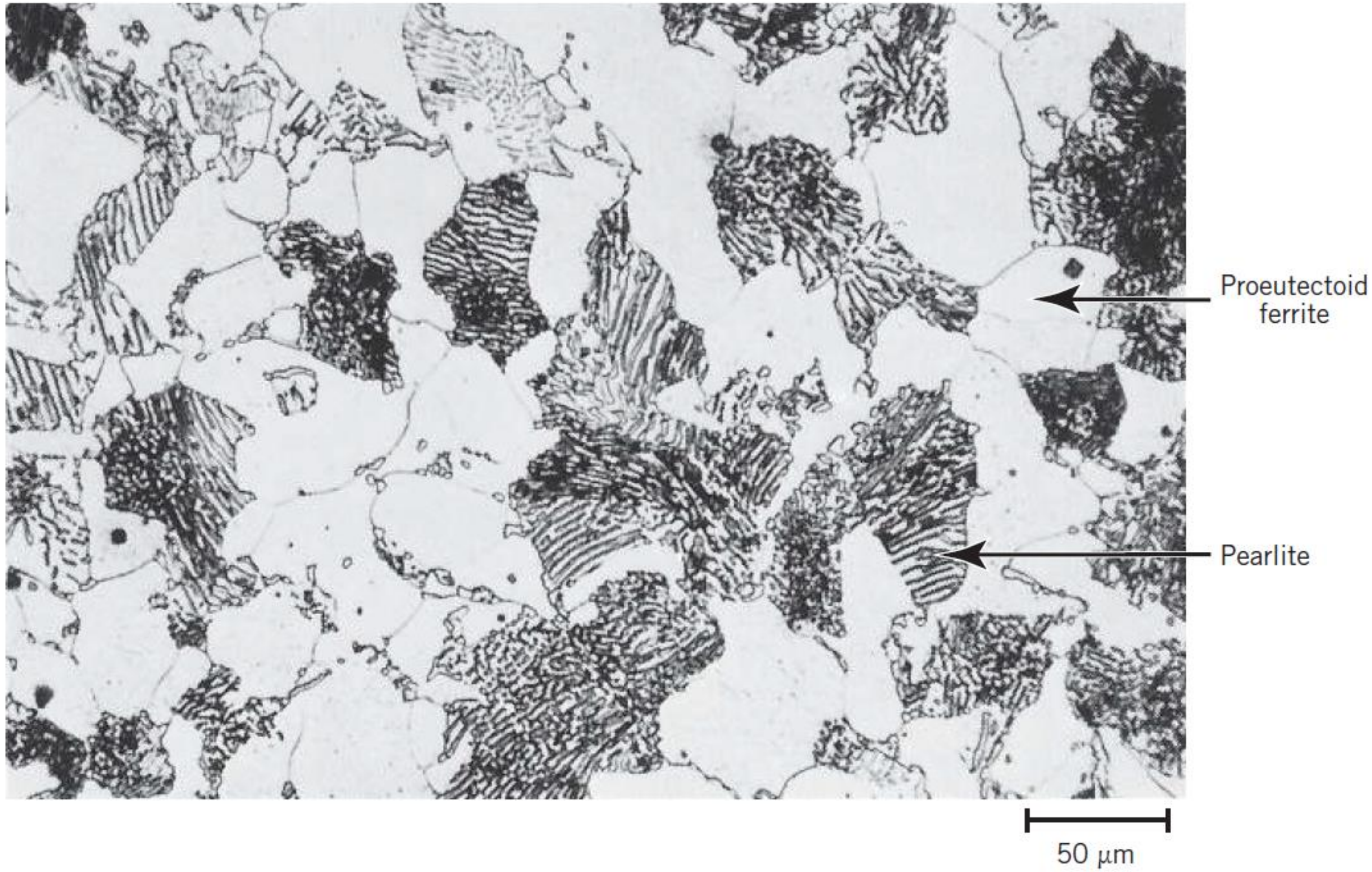
The microstructure at point f appears as the corresponding schematic inset. Thus the ferrite phase is present both in the pearlite and as the phase that formed while cooling through the $\alpha + \gamma$ phase region.

The ferrite present in the pearlite is called *eutectoid ferrite,* whereas the other, which formed above T_e, is termed **proeutectoid** (meaning "pre- or before eutectoid") **ferrite,** as labelled.



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

Photomicrograph of a 0.38 wt% C steel having a microstructure consisting of pearlite and proeutectoid ferrite. 635×. (Photomicrograph courtesy of Republic Steel Corporation.)



Photomicrograph of a 0.38-wt% C steel; large, white regions correspond to the proeutectoid ferrite. For pearlite, the spacing between the α and Fe_3C layers varies from grain to grain; some of the pearlite appears dark because the many close-spaced layers are unresolved at the magnification of the photomicrograph. Note that two microconstituents are present in this micrograph—proeutectoid ferrite and pearlite—which appear in all hypoeutectoid iron–carbon alloys that are slowly cooled to a temperature below the eutectoid.

DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

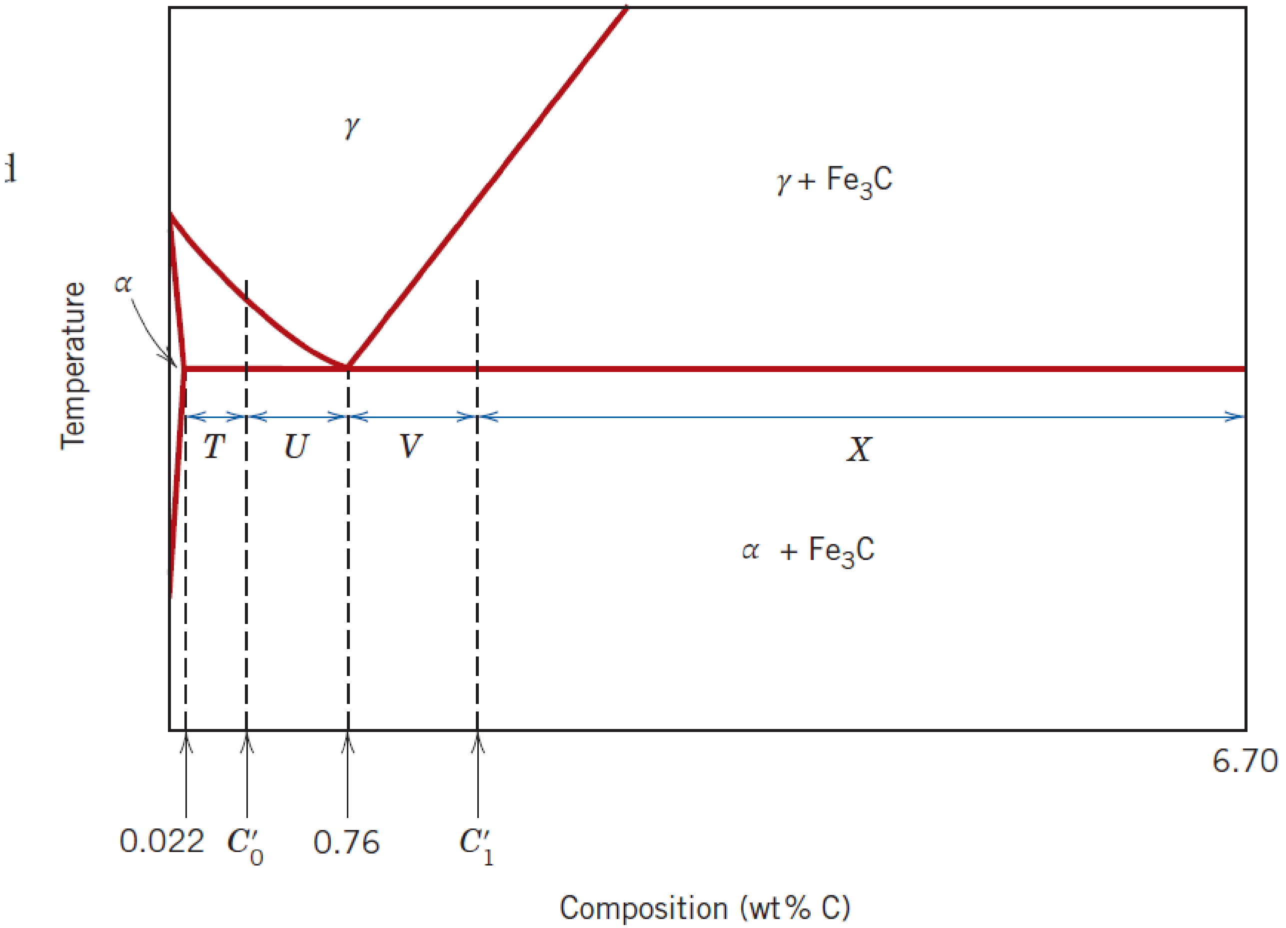
The relative amounts of the proeutectoid α and pearlite may be determined in a manner similar to that described previously for primary and eutectic microconstituents.

We use the lever rule in conjunction with a tie line that extends from the α–(α + Fe_3C) phase boundary (0.022-wt% C) to the eutectoid composition (0.76-wt% C) inasmuch as pearlite is the transformation product of austenite having this composition.

For example, let us consider an alloy of composition C_0'. The fraction of pearlite, W_p, may be determined according to

$$W_p = \frac{T}{T + U}$$

$$= \frac{C_0' - 0.022}{0.76 - 0.022} = \frac{C_0' - 0.022}{0.74}$$



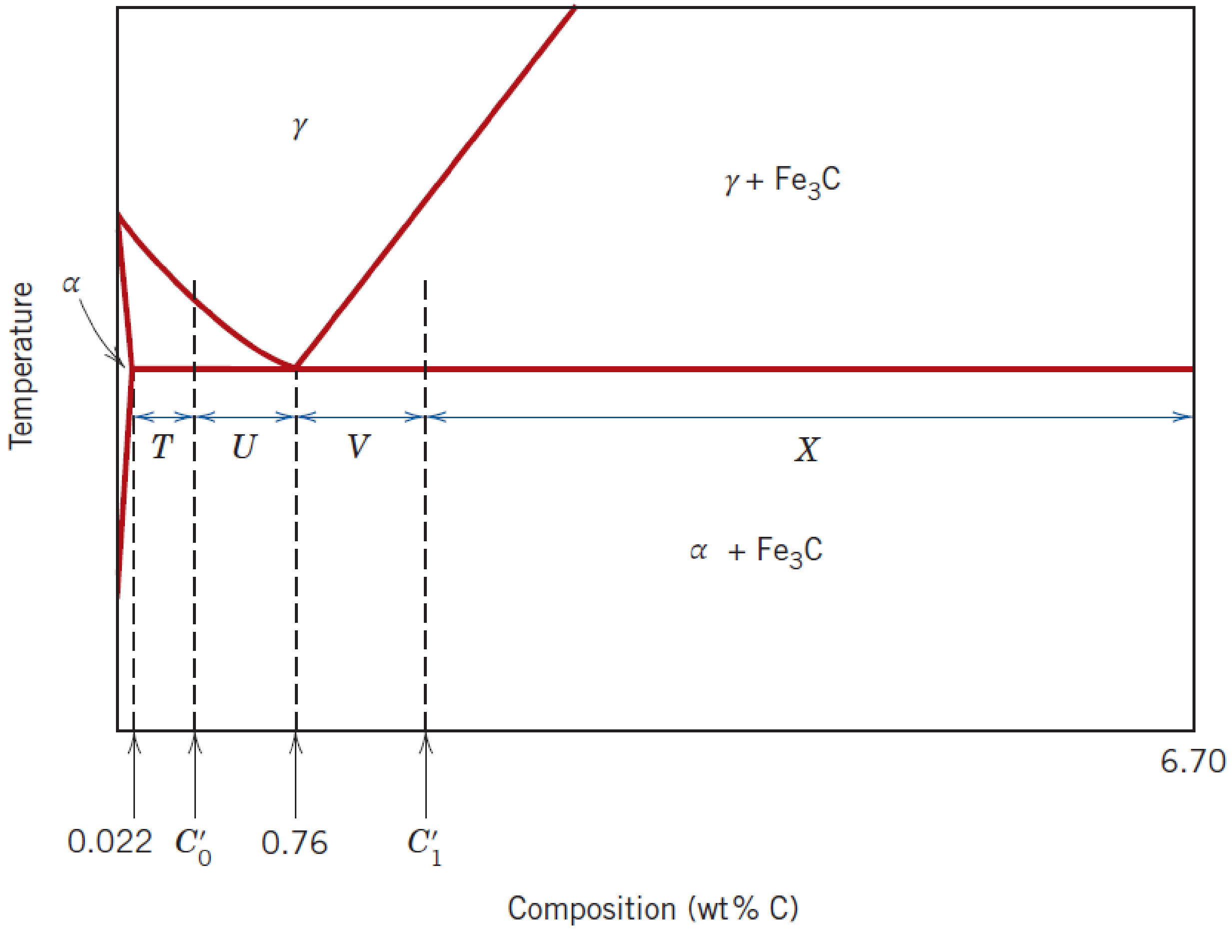
DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

The fraction of proeutectoid α, W_{α}', is computed as follows:

$$W_{\alpha'} = \frac{U}{T + U}$$

$$= \frac{0.76 - C_0'}{0.76 - 0.022} = \frac{0.76 - C_0'}{0.74}$$

Fractions of both total α (eutectoid and proeutectoid) and cementite are determined using the lever rule and a tie line that extends across the entirety of the α + Fe_3C phase region, from 0.022 to 6.70 wt% C.



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

Hypereutectoid Alloys

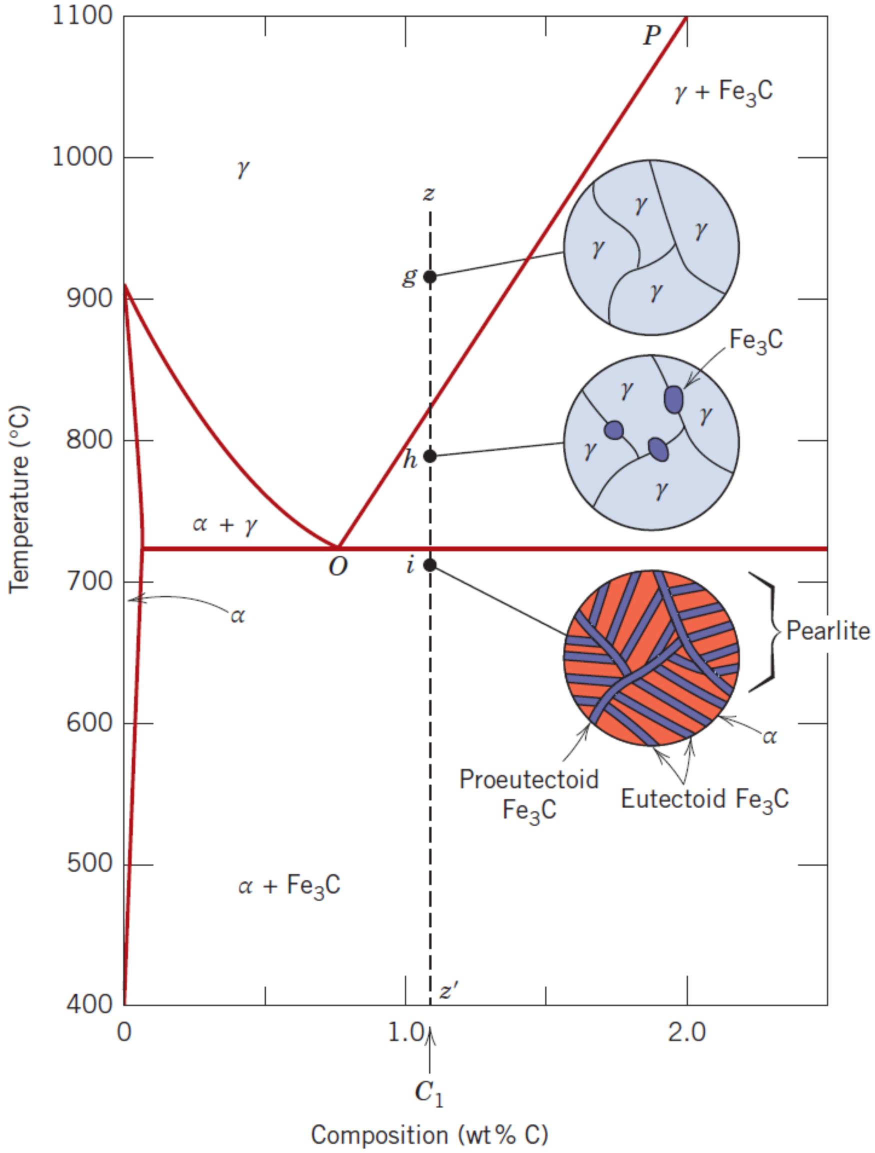
Analogous transformations and microstructures result for **hypereutectoid alloys**— those containing between 0.76 and 2.14 wt% C—that are cooled from temperatures within the γ-phase field.

Consider an alloy of composition C_1 that, upon cooling, moves down the line zz'. At point g, only the γ phase is present with a composition of C_1; the microstructure appears as shown, having only γ grains.

Upon cooling into the $\gamma + Fe_3C$ phase field—say, to point h—the cementite phase begins to form along the initial γ grain boundaries/

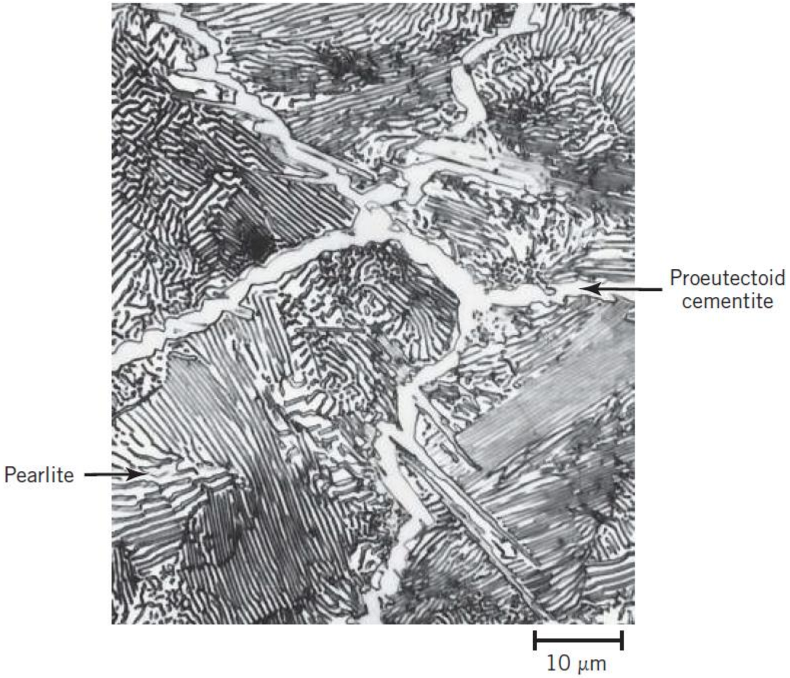
This cementite is called **proeutectoid cementite**—that which forms before the eutectoid reaction.

The cementite composition remains constant (6.70 wt% C) as the temperature changes. However, the composition of the austenite phase moves along line PO toward the eutectoid.

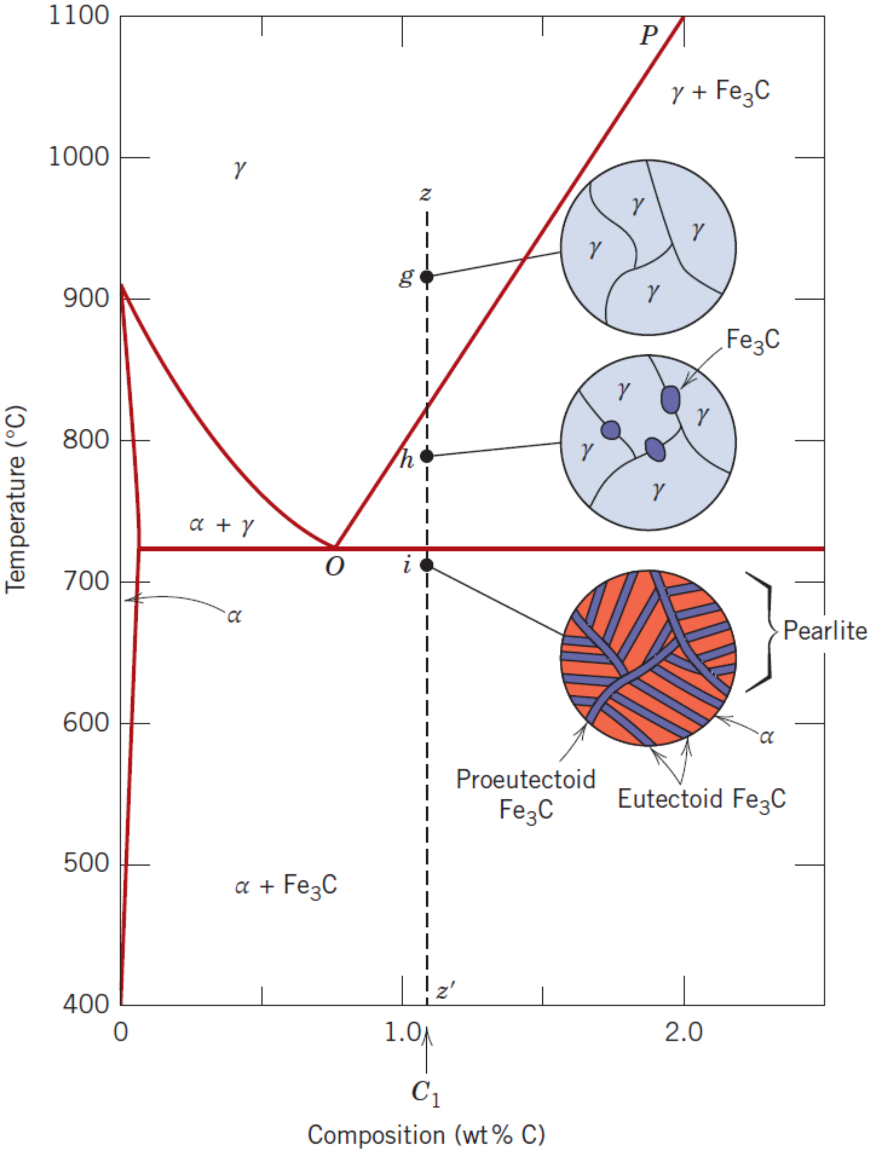


DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

As the temperature is lowered through the eutectoid to point *i*, all remaining austenite of eutectoid composition is converted into pearlite; thus, the resulting microstructure consists of pearlite and proeutectoid cementite as microconstituents.



In the photomicrograph of a 1.4-wt% C steel, note that the proeutectoid cementite appears light.



Because it has much the same appearance as proeutectoid ferrite, there is some difficulty in distinguishing between hypoeutectoid and hypereutectoid steels on the basis of microstructure.

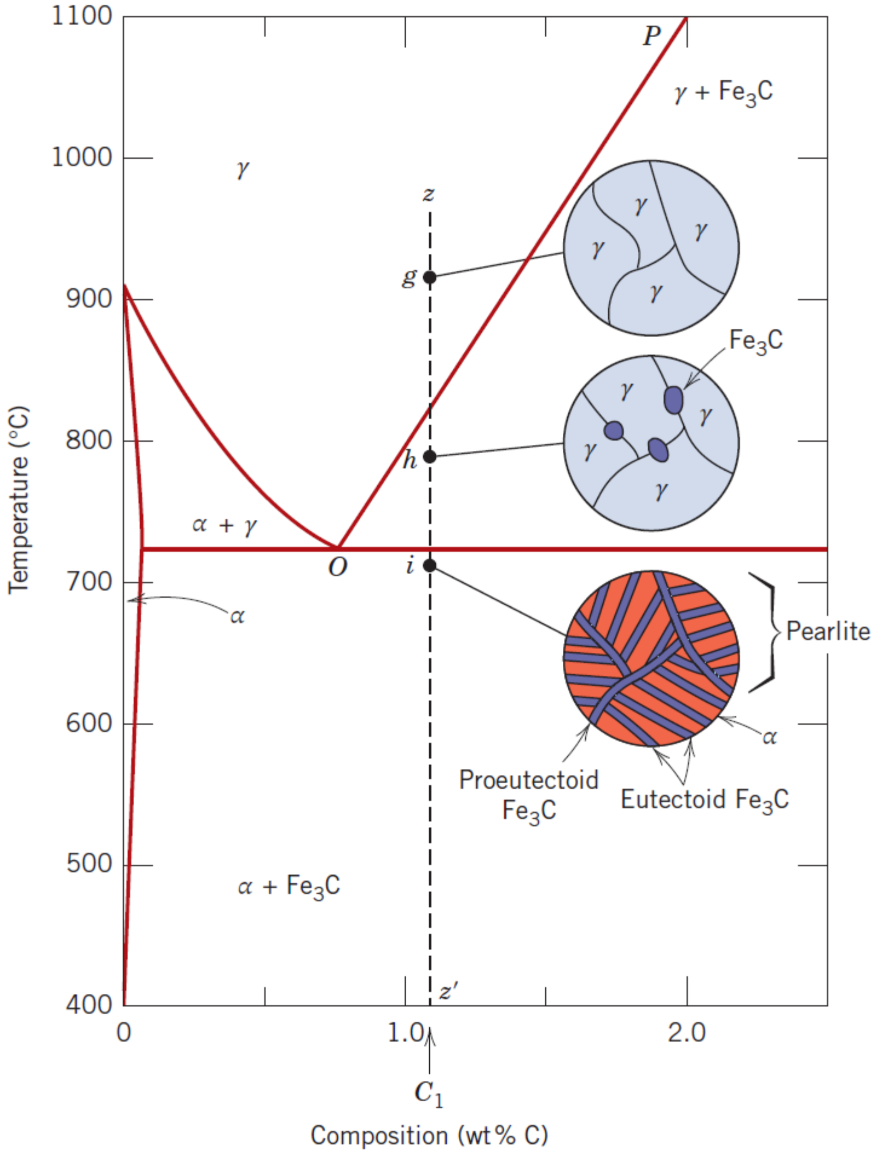
DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

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

Hypereutectoid reaction takes place when:

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

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



DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

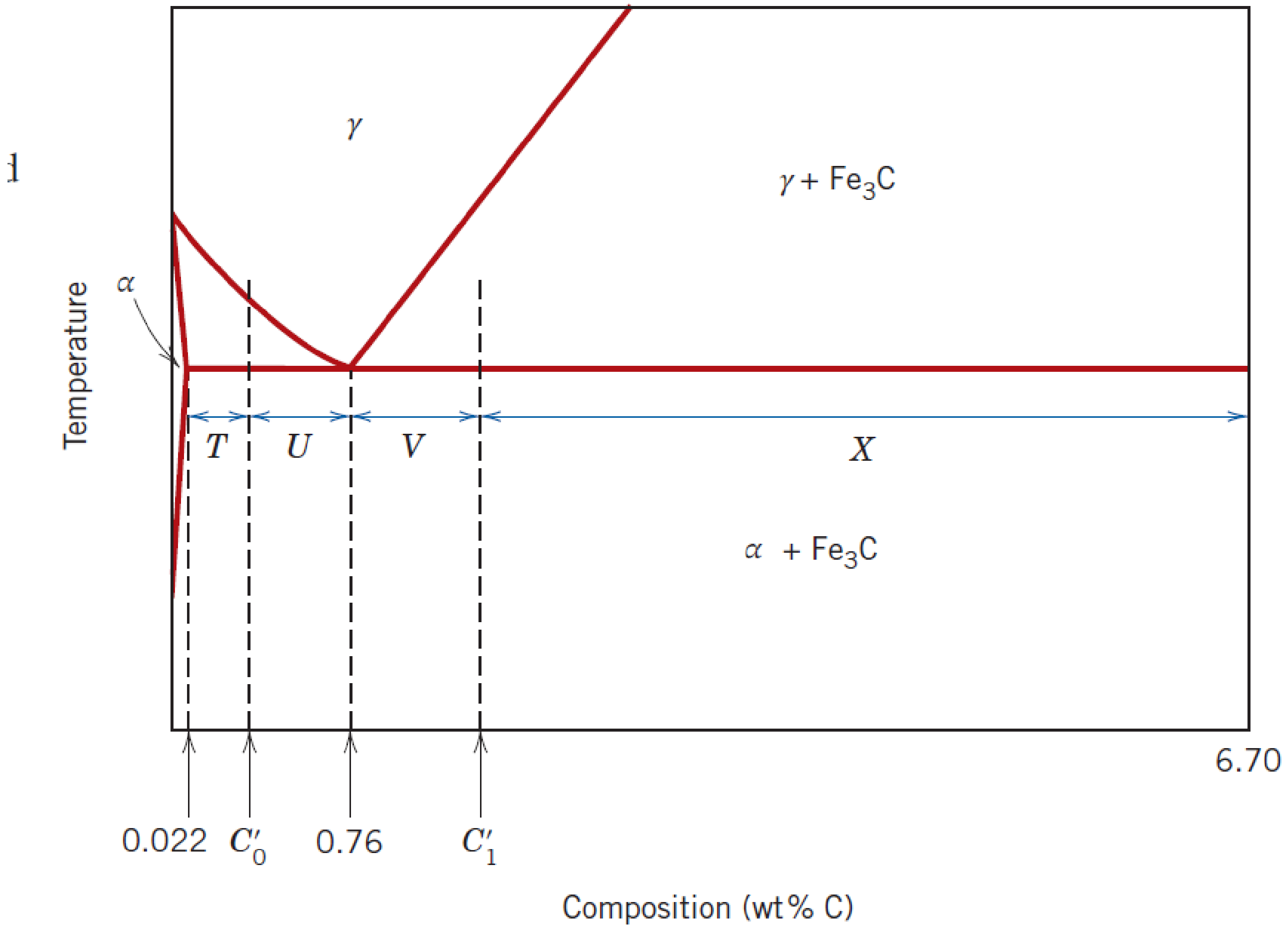
Relative amounts of both pearlite and proeutectoid Fe_3C microconstituents may be computed for hypereutectoid steel alloys in a manner analogous to that for hypoeutectoid materials; the appropriate tie line extends between 0.76 and 6.70 wt% C.

Thus, for an alloy having composition C_1', fractions of pearlite W_p and proeutectoid cementite W_{Fe3C}' are determined from the following lever rule expressions:

$$W_p = \frac{X}{V + X} = \frac{6.70 - C_1'}{6.70 - 0.76} = \frac{6.70 - C_1'}{5.94}$$

and

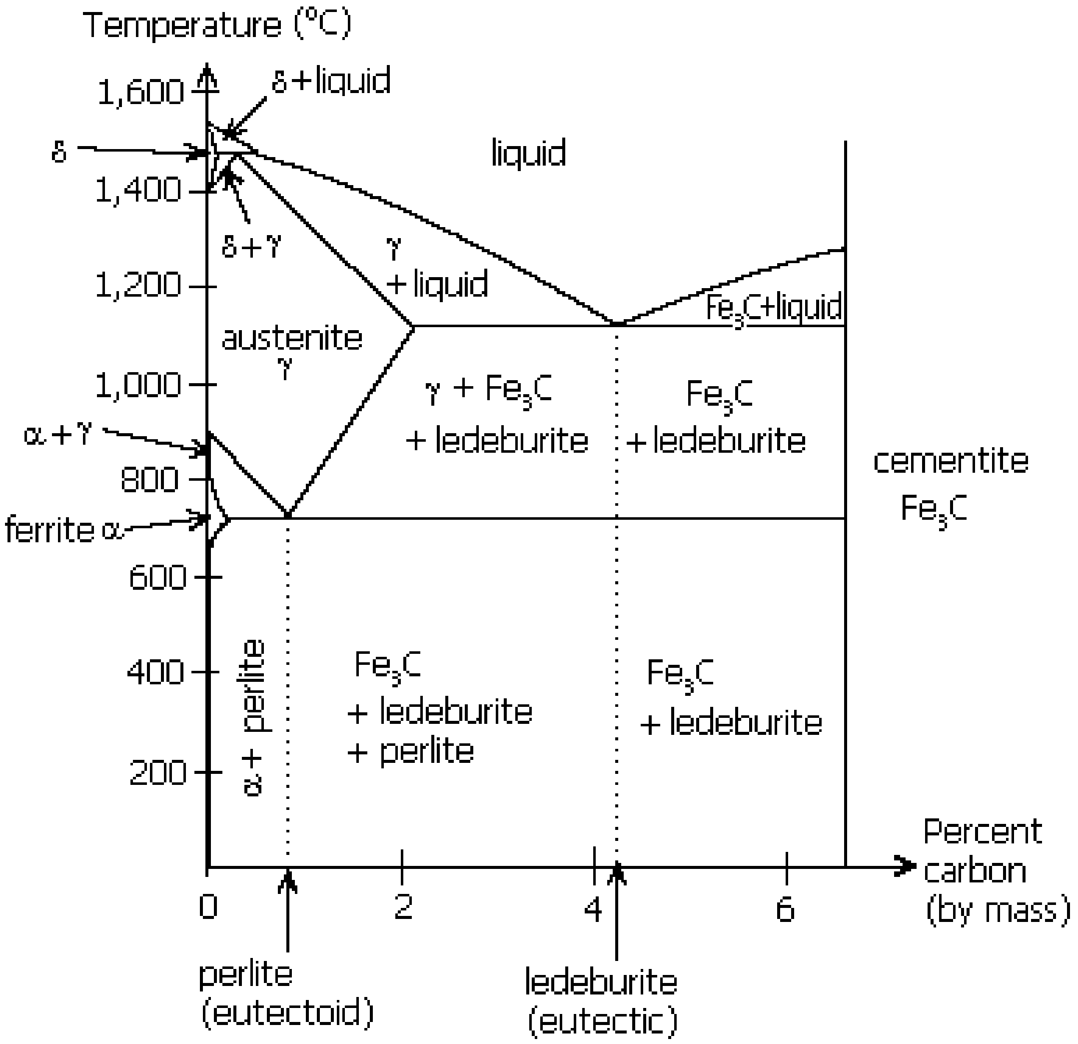
$$W_{Fe_3C'} = \frac{V}{V + X} = \frac{C_1' - 0.76}{6.70 - 0.76} = \frac{C_1' - 0.76}{5.94}$$



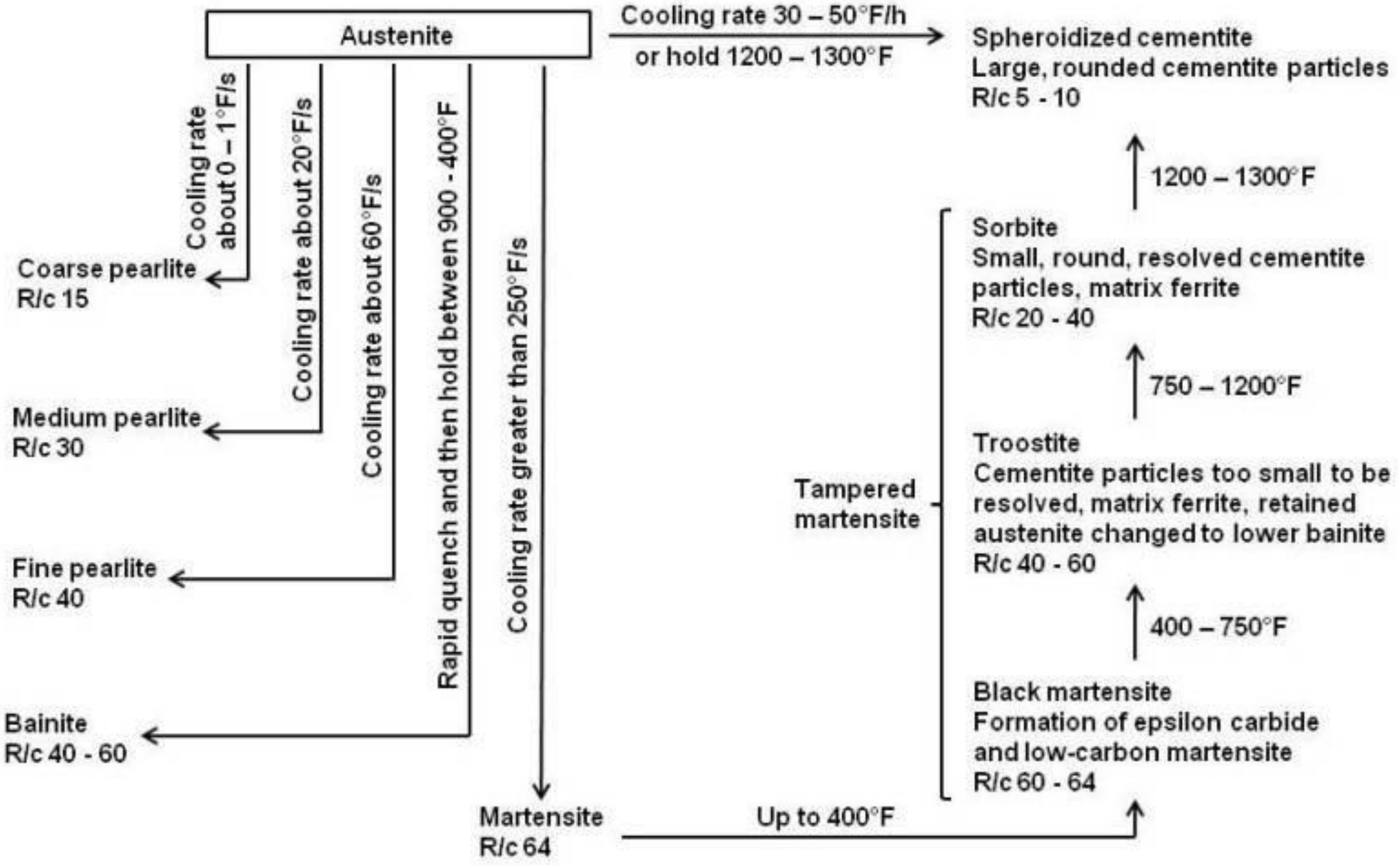
PRE-LECTURE QUESTION!

- Photomicrographs of alpha-ferrite, Gamma-Austenite and Delta-Ferrite
- Why FCC octahedral sites are larger than the BCC tetrahedral sites? Show!
- What's the difference between carbide, cementite and martensite?
- what is pearlite?
- what do you mean by metastable?
- Eutectic, eutectoid and hypoeutectoid, proeutectoid, hypereutectoid: what are these?

- What is quenching? Annealing?



PRE-LECTURE QUESTION!



Transformation products of austenite and martensite for a eutectoid steel

Austenite | Metallurgy for Dummies

DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

Nonequilibrium Cooling

In this discussion of the microstructural development of iron–carbon alloys, it has *been assumed* that, upon cooling, conditions of metastable equilibrium have been continuously maintained; that is, sufficient time has been allowed at each new temperature for any necessary adjustment in phase compositions and relative amounts as predicted from the Fe–Fe_3C phase diagram.

In most situations these cooling rates are impractically slow and unnecessary; in fact, on many occasions nonequilibrium conditions are desirable.

Two nonequilibrium effects of practical importance are

(1) the occurrence of phase changes or transformations at temperatures other than those predicted by phase boundary lines on the phase diagram, and

(2) the existence at room temperature of nonequilibrium phases that do not appear on the phase diagram.

THE INFLUENCE OF OTHER ALLOYING ELEMENTS

Additions of other alloying elements (Cr, Ni, Ti, etc.) bring about rather dramatic changes in the binary iron–iron carbide phase diagram. 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 carbon concentration.

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.