

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 relationships among heat treatment, microstructure, and mechanical properties are explored in Chapters 10 and 11.

9.18 THE IRON–IRON CARBIDE ($\text{Fe–Fe}_3\text{C}$) PHASE DIAGRAM

ferrite

austenite

A portion of the iron–carbon phase diagram is presented in Figure 9.24. Pure iron, upon heating, experiences two changes in crystal structure before it melts. At room temperature the stable form, called **ferrite**, or α iron, has a BCC crystal structure. Ferrite experiences a polymorphic transformation to FCC **austenite**, or γ iron, at 912°C (1674°F). This austenite persists to 1394°C (2541°F), at which temperature the FCC austenite reverts back to a BCC phase known as δ ferrite, which finally

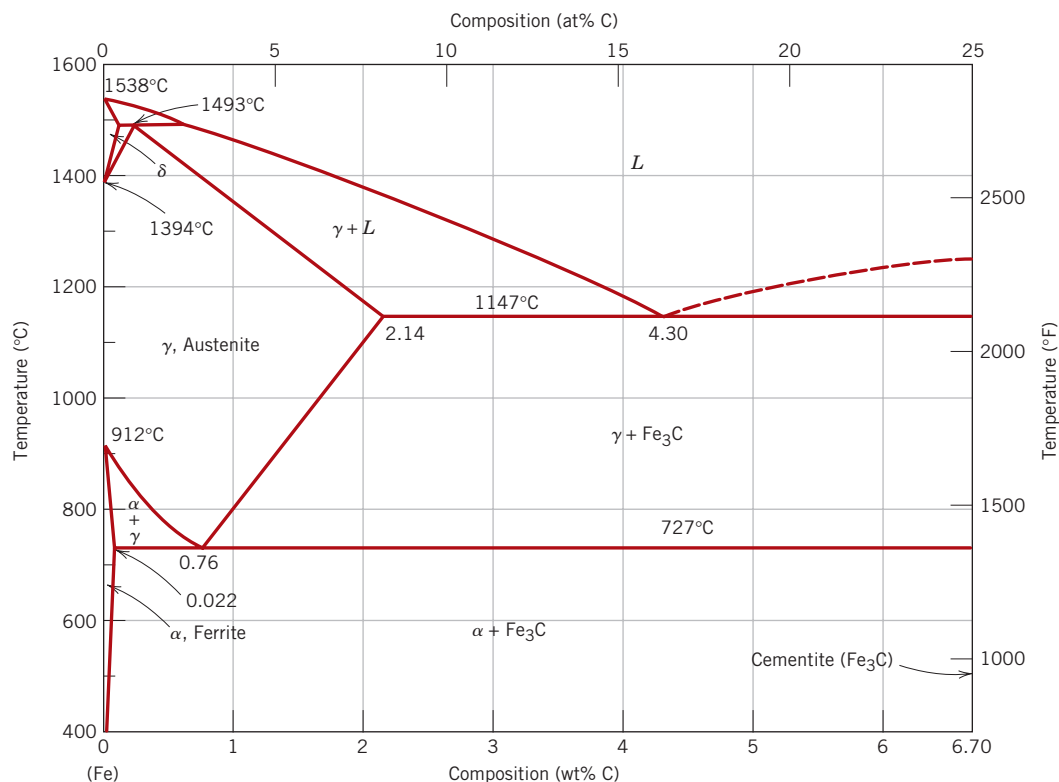
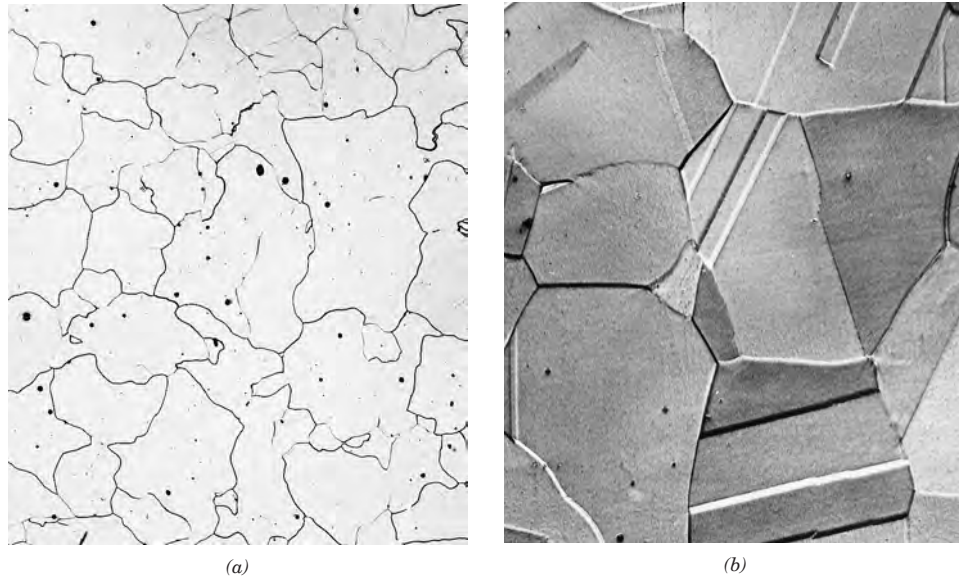


Figure 9.24 The iron–iron carbide phase diagram. [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

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Figure 9.25
Photomicrographs of
(a) α ferrite (90 \times)
and (b) austenite
(325 \times). (Copyright
1971 by United
States Steel
Corporation.)



cementite

melts at 1538°C (2800°F). All these changes are apparent along the left vertical axis of the phase diagram.¹

The composition axis in Figure 9.24 extends only to 6.70 wt% C; at this concentration the intermediate compound iron carbide, or **cementite** (Fe_3C), is formed, which is represented by a vertical line on the phase diagram. Thus, the iron–carbon system may be divided into two parts: an iron-rich portion, as in Figure 9.24, and the other (not shown) for compositions between 6.70 and 100 wt% C (pure graphite). In practice, all steels and cast irons have carbon contents less than 6.70 wt% C; therefore, we consider only the iron–iron carbide system. Figure 9.24 would be more appropriately labeled the $\text{Fe}-\text{Fe}_3\text{C}$ phase diagram, since Fe_3C is now considered to be a component. Convention and convenience dictate that composition still be expressed in “wt% C” rather than “wt% Fe_3C ”; 6.70 wt% C corresponds to 100 wt% Fe_3C .

Carbon is an interstitial impurity in iron and forms a solid solution with each of α and δ ferrites, and also with austenite, as indicated by the α , δ , and γ single-phase fields in Figure 9.24. In the BCC α ferrite, only small concentrations of carbon are soluble; the maximum solubility is 0.022 wt% at 727°C (1341°F). The limited solubility is explained by the shape and size of the BCC interstitial positions, which make it difficult to accommodate the carbon atoms. Even though present in relatively low concentrations, carbon significantly influences the mechanical properties of ferrite. This particular iron–carbon phase is relatively soft, may be made magnetic at temperatures below 768°C (1414°F), and has a density of 7.88 g/cm³. Figure 9.25a is a photomicrograph of α ferrite.

¹ The reader may wonder why no β phase is found on the $\text{Fe}-\text{Fe}_3\text{C}$ phase diagram, Figure 9.24 (consistent with the α , β , γ , etc. labeling scheme described previously). Early investigators observed that the ferromagnetic behavior of iron disappears at 768°C and attributed this phenomenon to a phase transformation; the “ β ” label was assigned to the high-temperature phase. Later it was discovered that this loss of magnetism did not result from a phase transformation (see Section 20.6) and, therefore, the presumed β phase did not exist.

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The austenite, or γ phase of iron, when alloyed with carbon alone, is not stable below 727°C (1341°F), as indicated in Figure 9.24. The maximum solubility of carbon in austenite, 2.14 wt%, occurs at 1147°C (2097°F). This solubility is approximately 100 times greater than the maximum for BCC ferrite, since the FCC interstitial positions are larger (see the results of Problem 4.5), and, therefore, the strains imposed on the surrounding iron atoms are much lower. As the discussions that follow demonstrate, phase transformations involving austenite are very important in the heat treating of steels. In passing, it should be mentioned that austenite is non-magnetic. Figure 9.25*b* shows a photomicrograph of this austenite phase.

The δ ferrite is virtually the same as α ferrite, except for the range of temperatures over which each exists. Since the δ ferrite is stable only at relatively high temperatures, it is of no technological importance and is not discussed further.

Cementite (Fe_3C) forms when the solubility limit of carbon in α ferrite is exceeded below 727°C (1341°F) (for compositions within the $\alpha + \text{Fe}_3\text{C}$ phase region). As indicated in Figure 9.24, Fe_3C will also coexist with the γ phase between 727 and 1147°C (1341 and 2097°F). Mechanically, cementite is very hard and brittle; the strength of some steels is greatly enhanced by its presence.

Strictly speaking, cementite is only metastable; that is, it will remain as a compound indefinitely at room temperature. However, if heated to between 650 and 700°C (1200 and 1300°F) for several years, it will gradually change or transform into α iron and carbon, in the form of graphite, which will remain upon subsequent cooling to room temperature. Thus, the phase diagram in Figure 9.24 is not a true equilibrium one because cementite is not an equilibrium compound. However, inasmuch as the decomposition rate of cementite is extremely sluggish, virtually all the carbon in steel will be as Fe_3C instead of graphite, and the iron–iron carbide phase diagram is, for all practical purposes, valid. As will be seen in Section 11.2, addition of silicon to cast irons greatly accelerates this cementite decomposition reaction to form graphite.

The two-phase regions are labeled in Figure 9.24. 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,

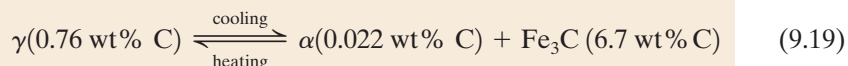
Eutectic reaction for
the iron-iron carbide
system



the liquid solidifies to form austenite and cementite phases. Of course, subsequent cooling to room temperature will promote additional phase changes.

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

Eutectoid reaction for
the iron-iron
carbide system



or, upon cooling, the solid γ phase is transformed into α iron and cementite. (Eutectoid phase transformations were addressed in Section 9.14.) The eutectoid phase changes described by Equation 9.19 are very important, being fundamental to the heat treatment of steels, as explained in subsequent discussions.

Ferrous alloys are those in which iron is the prime component, but carbon as well as other alloying elements may be present. In the classification scheme of ferrous alloys based on carbon content, there are three types: iron, steel, and cast iron. Commercially pure iron contains less than 0.008 wt% C and, from the phase diagram, is composed almost exclusively of the ferrite phase at room temperature. The

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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, as discussed below. Although a steel alloy may contain as much as 2.14 wt% C, in practice, carbon concentrations rarely exceed 1.0 wt%. The properties and various classifications of steels are treated in Section 11.2. Cast irons are classified as ferrous alloys that contain between 2.14 and 6.70 wt% C. However, commercial cast irons normally contain less than 4.5 wt% C. These alloys are discussed further also in Section 11.2.

9.19 DEVELOPMENT OF MICROSTRUCTURE IN IRON–CARBON ALLOYS

Several of the various microstructures that may be produced in steel alloys and their relationships to the iron–iron carbon phase diagram are now discussed, and it is shown that the microstructure that develops depends on both the carbon content and heat treatment. This discussion is confined to very slow cooling of steel alloys, in which equilibrium is continuously maintained. A more detailed exploration of the influence of heat treatment on microstructure, and ultimately on the mechanical properties of steels, is contained in Chapter 10.

Phase changes that occur upon passing from the γ region into the $\alpha + \text{Fe}_3\text{C}$ phase field (Figure 9.24) are relatively complex and similar to those described for the eutectic systems in Section 9.12. 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* in Figure 9.26 and moving down the

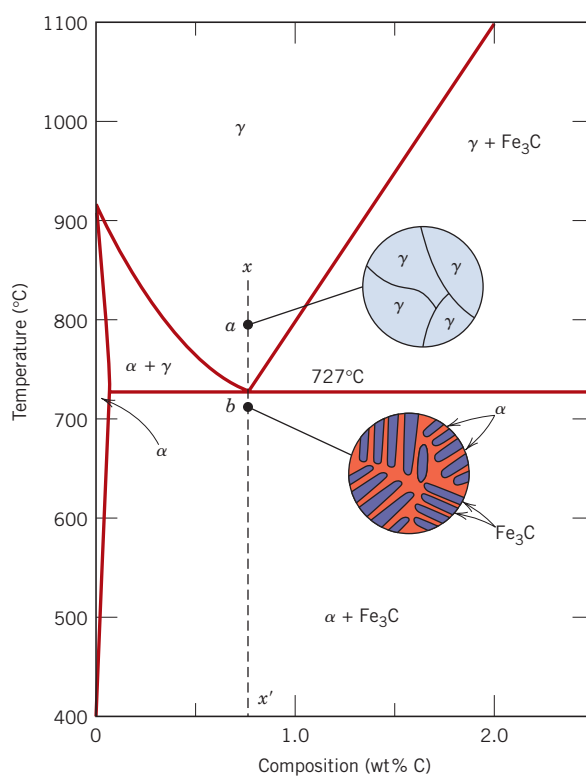


Figure 9.26 Schematic representations of the microstructures for an iron–carbon alloy of eutectoid composition (0.76 wt% C) above and below the eutectoid temperature.

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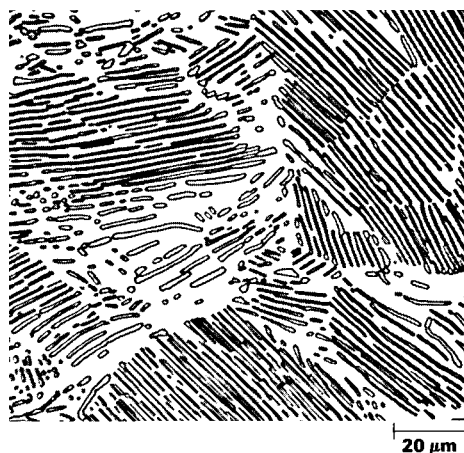


Figure 9.27 Photomicrograph of a eutectoid steel showing the pearlite microstructure consisting of alternating layers of α ferrite (the light phase) and Fe_3C (thin layers most of which appear dark). 500 \times . (Reproduced with permission from *Metals Handbook*, 9th edition, Vol. 9, *Metallography and Microstructures*, American Society for Metals, Materials Park, OH, 1985.)

pearlite

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 in Figure 9.26. As the alloy is cooled, there will occur no changes until the eutectoid temperature (727°C) is reached. Upon crossing this temperature to point b , the austenite transforms according to Equation 9.19.

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. This microstructure, represented schematically in Figure 9.26, point b , is called **pearlite** because it has the appearance of mother of pearl when viewed under the microscope at low magnifications. Figure 9.27 is a photomicrograph of a eutectoid steel showing the pearlite. 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 the soft, ductile ferrite and the hard, brittle cementite.

The alternating α and Fe_3C layers in pearlite form as such for the same reason that the eutectic structure (Figures 9.13 and 9.14) forms—because the composition of the parent phase [in this case austenite (0.76 wt% C)] is different from either of the product phases [ferrite (0.022 wt% C) and cementite (6.7 wt% C)], and the phase transformation requires that there be a redistribution of the carbon by diffusion. Figure 9.28 illustrates schematically 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 6.7 wt% cementite layers, as the pearlite extends from the grain boundary into the unreacted austenite grain. The layered pearlite forms because carbon atoms need diffuse only minimal distances with the formation of this structure.

Furthermore, subsequent cooling of the pearlite from point b in Figure 9.26 will produce relatively insignificant microstructural changes.

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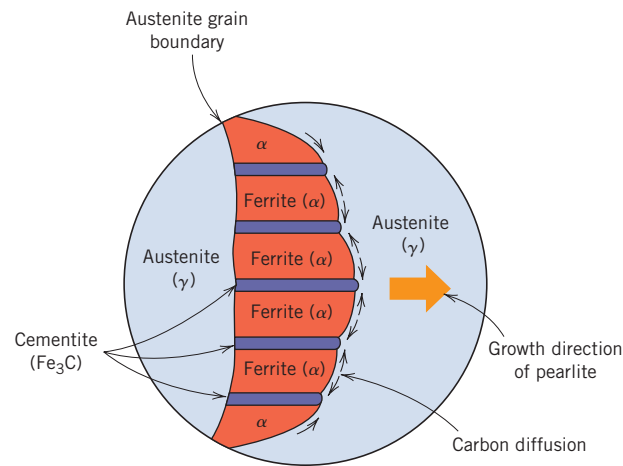


Figure 9.28 Schematic representation of the formation of pearlite from austenite; direction of carbon diffusion indicated by arrows.

Hypoeutectoid Alloys

hypoeutectoid alloy

Microstructures for iron–iron carbide alloys having other than the eutectoid composition are now explored; these are analogous to the fourth case described in Section 9.12 and illustrated in Figure 9.16 for the eutectic system. 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' in Figure 9.29. At about 875°C, point c , the microstructure will consist entirely of grains of the γ phase, as shown

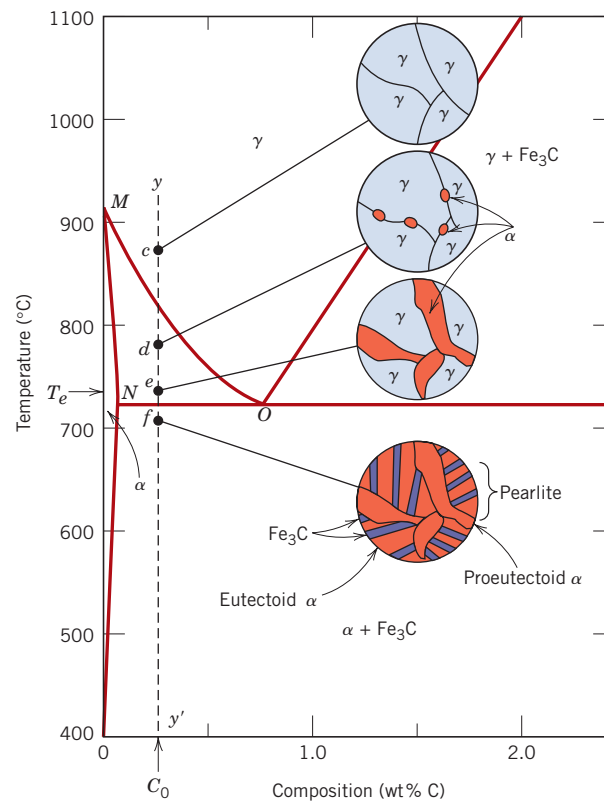


Figure 9.29 Schematic representations of the microstructures for an iron–carbon alloy of hypoeutectoid composition C_0 (containing less than 0.76 wt% C) as it is cooled from within the austenite phase region to below the eutectoid temperature.

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schematically in the figure. In cooling to point *d*, about 775°C, which is within the $\alpha + \gamma$ phase region, both these phases will coexist as in the schematic microstructure. Most of the small α particles will 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.

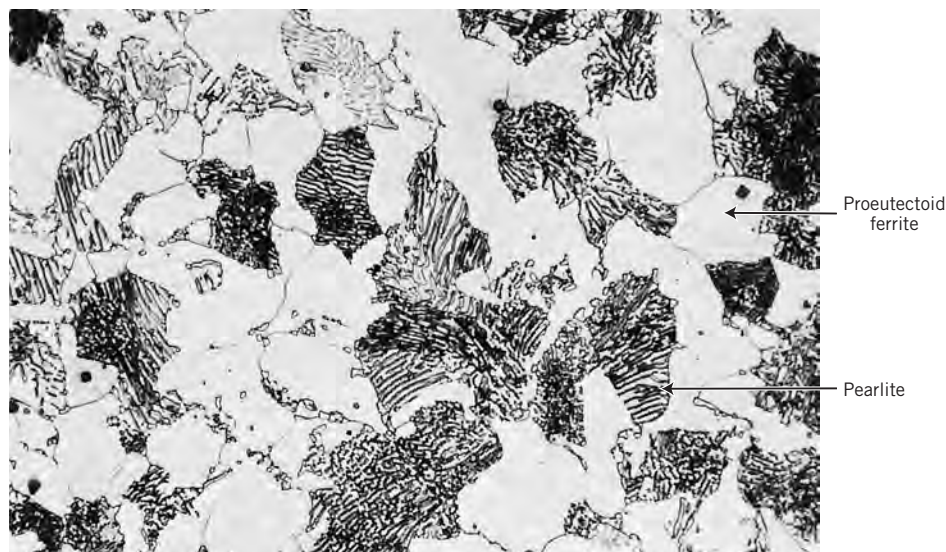
While cooling an alloy through the $\alpha + \gamma$ phase region, the composition of the ferrite phase changes with temperature along the $\alpha - (\alpha + \gamma)$ phase boundary, line *MN*, becoming slightly richer in carbon. On the other hand, the change in composition of the austenite is more dramatic, proceeding along the $(\alpha + \gamma) - \gamma$ 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, will produce 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 will contain 0.022 wt% C, while the γ phase will be of the eutectoid composition, 0.76 wt% C.

As the temperature is lowered just below the eutectoid, to point *f*, all the γ phase that was present at temperature T_e (and having the eutectoid composition) will transform to pearlite, according to the reaction in Equation 9.19. There will be virtually no change in the α phase that existed at point *e* in crossing the eutectoid temperature—it will normally be present as a continuous matrix phase surrounding the isolated pearlite colonies. The microstructure at point *f* will appear as the corresponding schematic inset of Figure 9.29. Thus the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the $\alpha + \gamma$ phase region. The ferrite that is present in the pearlite is called *eutectoid ferrite*, whereas the other, that formed above T_e , is termed **proeutectoid** (meaning pre- or before eutectoid) **ferrite**, as labeled in Figure 9.29. Figure 9.30 is a 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. The

proeutectoid ferrite

Figure 9.30
Photomicrograph
of a 0.38 wt% C
steel having a
microstructure
consisting of pearlite
and proeutectoid
ferrite. 635 \times .
(Photomicrograph
courtesy of Republic
Steel Corporation.)



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chapter-opening photograph for this chapter is a scanning electron micrograph of a hypoeutectoid (0.44 wt% C) steel in which may also be seen both pearlite and proeutectoid ferrite, only at a higher magnification. Note also that two microconstituents are present in these micrographs—proeutectoid ferrite and pearlite—which will appear in all hypoeutectoid iron–carbon alloys that are slowly cooled to a temperature below the eutectoid.

The relative amounts of the proeutectoid α and pearlite may be determined in a manner similar to that described in Section 9.12 for primary and eutectic microconstituents. We use the lever rule in conjunction with a tie line that extends from the $\alpha - (\alpha + \text{Fe}_3\text{C})$ 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 in Figure 9.31. Thus, the fraction of pearlite, W_p , may be determined according to

Lever rule
expression for
computation of
pearlite mass
fraction
(composition C'_0 ,
Figure 9.31)

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

$$= \frac{C'_0 - 0.022}{0.76 - 0.022} = \frac{C'_0 - 0.022}{0.74} \quad (9.20)$$

Furthermore, the fraction of proeutectoid α , $W_{\alpha'}$, is computed as follows:

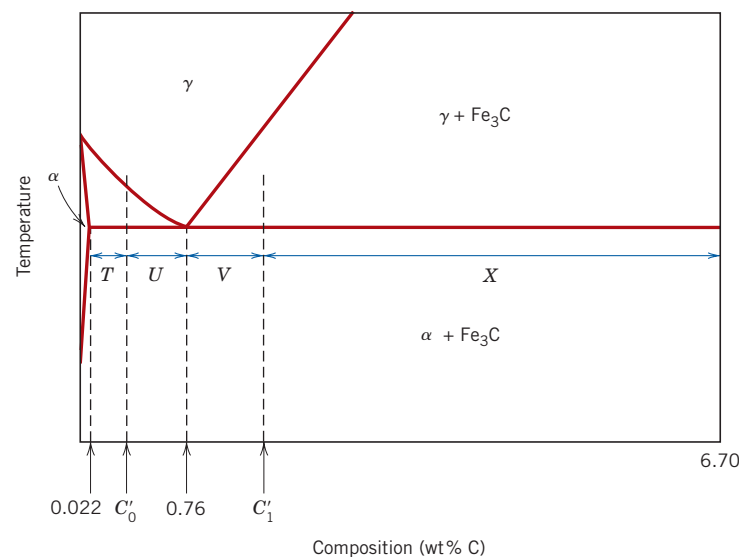
Lever rule
expression for
computation of
proeutectoid ferrite
mass fraction

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

$$= \frac{0.76 - C'_0}{0.76 - 0.022} = \frac{0.76 - C'_0}{0.74} \quad (9.21)$$

Of course, 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 $\alpha + \text{Fe}_3\text{C}$ phase region, from 0.022 to 6.7 wt% C.

Figure 9.31 A portion of the Fe–Fe₃C phase diagram used in computations for relative amounts of proeutectoid and pearlite microconstituents for hypoeutectoid (C'_0) and hypereutectoid (C'_1) compositions.



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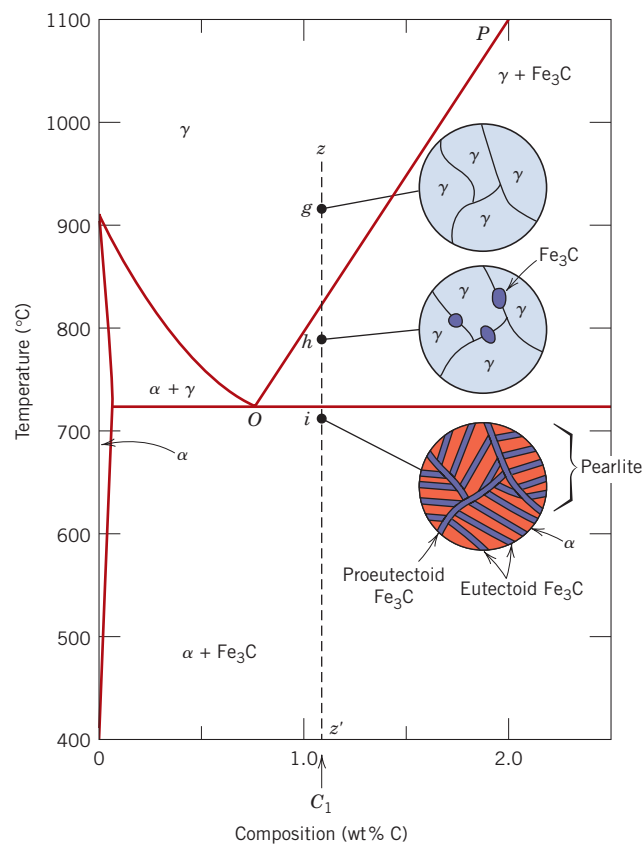


Figure 9.32 Schematic representations of the microstructures for an iron–carbon alloy of hypereutectoid composition C_1 (containing between 0.76 and 2.14 wt% C), as it is cooled from within the austenite phase region to below the eutectoid temperature.

Hypereutectoid Alloys

hypereutectoid
alloy

proeutectoid
cementite

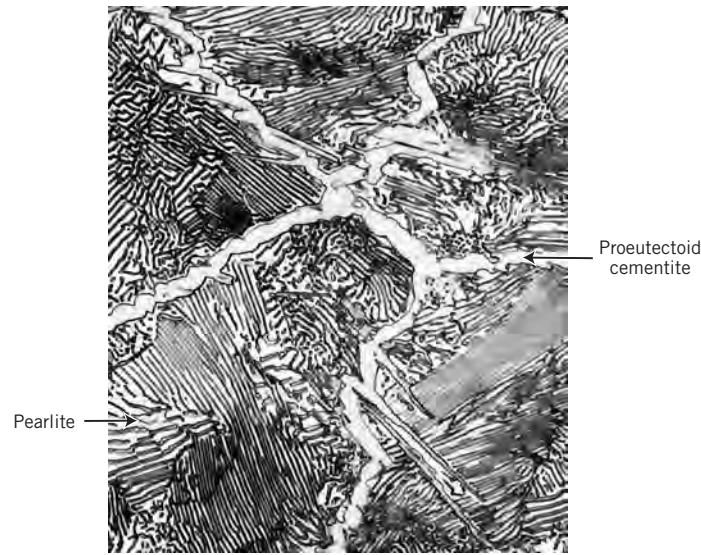
Analogous transformations and microstructures result for **hypereutectoid alloys**, those containing between 0.76 and 2.14 wt% C, which are cooled from temperatures within the γ phase field. Consider an alloy of composition C_1 in Figure 9.32 that, upon cooling, moves down the line zz' . At point g only the γ phase will be present with a composition of C_1 ; the microstructure will appear as shown, having only γ grains. Upon cooling into the $\gamma + \text{Fe}_3\text{C}$ phase field—say, to point h —the cementite phase will begin to form along the initial γ grain boundaries, similar to the α phase in Figure 9.29, point d . This cementite is called **proeutectoid cementite**—that which forms before the eutectoid reaction. Of course, the cementite composition remains constant (6.70 wt% C) as the temperature changes. However, the composition of the austenite phase will move along line PO toward the eutectoid. 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 (Figure 9.32). In the photomicrograph of a 1.4 wt% C steel (Figure 9.33), note that the proeutectoid cementite appears light. Since it has much the same appearance as proeutectoid ferrite (Figure 9.30), there is some difficulty in distinguishing between hypoeutectoid and hypereutectoid steels on the basis of microstructure.

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

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Figure 9.33

Photomicrograph of a 1.4 wt% C steel having a microstructure consisting of a white proeutectoid cementite network surrounding the pearlite colonies. 1000 \times . (Copyright 1971 by United States Steel Corporation.)



wt% C. Thus, for an alloy having composition C'_1 in Figure 9.31, fractions of pearlite W_p and proeutectoid cementite $W_{\text{Fe}_3\text{C}'}$ are determined from the following lever rule expressions:

$$W_p = \frac{X}{V + X} = \frac{6.70 - C'_1}{6.70 - 0.76} = \frac{6.70 - C'_1}{5.94} \quad (9.22)$$

and

$$W_{\text{Fe}_3\text{C}'} = \frac{V}{V + X} = \frac{C'_1 - 0.76}{6.70 - 0.76} = \frac{C'_1 - 0.76}{5.94} \quad (9.23)$$

Concept Check 9.8

Briefly explain why a proeutectoid phase (ferrite or cementite) forms along austenite grain boundaries. *Hint:* Consult Section 4.6.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

EXAMPLE PROBLEM 9.4

Determination of Relative Amounts of Ferrite, Cementite, and Pearlite Microconstituents

For a 99.65 wt% Fe–0.35 wt% C alloy at a temperature just below the eutectoid, determine the following:

- The fractions of total ferrite and cementite phases
- The fractions of the proeutectoid ferrite and pearlite
- The fraction of eutectoid ferrite