

steel sheet and plate (see Figs. 9.4 and 6.4 to 6.8). The billets are hot- and cold-rolled into bars, rods, and wire, while blooms are hot- and cold-rolled into shapes such as I beams and rails. Figure 9.5 is a flow diagram that summarizes the principal process steps involved in converting raw materials into major steel product forms.

9.2 THE IRON-CARBON SYSTEM

Iron-carbon alloys containing from a very small amount (about 0.03 percent) to about 1.2 percent carbon, 0.25 to 1.00 percent manganese, and minor amounts of other elements³ are termed *plain-carbon steels*. However, for purposes of this section of the book, plain-carbon steels will be treated as essentially iron-carbon binary alloys. The effects of other elements in steels will be dealt with in later sections.

9.2.1 The Iron-Iron-Carbide Phase Diagram

The phases present in very slowly cooled iron-carbon alloys at various temperatures and compositions of iron with up to 6.67 percent carbon are shown in the Fe-Fe₃C phase diagram of Fig. 9.6. This phase diagram is not a true equilibrium diagram since the compound iron carbide (Fe₃C) that is formed is not a true equilibrium phase. Under certain conditions, Fe₃C, which is called **cementite**, can decompose into the more stable phases of iron and carbon (graphite). However, for most practical conditions, Fe₃C is very stable and will therefore be treated as an equilibrium phase.

9.2.2 Solid Phases in the Fe-Fe₃C Phase Diagram

The Fe-Fe₃C diagram contains the following solid phases: α ferrite, austenite (γ), cementite (Fe₃C), and δ ferrite.

α ferrite. This phase is an interstitial solid solution of carbon in the BCC iron crystal lattice. As indicated by the Fe-Fe₃C phase diagram, carbon is only slightly soluble in α ferrite, reaching a maximum solid solubility of 0.02 percent at 723°C. The solubility of carbon in α ferrite decreases to 0.005 percent at 0°C.

Austenite (γ). The interstitial solid solution of carbon in γ iron is called *austenite*. Austenite has an FCC crystal structure and a much higher solid solubility for carbon than α ferrite. The solid solubility of carbon in austenite is a maximum of 2.08 percent at 1148°C and decreases to 0.8 percent at 723°C (Fig. 9.6).

Cementite (Fe₃C). The intermetallic compound Fe₃C is called *cementite*. Cementite has negligible solubility limits and a composition of 6.67 percent C and 93.3 percent Fe. Cementite is a hard and brittle compound.

δ ferrite. The interstitial solid solution of carbon in δ iron is called *δ ferrite*. It has a BCC crystal structure like α ferrite but with a greater lattice constant. The maximum solid solubility of carbon in δ ferrite is 0.09 percent at 1465°C.

³Plain-carbon steels also contain impurities of silicon, phosphorus, and sulfur as well as others.

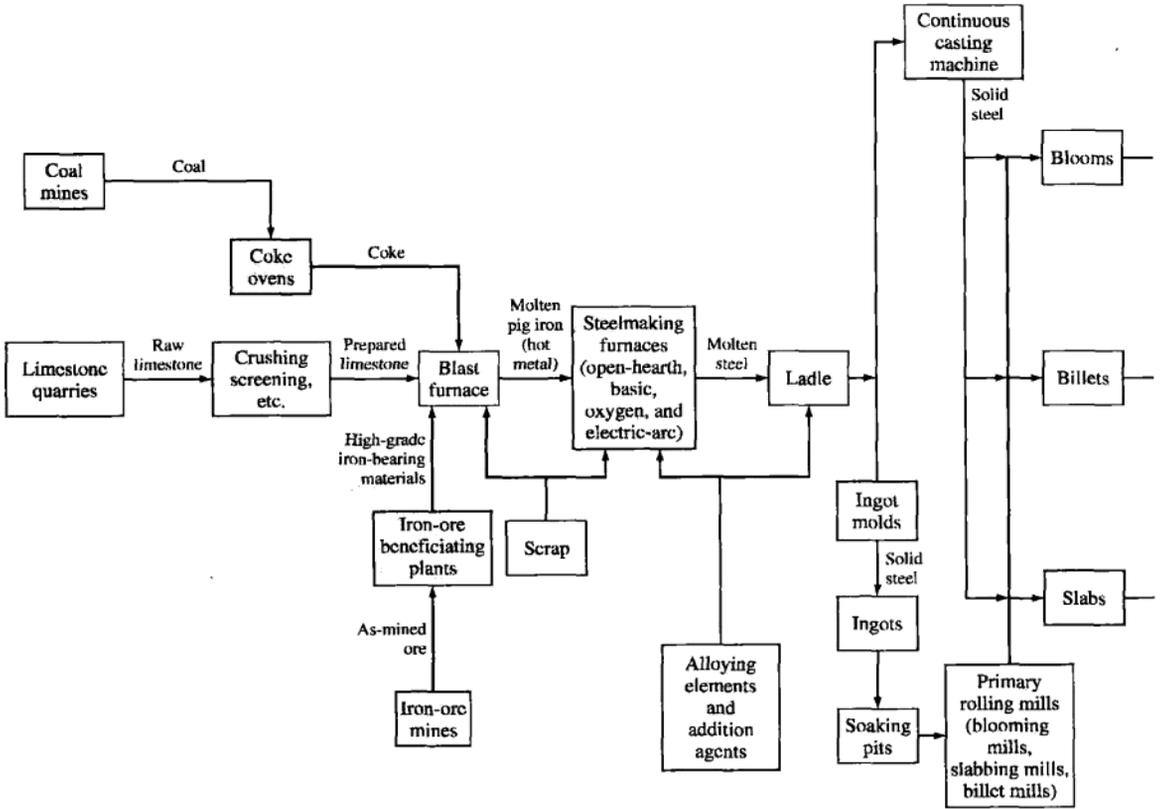


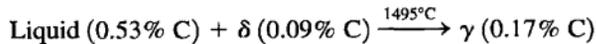
Figure 9.5

Flow diagram showing the principal process steps involved in converting raw materials into the major product forms, excluding coated products.

[From H.E. McGannon (ed.), "The Making, Shaping, and Treating of Steel," 9th ed., United States Steel, 1971, p. 2. Courtesy of United States Steel Corporation.]

9.2.3 Invariant Reactions in the Fe-Fe₃C Phase Diagram

Peritectic Reaction At the peritectic reaction point, liquid of 0.53 percent C combines with δ ferrite of 0.09 percent C to form γ austenite of 0.17 percent C. This reaction, which occurs at 1495°C, can be written as



δ Ferrite is a high-temperature phase and so is not encountered in plain-carbon steels at lower temperatures.

Eutectic Reaction At the eutectic reaction point, liquid of 4.3 percent forms γ austenite of 2.08 percent C and the intermetallic compound Fe₃C (cementite),

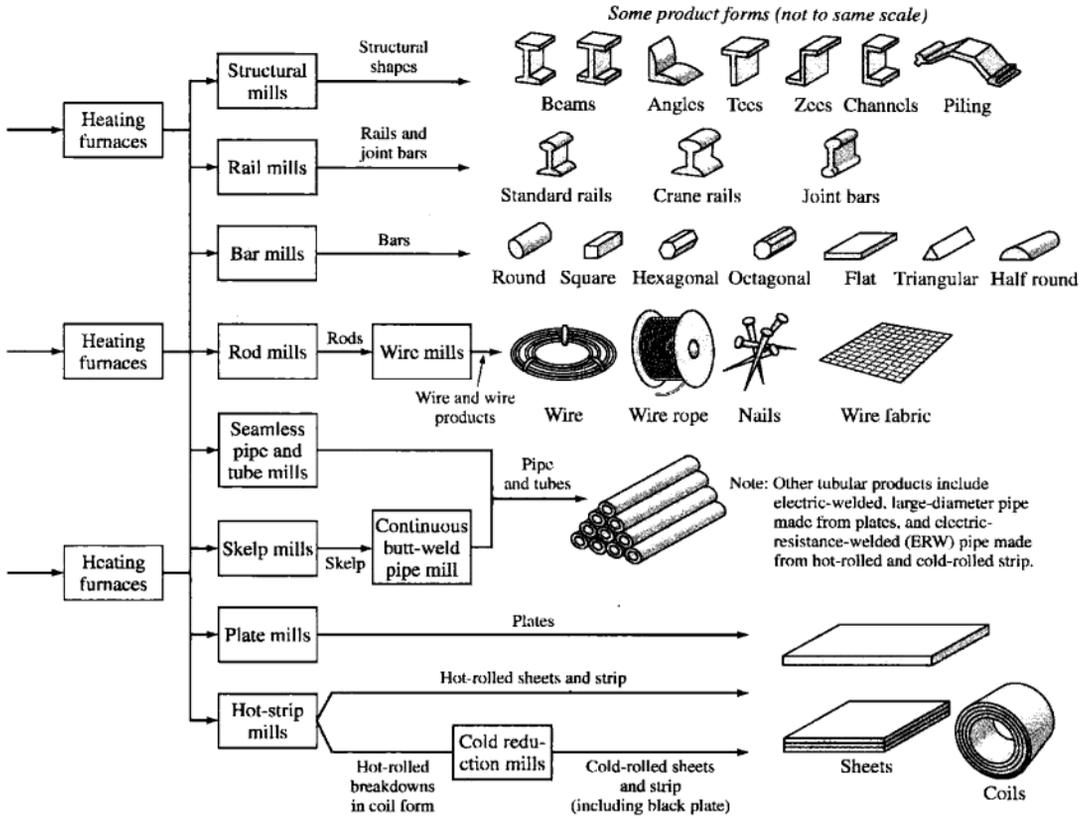
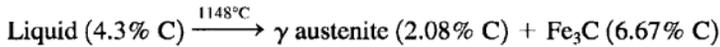


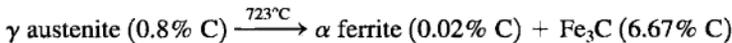
Figure 9.5 (continued)

which contains 6.67 percent C. This reaction, which occurs at 1148°C, can be written as



This reaction is not encountered in plain-carbon steels because their carbon contents are too low.

Eutectoid Reaction At the eutectoid reaction point, solid austenite of 0.8 percent C produces α ferrite with 0.02 percent C and Fe_3C (cementite) that contains 6.67 percent C. This reaction, which occurs at 723°C, can be written as



This eutectoid reaction, which takes place completely in the solid state, is important for some of the heat treatments of plain-carbon steels.

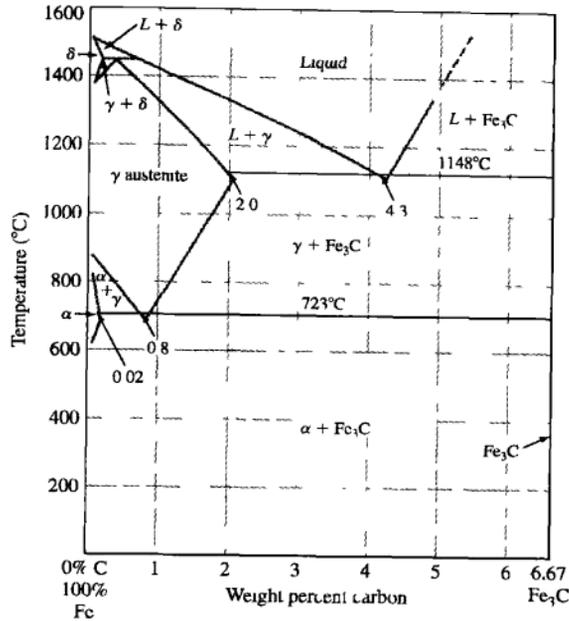
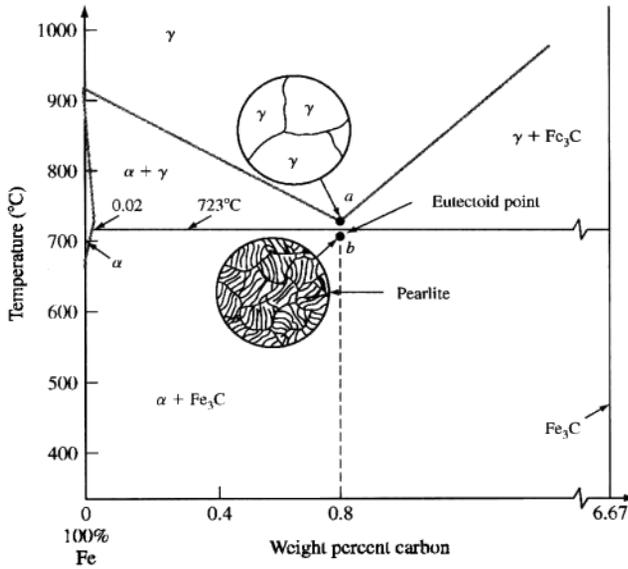


Figure 9.6
The iron-iron-carbide phase diagram

A plain-carbon steel that contains 0.8 percent C is called a **eutectoid steel** since an all-eutectoid structure of α ferrite and Fe_3C is formed when austenite of this composition is slowly cooled below the eutectoid temperature. If a plain-carbon steel contains less than 0.8 percent C, it is termed a **hypoeutectoid steel**, and if the steel contains more than 0.8 percent C, it is designated a **hypereutectoid steel**.

9.2.4 Slow Cooling of Plain-Carbon Steels

Eutectoid Plain-Carbon Steels If a sample of a 0.8 percent (eutectoid) plain-carbon steel is heated to about 750°C and held for a sufficient time, its structure will become homogeneous austenite. This process is called **austenitizing**. If this eutectoid steel is then cooled very slowly to just above the eutectoid temperature, its structure will remain austenitic, as indicated in Fig. 9.7 at point *a*. Further cooling to the eutectoid temperature or just below it will cause the entire structure to transform from austenite to a lamellar structure of alternate plates of α ferrite and cementite (Fe_3C). Just below the eutectoid temperature, at point *b* in Fig. 9.7, the lamellar structure will appear as shown in Fig. 9.8. This eutectoid structure is called **pearlite** since it resembles mother-of-pearl. Since the solubility of carbon in α ferrite and Fe_3C changes very little from 723°C to room temperature, the pearlite structure will remain essentially unchanged in this temperature interval.

**Figure 9.7**

Transformation of a eutectoid steel (0.8 percent C) with slow cooling.

(From W.F. Smith, "Structure and Properties of Engineering Alloys," 2d ed., McGraw-Hill, 1993, p. 8. Reproduced with permission of The McGraw-Hill Companies.)

**Figure 9.8**

Microstructure of a slowly cooled eutectoid steel. The microstructure consists of lamellar eutectoid pearlite. The dark etched phase is cementite, and the white phase is ferrite. (Etch: picral; magnification 650 \times .)

(United States Steel Corporation, as presented in "Metals Handbook," vol. 8, 8th ed., American Society for Metals, 1973, p. 188.)

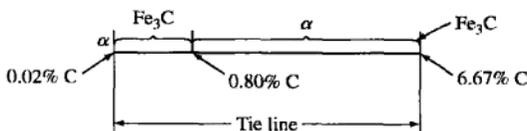
**EXAMPLE
PROBLEM 9.1**

A 0.80 percent C eutectoid plain-carbon steel is slowly cooled from 750°C to a temperature just slightly below 723°C. Assuming that the austenite is completely transformed to α ferrite and cementite:

- Calculate the weight percent eutectoid ferrite formed.
- Calculate the weight percent eutectoid cementite formed.

■ Solution

Referring to Fig. 9.6, we first draw a tie line just below 723°C from the α ferrite phase boundary to the Fe_3C phase boundary and indicate the 0.80 percent C composition on the tie line as shown in the following figure:



- The weight fraction of ferrite is calculated from the ratio of the segment of the tie line to the right of 0.80 percent C over the whole length of the tie line. Multiplying by 100 percent gives the weight percent ferrite:

$$\text{Wt \% ferrite} = \frac{6.67 - 0.80}{6.67 - 0.02} \times 100\% = \frac{5.87}{6.65} \times 100\% = 88.3\% \blacktriangleleft$$

- The weight percent cementite is calculated in a similar way by using the ratio of the segment of the tie line to the left of 0.80 percent C over the length of the whole tie line and multiplying by 100 percent:

$$\text{Wt \% cementite} = \frac{0.80 - 0.02}{6.67 - 0.02} \times 100\% = \frac{0.78}{6.65} \times 100\% = 11.7\% \blacktriangleleft$$

Hypoeutectoid Plain-Carbon Steels If a sample of a 0.4 percent C plain-carbon steel (hypoeutectoid steel) is heated to about 900°C (point *a* in Fig. 9.9) for a sufficient time, its structure will become homogeneous austenite. Then, if this steel is slowly cooled to temperature *b* in Fig. 9.9 (about 775°C), **proeutectoid⁴ ferrite** will nucleate and grow mostly at the austenitic grain boundaries. If this alloy is slowly cooled from temperature *b* to *c* in Fig. 9.9, the amount of proeutectoid ferrite formed will continue to increase until about 50 percent of the austenite is transformed. While the steel is cooling from *b* to *c*, the carbon content of the remaining austenite will be increased from 0.4 to 0.8 percent. At 723°C, if very slow cooling conditions prevail, the remaining austenite will transform isothermally

⁴The prefix *pro-* means "before," and thus the term *proeutectoid ferrite* is used to distinguish this constituent, which forms earlier, from eutectoid ferrite, which forms by the eutectoid reaction later in the cooling.

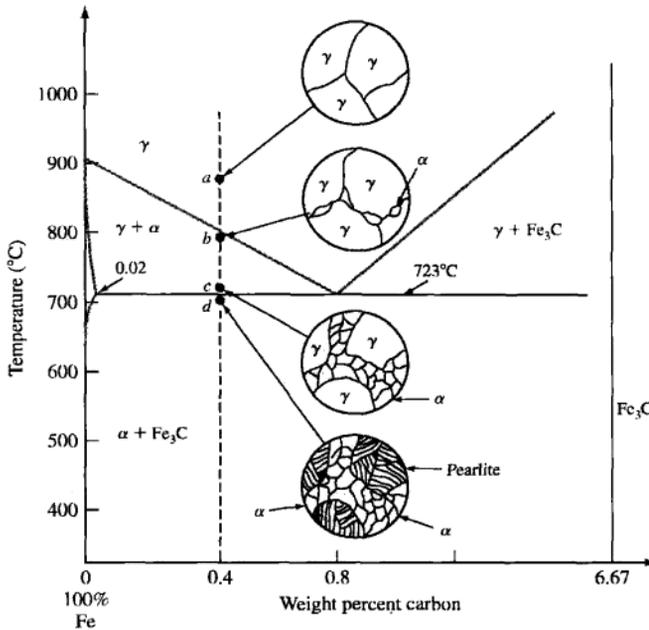


Figure 9.9

Transformation of a 0.4 percent C hypoeutectoid plain-carbon steel with slow cooling.

(From W.F. Smith, "Structure and Properties of Engineering Alloys," 2d ed., McGraw-Hill, 1993, p. 10. Reproduced with permission of The McGraw-Hill Companies.)

into pearlite by the eutectoid reaction austenite \rightarrow ferrite + cementite. The α ferrite in the pearlite is called **eutectoid ferrite** to distinguish it from the proeutectoid ferrite that forms first above 723°C. Figure 9.10 is an optical micrograph of the structure of a 0.35 percent C hypoeutectoid steel that was austenitized and slowly cooled to room temperature.

- a. A 0.40 percent C hypoeutectoid plain-carbon steel is slowly cooled from 940°C to a temperature just slightly above 723°C.
 - (i) Calculate the weight percent austenite present in the steel.
 - (ii) Calculate the weight percent proeutectoid ferrite present in the steel.
- b. A 0.40 percent C hypoeutectoid plain-carbon steel is slowly cooled from 940°C to a temperature just slightly below 723°C.
 - (i) Calculate the weight percent proeutectoid ferrite present in the steel.
 - (ii) Calculate the weight percent eutectoid ferrite and weight percent eutectoid cementite present in the steel.

**EXAMPLE
PROBLEM 9.2**

■ Solution

Referring to Fig. 9.6 and using tie lines:

$$a. \quad (i) \quad \text{Wt \% austenite} = \frac{0.40 - 0.02}{0.80 - 0.02} \times 100\% = 50\% \blacktriangleleft$$

$$(ii) \quad \text{Wt \% proeutectoid ferrite} = \frac{0.80 - 0.40}{0.80 - 0.02} \times 100\% = 50\% \blacktriangleleft$$

b. (i) The weight percent proeutectoid ferrite present in the steel just below 723°C will be the same as that just above 723°C, which is 50 percent.

(ii) The weight percent total ferrite and cementite just below 723°C are

$$\text{Wt \% total ferrite} = \frac{6.67 - 0.40}{6.67 - 0.02} \times 100\% = 94.3\%$$

$$\text{Wt \% total cementite} = \frac{0.40 - 0.02}{6.67 - 0.02} \times 100\% = 5.7\%$$

$$\begin{aligned} \text{Wt \% eutectoid ferrite} &= \text{total ferrite} - \text{proeutectoid ferrite} \\ &= 94.3 - 50 = 44.3\% \blacktriangleleft \end{aligned}$$

$$\text{Wt \% eutectoid cementite} = \text{wt \% total cementite} = 5.7\% \blacktriangleleft$$

(No proeutectoid cementite was formed during cooling.)

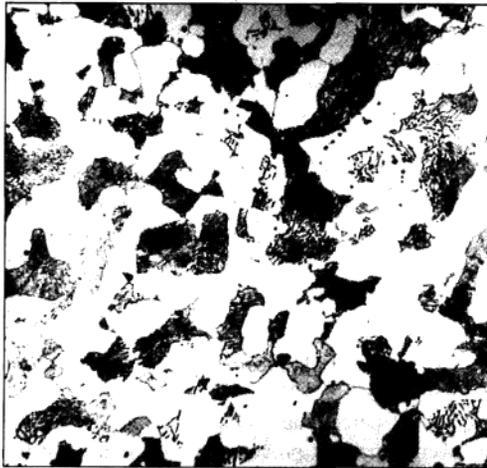


Figure 9.10

Microstructure of a 0.35 percent C hypoeutectoid plain-carbon steel slowly cooled from the austenite region. The white constituent is proeutectoid ferrite; the dark constituent is pearlite. (Etchant: 2% nital; magnification 500×.)

(After W.F. Smith, "Structure and Properties of Engineering Alloys," 2d ed., McGraw-Hill, 1993, p. 11.)

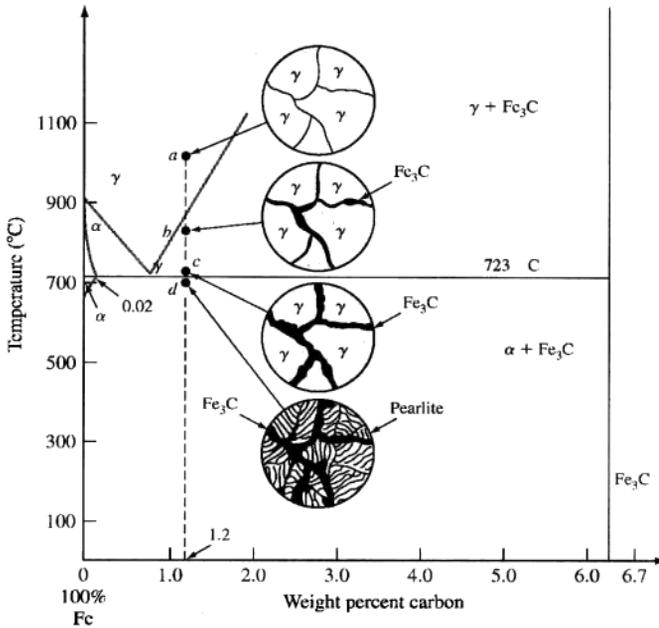


Figure 9.11

Transformation of a 1.2 percent C hypereutectoid plain-carbon steel with slow cooling.

(From W.F. Smith, "Structure and Properties of Engineering Alloys," 2d ed., McGraw-Hill, 1993, p. 12. Reproduced with permission of The McGraw-Hill Companies.)

Hypereutectoid Plain-Carbon Steels If a sample of a 1.2 percent C plain-carbon steel (hypereutectoid steel) is heated to about 950°C and held for a sufficient time, its structure will become essentially all austenite (point *a* in Fig. 9.11). Then, if this steel is cooled very slowly to temperature *b* in Fig. 9.11, **proeutectoid cementite** will begin to nucleate and grow primarily at the austenite grain boundaries. With further slow cooling to point *c* of Fig. 9.11, which is just above 723°C, more proeutectoid cementite will be formed at the austenite grain boundaries. If conditions approaching equilibrium are maintained by the slow cooling, the overall carbon content of the austenite remaining in the alloy will change from 1.2 to 0.8 percent.

With still further slow cooling to 723°C or just slightly below this temperature, the remaining austenite will transform to pearlite by the eutectoid reaction, as indicated at point *d* of Fig. 9.11. The cementite formed by the eutectoid reaction is called **eutectoid cementite** to distinguish it from the proeutectoid cementite formed at temperatures above 723°C. Similarly, the ferrite formed by the eutectoid reaction is

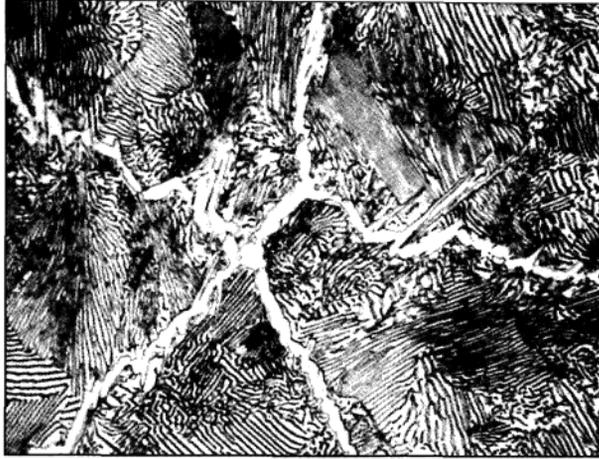


Figure 9.12

Microstructure of a 1.2 percent C hypereutectoid steel slowly cooled from the austenite region. In this structure, the proeutectoid cementite appears as the white constituent that has formed at the former austenite grain boundaries. The remaining structure consists of coarse lamellar pearlite. (Etchant: picral; magnification 1000 \times .) (Courtesy of United States Steel Corp.)

termed *eutectoid ferrite*. Figure 9.12 is an optical micrograph of the structure of a 1.2 percent C hypereutectoid steel that was austenitized and slowly cooled to room temperature.

**EXAMPLE
PROBLEM 9.3**

A hypoeutectoid plain-carbon steel that was slow-cooled from the austenitic region to room temperature contains 9.1 wt % eutectoid ferrite. Assuming no change in structure on cooling from just below the eutectoid temperature to room temperature, what is the carbon content of the steel?

■ **Solution**

Let x = the weight percent carbon of the hypoeutectoid steel. Now we can use the equation that relates the eutectoid ferrite to the total ferrite and the proeutectoid ferrite, which is

$$\text{Eutectoid ferrite} = \text{total ferrite} - \text{proeutectoid ferrite}$$

Using Fig. EP9.3 and the lever rule, we can make the equation

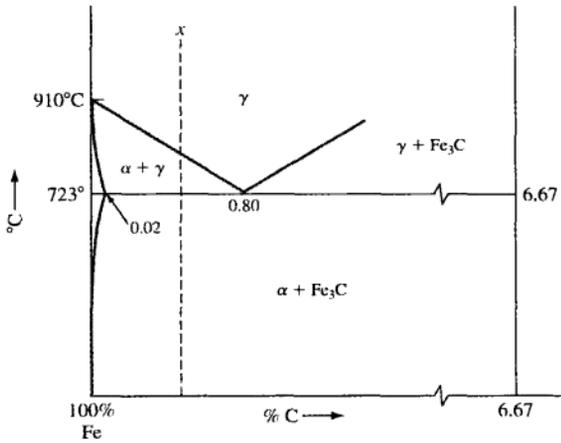


Figure EP9.3

$$0.091 = \frac{\text{Eutectoid ferrite}}{6.67 - 0.02} = \frac{6.67 - x}{6.67 - 0.02} - \frac{\text{Proeutectoid ferrite}}{0.80 - 0.02} = \frac{6.67}{6.65} - \frac{x}{6.65} - \frac{0.80}{0.78} + \frac{x}{0.78}$$

or $1.28x - 0.150x = 0.091 - 1.003 + 1.026 = 0.114$

$$x = \frac{0.114}{1.13} = 0.101\% \text{ C} \blacktriangleleft$$

9.3 HEAT TREATMENT OF PLAIN-CARBON STEELS

By varying the manner in which plain-carbon steels are heated and cooled, different combinations of mechanical properties for steels can be obtained. In this section, we shall examine some of the structural and property changes that take place during some of the important heat treatments given to plain-carbon steels.

9.3.1 Martensite

Formation of Fe-C Martensite by Rapid Quenching If a sample of a plain-carbon steel in the austenitic condition is rapidly cooled to room temperature by quenching it in water, its structure will be changed from austenite to **martensite**. Martensite in plain-carbon steels is a metastable phase consisting of a supersaturated interstitial solid solution of carbon in body-centered cubic iron or body-centered tetragonal iron (the tetragonality is caused by a slight distortion of the BCC iron unit cell). The temperature,

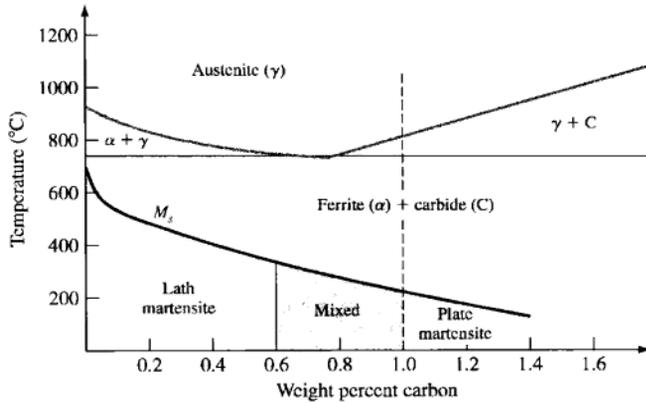


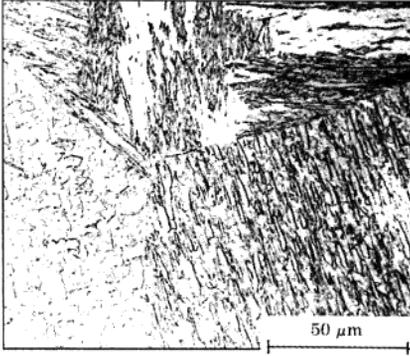
Figure 9.13
Effect of carbon content on the martensite-transformation start temperature, M_s , for iron-carbon alloys.
(From A.R. Marder and G. Krauss, as presented in "Hardenability Concepts with Applications to Steel," AIME, 1978, p. 238.)

upon cooling, at which the austenite-to-martensite transformation starts is called the *martensite start*, M_s , temperature, and the temperature at which the transformation finishes is called the *martensite finish*, M_f , temperature. The M_s temperature for Fe-C alloys decreases as the weight percent carbon increases in these alloys, as shown in Fig. 9.13.

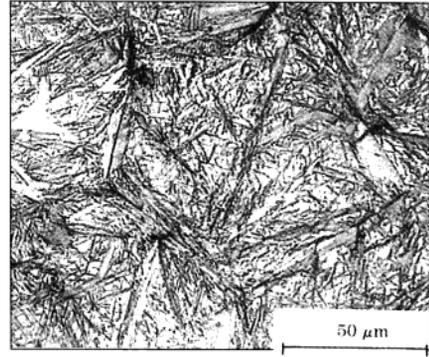
Microstructure of Fe-C Martensites The microstructure of martensites in plain-carbon steels depends on the carbon content of the steel. If the steel contains less than about 0.6 percent C, the martensite consists of *domains* of laths of different but limited orientations through a whole domain. The structure within the laths is highly distorted, consisting of regions with high densities of dislocation tangles. Figure 9.14a is an optical micrograph of *lath martensite* in an Fe-0.2% C alloy at 600 \times , while Fig. 9.15 shows the substructure of lath martensite in this alloy in an electron micrograph at 60,000 \times .

As the carbon content of the Fe-C martensites is increased to above about 0.6 percent C, a different type of martensite, called *plate martensite*, begins to form. Above about 1 percent C, Fe-C alloys consist entirely of plate martensite. Figure 9.14b is an optical micrograph of plate martensite in an Fe-1.2% C alloy at 600 \times . The plates in high-carbon Fe-C martensites vary in size and have a fine structure of parallel twins, as shown in Fig. 9.16. The plates are often surrounded by large amounts of untransformed (retained) austenite. Fe-C martensites with carbon contents between about 0.6 and 1.0 percent C have microstructures consisting of both lath- and plate-type martensites.

Structure of Fe-C Martensites on an Atomic Scale The transformation of austenite to martensite in Fe-C alloys (plain-carbon steels) is considered to be *diffusionless*



(a)



(b)

Figure 9.14

Effect of carbon content on the structure of martensite in plain-carbon steels: (a) lath type, (b) plate type. (Etchant: sodium bisulfite; optical micrographs.)

[After A.R. Marder and G. Krauss, *Trans. ASM*, 60:651(1967). Reprinted with permission of ASM International. All rights reserved. www.asminternational.org.]



Figure 9.15

Structure of lath martensite in an Fe-0.2% C alloy. (Note the parallel alignment of the laths.)

[After A.R. Marder and G. Krauss, *Trans. ASM*, 60:651 (1967). Reprinted with permission of ASM International. All rights reserved. www.asminternational.org.]

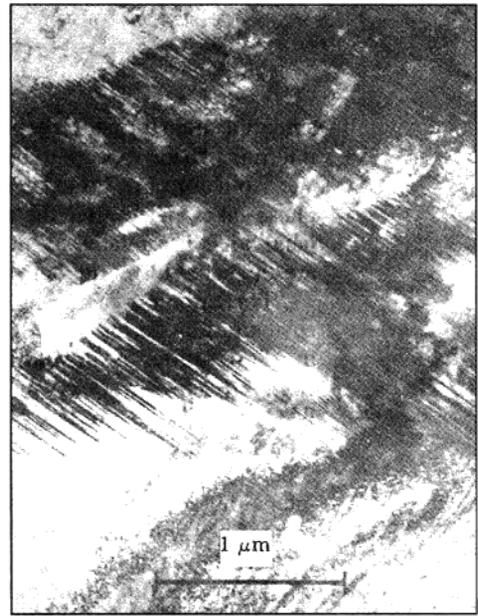


Figure 9.16

Plate martensite showing fine transformation twins.

[After M. Oka and C.M. Wayman, *Trans. ASM*, 62:370(1969). Reprinted with permission of ASM International. All rights reserved. www.asminternational.org.]

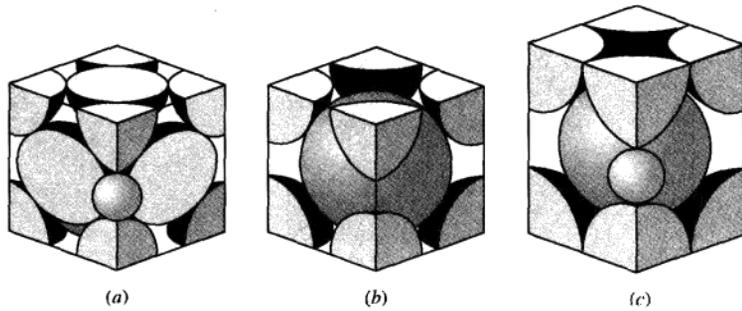


Figure 9.17

(a) FCC γ iron unit cell showing a carbon atom in a large interstitial hole along the cube edge of the cell. (b) BCC α iron unit cell indicating a smaller interstitial hole between cube-edge atoms of the unit cell. (c) BCT (body-centered tetragonal) iron unit cell produced by the distortion of the BCC unit cell by the interstitial carbon atom.

(From E.R. Parker and V.F. Zackay, "Strong and Ductile Steels," *Scientific American*, November 1968, p. 42.)

MatVis

since the transformation takes place so rapidly that the atoms do not have time to intermix. There appears to be no thermal-activation energy barrier to prevent martensite from forming. Also, it is believed that no compositional change in the parent phase takes place after the reaction and that each atom tends to retain its original neighbors. The relative positions of the carbon atoms with respect to the iron atoms are the same in the martensite as they were in the austenite.

For carbon contents in Fe-C martensites of less than about 0.2 percent C, the austenite transforms to a BCC α ferrite crystal structure. As the carbon content of the Fe-C alloys is increased, the BCC structure is distorted into a BCT (*body-centered tetragonal*) crystal structure. The largest interstitial hole in the γ iron FCC crystal structure has a diameter of 0.104 nm (Fig. 9.17a), whereas the largest interstitial hole in the α iron BCC structure has a diameter of 0.072 nm (Fig. 9.17b). Since the carbon atom has a diameter of 0.154 nm, it can be accommodated in interstitial solid solution to a greater extent in the FCC γ iron lattice. When Fe-C martensites with more than about 0.2 percent C are produced by rapid cooling from austenite, the reduced interstitial spacings of the BCC lattice cause the carbon atoms to distort the BCC unit cell along its c axis to accommodate the carbon atoms (Fig. 9.17c). Figure 9.18 shows how the c axis of the Fe-C martensite lattice is elongated as its carbon content increases.

Hardness and Strength of Fe-C Martensites The hardness and strength of Fe-C martensites are directly related to their carbon content and increase as the carbon content is increased (Fig. 9.19). However, ductility and toughness also decrease with increasing carbon content, and so most martensitic plain-carbon steels are tempered by reheating at a temperature below the transformation temperature of 723°C.

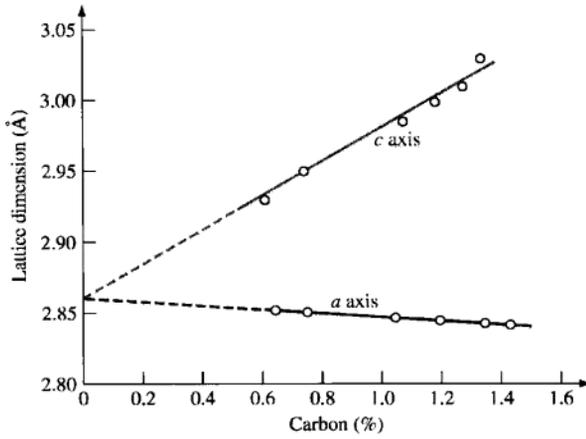


Figure 9.18
 Variation of a and c axes of the Fe-C martensite lattice as a function of carbon content.
 (From p. 36 in E.C. Bain and H.W. Paxton, "Alloying Elements in Steel," 2d ed., American Society for Metals, 1966. Used by permission of ASM International.)

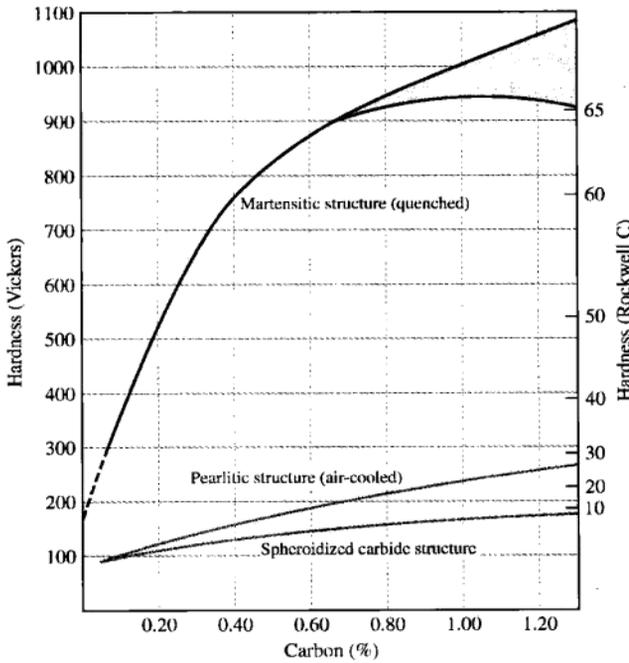


Figure 9.19
 Approximate hardness of fully hardened martensitic plain-carbon steel as a function of carbon content. The shaded region indicates some possible loss of hardness due to the formation of retained austenite, which is softer than martensite.
 (From p. 37 in E.C. Bain and H.W. Paxton, "Alloying Elements in Steel," 2d ed., American Society for Metals, 1966. Used by permission of ASM International.)

Low-carbon Fe-C martensites are strengthened by a high concentration of dislocations being formed (lath martensite) and by interstitial solid-solution strengthening by carbon atoms. The high concentration of dislocations in networks (lath martensite) makes it difficult for other dislocations to move. As the carbon content increases above 0.2 percent, interstitial solid-solution strengthening becomes more important and the BCC iron lattice becomes distorted into tetragonality. However, in high-carbon Fe-C martensites, the numerous twinned interfaces in plate martensite also contribute to the hardness.

9.3.2 Isothermal Decomposition of Austenite

Isothermal Transformation Diagram for a Eutectoid Plain-Carbon Steel In previous sections, the reaction products from the decomposition of austenite of eutectoid plain-carbon steels for very slow and rapid cooling conditions have been described. Let us now consider what reaction products form when austenite of eutectoid steels is rapidly cooled to temperatures below the eutectoid temperature and then *isothermally transformed*.

Isothermal transformation experiments to investigate the microstructural changes for the decomposition of eutectoid austenite can be made by using a number of small samples, each about the size of a dime. The samples are first austenitized in a furnace at a temperature above the eutectoid temperature (Fig. 9.20a). The samples are then rapidly cooled (quenched) in a liquid salt bath at the desired temperature below the eutectoid temperature (Fig. 9.20b). After various time intervals, the samples are removed from the salt bath one at a time and quenched into water at room temperature (Fig. 9.20c). The microstructure after each transformation time can then be examined at room temperature.

Consider the microstructural changes that take place during the isothermal transformation of a eutectoid plain-carbon steel at 705°C, as schematically shown in

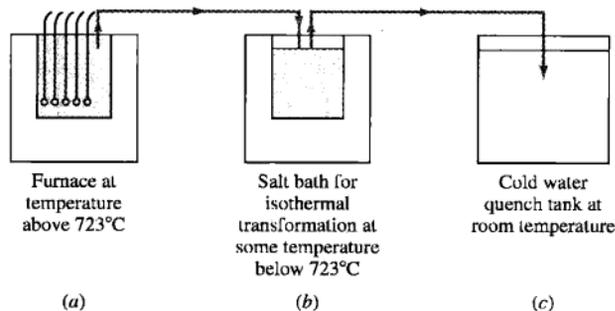


Figure 9.20

Experimental arrangement for determining the microscopic changes that occur during the isothermal transformation of austenite in a eutectoid plain-carbon steel.

(From W.F. Smith, "Structure and Properties of Engineering Alloys," McGraw-Hill, 1981, p. 14. Reproduced with permission of The McGraw-Hill Companies.)

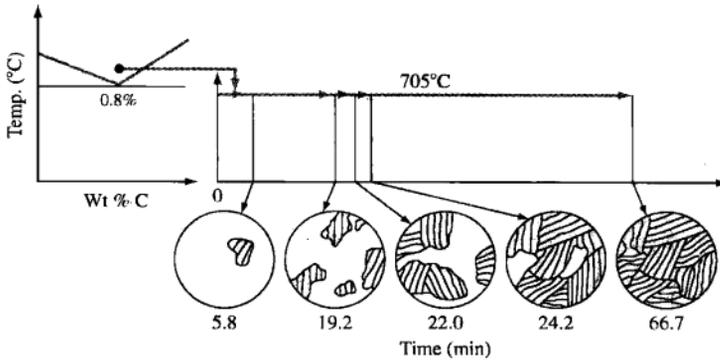


Figure 9.21

Experiment for following the microstructural changes that occur during the isothermal transformation of a eutectoid plain-carbon steel at 705°C. After austenitizing, samples are quenched in a salt bath at 705°C, held for the times indicated, and then quenched in water at room temperature.

(From W.F. Smith, "Structure and Properties of Engineering Alloys," McGraw-Hill, 1981, p. 14. Reproduced with permission of The McGraw-Hill Companies.)

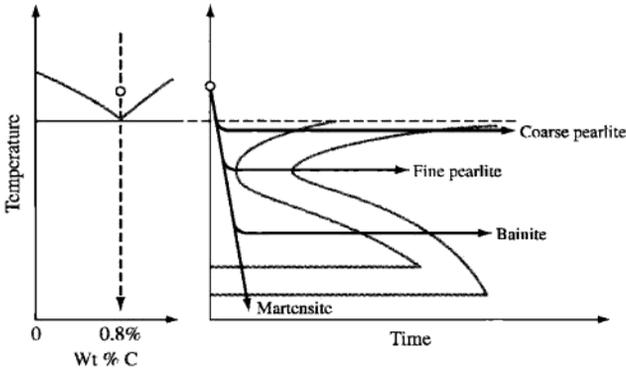


Figure 9.22

Isothermal transformation diagram for a eutectoid plain-carbon steel showing its relationship to the Fe-Fe₃C phase diagram.

Fig. 9.21. After being austenitized, the samples are hot-quenched into a salt bath at 705°C. After about 6 min, coarse pearlite has formed to a small extent. After about 67 min, the austenite is completely transformed to coarse pearlite.

By repeating the same procedure for the isothermal transformation of eutectoid steels at progressively lower temperatures, an **isothermal transformation (IT) diagram** can be constructed, as shown schematically in Fig. 9.22 and from experimental

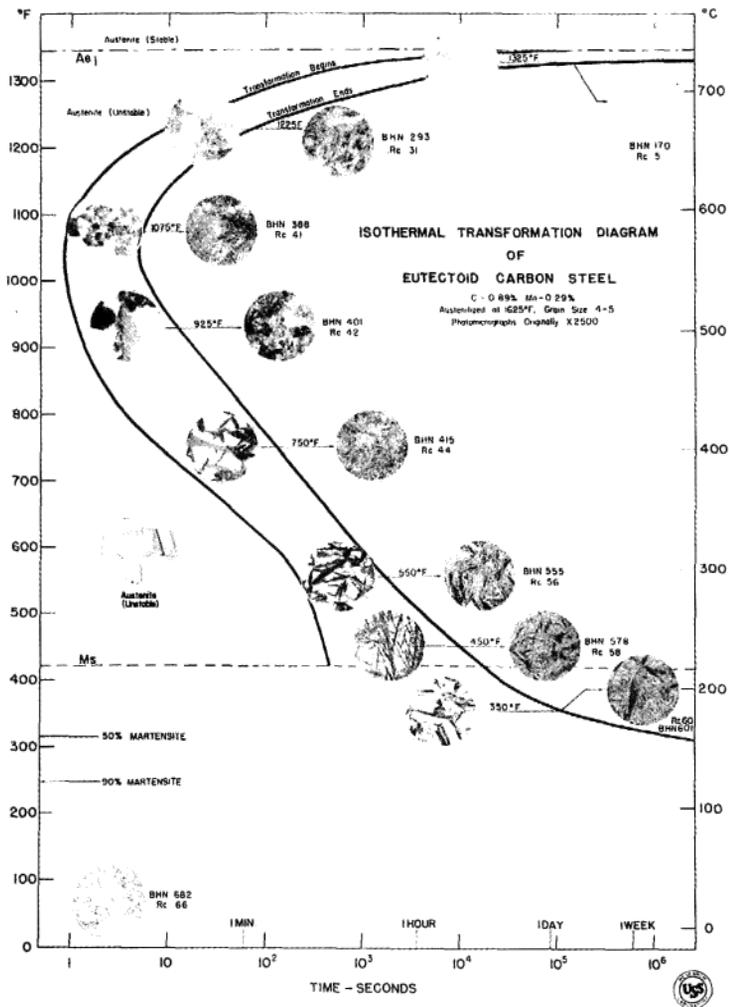
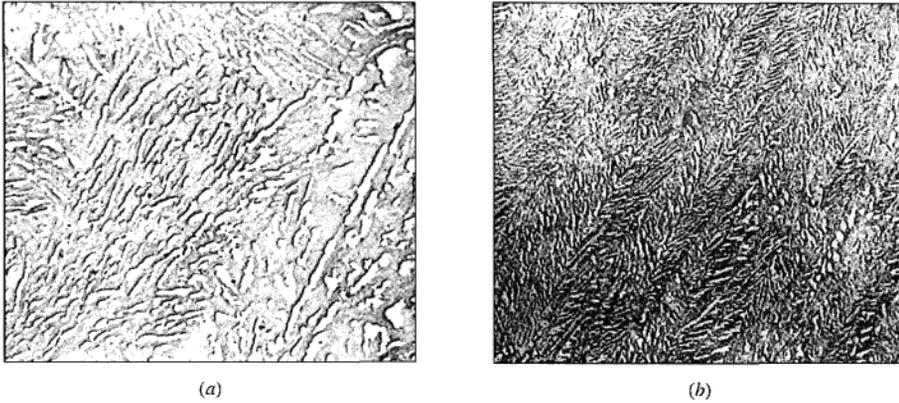


Figure 9.23 Isothermal transformation diagram of a eutectoid steel. (Courtesy of United States Steel Corporation.)

data in Fig. 9.23. The S-shaped curve next to the temperature axis indicates the time necessary for the isothermal transformation of austenite to begin, and the second S curve indicates the time required for the transformation to be completed.

Isothermal transformations of eutectoid steels at temperatures between 723°C and about 550°C produce pearlitic microstructures. As the transformation tempera-

**Figure 9.24**

(a) Microstructure of upper bainite formed by a complete transformation of a eutectoid steel at 450°C (850°F). (b) Microstructure of lower bainite formed by a complete transformation of a eutectoid steel at 260°C (500°F). The white particles are Fe_3C , and the dark matrix is ferrite. (Electron micrographs, replica-type; magnification 15,000 \times .)

[After H.E. McGannon (ed.), "The Making, Shaping, and Treating of Steel," 9th ed., United States Steel Corp., 1971.]

ture is decreased in this range, the pearlite changes from a coarse to a fine structure (Fig. 9.23). Rapid quenching (cooling) of a eutectoid steel from temperatures above 723°C, where it is in the austenitic condition, transforms the austenite into martensite, as has been previously discussed.

If eutectoid steels in the austenitic condition are hot-quenched to temperatures in the 550°C to 250°C range and are isothermally transformed, a structure intermediate between pearlite and martensite, called **bainite**,⁵ is produced. Bainite in Fe-C alloys can be defined as an austenitic decomposition product that has a *non-lamellar eutectoid structure* of α ferrite and cementite (Fe_3C). For eutectoid plain-carbon steels, a distinction is made between *upper bainite*, which is formed by isothermal transformation at temperatures between about 550°C and 350°C, and *lower bainite*, which is formed between about 350°C and 250°C. Figure 9.24a shows an electron micrograph (replica-type) of the microstructure of upper bainite for a eutectoid plain-carbon steel, and Fig. 9.24b shows one for lower bainite. Upper bainite has large, rodlike cementite regions, whereas lower bainite has much finer cementite particles. As the transformation temperature is decreased, the carbon atoms cannot diffuse as easily, and hence the lower bainite structure has smaller particles of cementite.

⁵Bainite is named after E.C. Bain, the American metallurgist who first intensively studied the isothermal transformations of steels. See E.S. Davenport and E.C. Bain, *Trans. AIME*, **90**:117 (1930).

**EXAMPLE
PROBLEM 9.4**

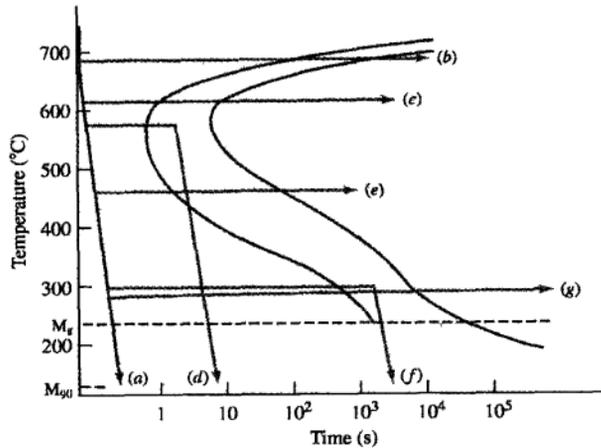
Small, thin pieces of 0.25 mm thick hot-rolled strips of 1080 steel are heated for 1 h at 850°C and then given the heat treatments shown in the following list. Using the isothermal transformation diagram of Fig. 9.23, determine the microstructures of the samples after each heat treatment.

- Water-quench to room temperature.
- Hot-quench in molten salt to 690°C and hold 2 h; water-quench.
- Hot-quench to 610°C and hold 3 min; water-quench.
- Hot-quench to 580°C and hold 2 s; water-quench.
- Hot-quench to 450°C and hold 1 h; water-quench.
- Hot-quench to 300°C and hold 30 min; water-quench.
- Hot-quench to 300°C and hold 5 h; water-quench.

■ Solution

The cooling paths are indicated on Fig. EP9.4 and the microstructures obtained are listed as follows:

- All martensite.
- All coarse pearlite.
- All fine pearlite.
- Approximately 50 percent fine pearlite and 50 percent martensite.
- All upper bainite.
- Approximately 50 percent lower bainite and 50 percent martensite.
- All lower bainite.

**Figure EP9.4**

Isothermal transformation diagram for a eutectoid plain-carbon steel indicating various cooling paths.

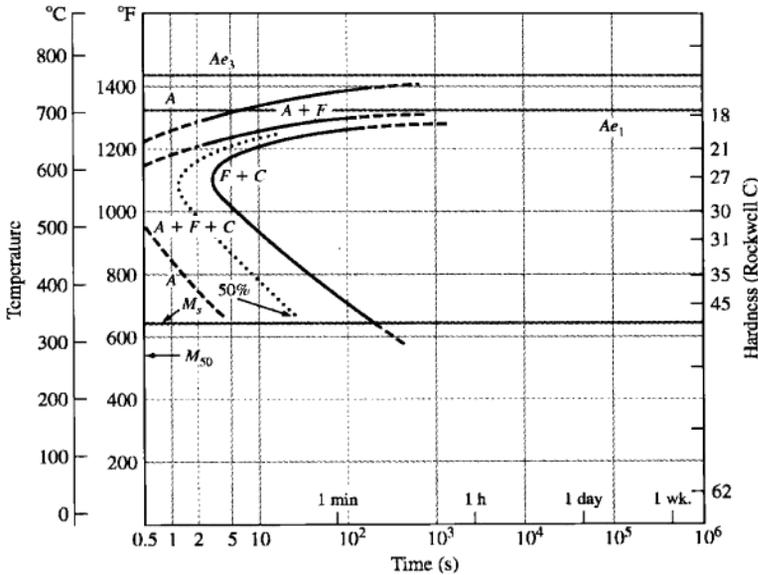


Figure 9.25

Isothermal transformation diagram for a hypoeutectoid steel containing 0.47 percent C and 0.57 percent Mn (austenitizing temperature: 843°C).

[From R.A. Grange and J.K. Kieffer as adapted in E.C. Bain and H.W. Paxton, "Alloying Elements in Steel," 2d ed., American Society for Metals, 1966.]

Isothermal Transformation Diagrams for Noneutectoid Plain-Carbon Steels

Isothermal transformation diagrams have been determined for noneutectoid plain-carbon steels. Figure 9.25 shows an IT diagram for a 0.47 percent hypoeutectoid plain-carbon steel. Several differences are evident between the IT diagram for a noneutectoid plain-carbon steel and the diagram for a eutectoid one (Fig. 9.23). One major difference is that the S curves of the hypoeutectoid steel have been shifted to the left, so that it is not possible to quench this steel from the austenitic region to produce an entirely martensitic structure.

A second major difference is that another transformation line has been added to the upper part of the eutectoid steel IT diagram that indicates the start of the formation of proeutectoid ferrite. Thus, at temperatures between 723°C and about 765°C, only proeutectoid ferrite is produced by isothermal transformation.

Similar IT diagrams have been determined for hypereutectoid plain-carbon steels. However, in this case, the uppermost line of the diagram for these steels is for the start of the formation of proeutectoid cementite.

9.3.3 Continuous-Cooling Transformation Diagram for a Eutectoid Plain-Carbon Steel

In industrial heat-treating operations, in most cases a steel is not isothermally transformed at a temperature above the martensite start temperature but is continuously

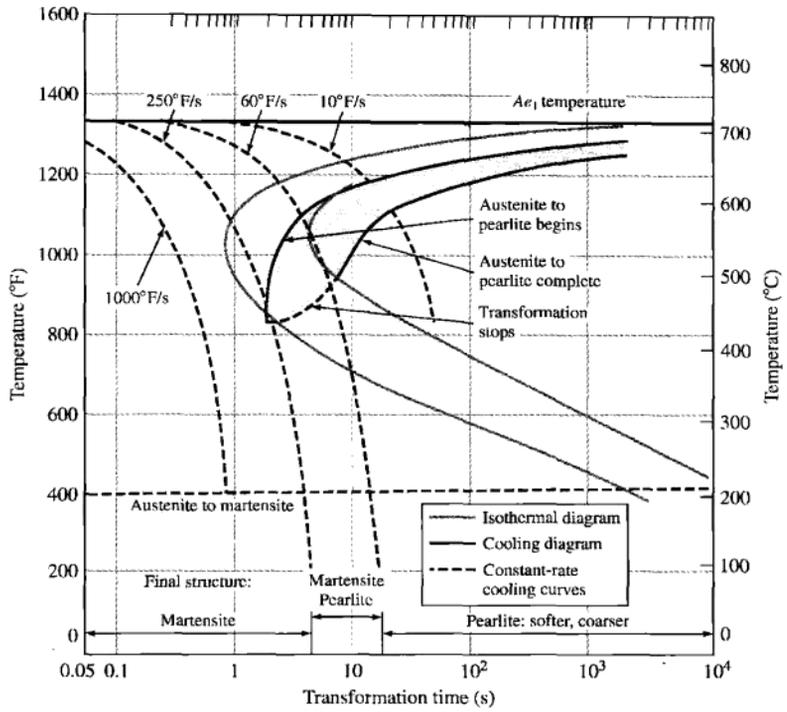


Figure 9.26

Continuous-cooling diagram for a plain-carbon eutectoid steel.

(After R.A. Grange and J.M. Kieffer as adapted in E.C. Bain and H.W. Paxton, "Alloying Elements in Steel," 2d ed., American Society for Metals, 1966, p. 254.)

cooled from the austenitic temperature to room temperature. In continuously cooling a plain-carbon steel, the transformation from austenite to pearlite occurs over a range of temperatures rather than at a single isothermal temperature. As a result, the final microstructure after continuous cooling will be complex since the reaction kinetics change over the temperature range in which the transformation takes place. Figure 9.26 shows a **continuous-cooling transformation (CCT) diagram** for a eutectoid plain-carbon steel superimposed over an IT diagram for this steel. The continuous-cooling diagram transformation start and finish lines are shifted to longer times and slightly lower temperatures in relation to the isothermal diagram. Also, there are no transformation lines below about 450°C for the austenite-to-bainite transformation.

Figure 9.27 shows different rates of cooling for thin samples of eutectoid plain-carbon steels cooled continuously from the austenitic region to room temperature. Cooling curve *A* represents very slow cooling, such as would be obtained by shutting off the power of an electric furnace and allowing the steel to cool as the furnace cools. The microstructure in this case would be coarse pearlite. Cooling curve *B* represents

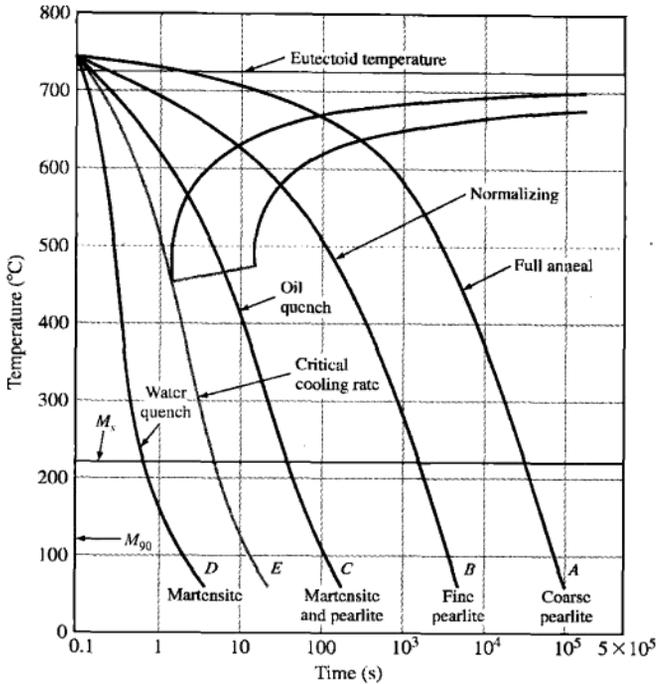


Figure 9.27

Variation in the microstructure of a eutectoid plain-carbon steel by continuously cooling at different rates.

(From R.E. Reed-Hill, "Physical Metallurgy Principles," 2d ed., D. Van Nostrand Co., 1973 © PWS Publishers.)

more rapid cooling, such as would be obtained by removing an austenitized steel from a furnace and allowing the steel to cool in still air. A fine pearlite microstructure is formed in this case.

Cooling curve C of Fig. 9.27 starts with the formation of pearlite, but there is insufficient time to complete the austenite-to-pearlite transformation. The remaining austenite that does not transform to pearlite at the upper temperatures will transform to martensite at lower temperatures starting at about 220°C. This type of transformation, since it takes place in two steps, is called a *split transformation*. The microstructure of this steel will thus consist of a mixture of pearlite and martensite. Cooling at a rate faster than curve E of Fig. 9.27, which is called the *critical cooling rate*, will produce a fully hardened martensitic structure.

Continuous-cooling diagrams have been determined for many hypoeutectoid plain-carbon steels and are more complex since at low temperatures some bainitic structure is also formed during continuous cooling. The discussion of these diagrams is beyond the scope of this book.

9.3.4 Annealing and Normalizing of Plain-Carbon Steels

In Chapter 6, the cold-working and annealing processes for metals were discussed, and reference should be made to that section. The two most common types of annealing processes applied to commercial plain-carbon steels are *full annealing* and *process annealing*.

In full annealing, hypoeutectoid and eutectoid steels are heated in the austenite region about 40°C above the austenite-ferrite boundary (Fig. 9.28), held the necessary time at the elevated temperature, and then slowly cooled to room temperature, usually in the furnace in which they were heated. For hypereutectoid steels, it is customary to austenitize in the two-phase austenite plus cementite (Fe_3C) region, about 40°C above the eutectoid temperature. The microstructure of hypoeutectoid steels after full annealing consists of proeutectoid ferrite and pearlite (Fig. 9.10).

Process annealing, which is often referred to as a *stress relief*, partially softens cold-worked low-carbon steels by relieving internal stresses from cold working. This treatment, which is usually applied to hypoeutectoid steels with less than 0.3 percent C, is carried out at a temperature below the eutectoid temperature, usually between 550°C and 650°C (Fig. 9.28).

Normalizing is a heat treatment in which the steel is heated in the austenitic region and then cooled in still air. The microstructure of thin sections of normalized

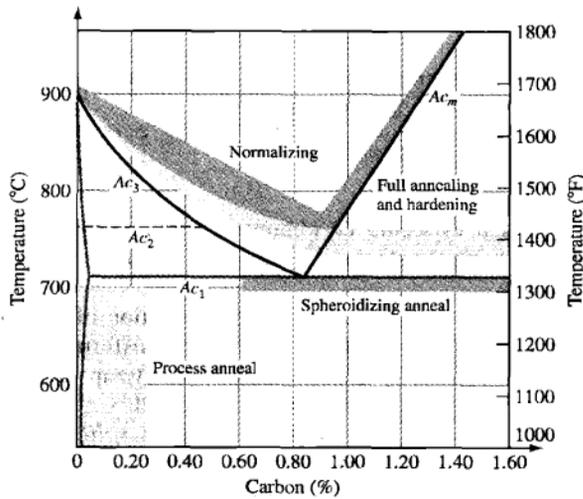


Figure 9.28

Commonly used temperature ranges for annealing plain-carbon steels.

(From T.G. Digges et al., "Heat treatment and Properties of Iron and Steel," NBS Monograph 88, 1966, p. 10.)

hypoeutectoid plain-carbon steels consists of proeutectoid ferrite and fine pearlite. The purposes for normalizing vary. Some of these are:

1. To refine the grain structure
2. To increase the strength of the steel (compared to annealed steel)
3. To reduce compositional segregation in castings or forgings and thus provide a more uniform structure

The austenitizing temperature ranges used for normalizing plain-carbon steels are shown in Fig. 9.28. Normalizing is more economical than full annealing since no furnace is required to control the cooling rate of the steel.

9.3.5 Tempering of Plain-Carbon Steels

The Tempering Process Tempering is the process of heating a martensitic steel at a temperature below the eutectoid transformation temperature to make it softer and more ductile. Figure 9.29 schematically illustrates the customary quenching and tempering process for a plain-carbon steel. As shown in Fig. 9.29, the steel is first austenitized and then quenched at a rapid rate to produce martensite and to avoid the transformation of austenite to ferrite and cementite. The steel is then subsequently reheated at a temperature below the eutectoid temperature to soften the martensite by transforming it to a structure of iron carbide particles in a matrix of ferrite.

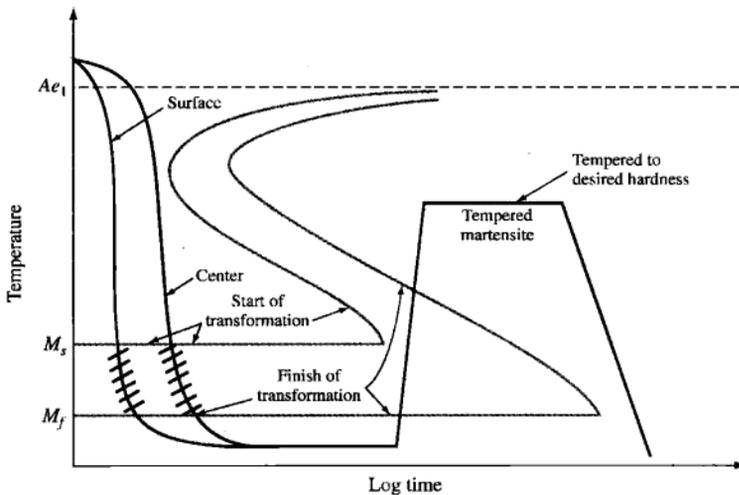


Figure 9.29

Schematic diagram illustrating the customary quenching and tempering process for a plain-carbon steel.

(From "Suiting the Heat Treatment to the Job," United States Steel Corp., 1968, p. 34. Courtesy of United States Steel Corporation.)

Microstructural Changes in Martensite Upon Tempering Martensite is a metastable structure and decomposes upon reheating. In lath martensites of low-carbon plain-carbon steels, there is a high dislocation density, and these dislocations provide lower-energy sites for carbon atoms than their regular interstitial positions. Thus, when low-carbon martensitic steels are first tempered in the 20°C to 200°C range, the carbon atoms segregate themselves to these lower-energy sites.

For martensitic plain-carbon steels with more than 0.2 percent carbon, the main mode of carbon redistribution at tempering temperatures below 200°C is by precipitation clustering. In this temperature range, a very small-sized precipitate called *epsilon* (ϵ) carbide forms. The carbide that forms when martensitic steels are tempered from 200°C to 700°C is *cementite*, Fe_3C . When the steels are tempered between 200°C and 300°C, the shape of the precipitate is rodlike (Fig. 9.30). At higher tempering temperatures from 400°C to 700°C, the rodlike carbides coalesce to form sphere-like particles. Tempered martensite that shows the coalesced cementite in the optical microscope is called **spheroidite** (Fig. 9.31).



Figure 9.30
Precipitation of Fe_3C in Fe-0.39% C martensite tempered 1 h at 300°C. (Electron micrograph.)
[After G.R. Speich and W.C. Leslie, *Met. Trans.*, 31:1043(1972).]

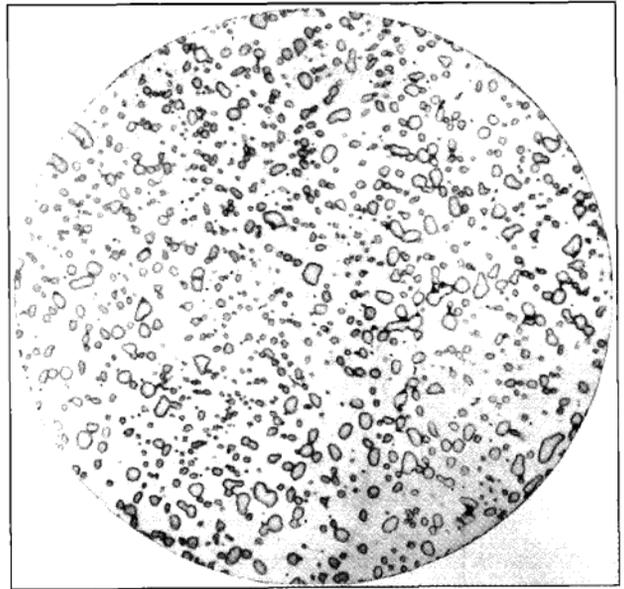


Figure 9.31
Spheroidite in a 1.1 percent C hypereutectoid steel. (Magnification 1000 \times .)
(After J. Vilella, E.C. Bain, and H.W. Paxton, "Alloying Elements in Steel," 2d ed., American Society for Metals, 1966, p. 101. Reprinted with permission of ASM International. All rights reserved. www.asminternational.org.)

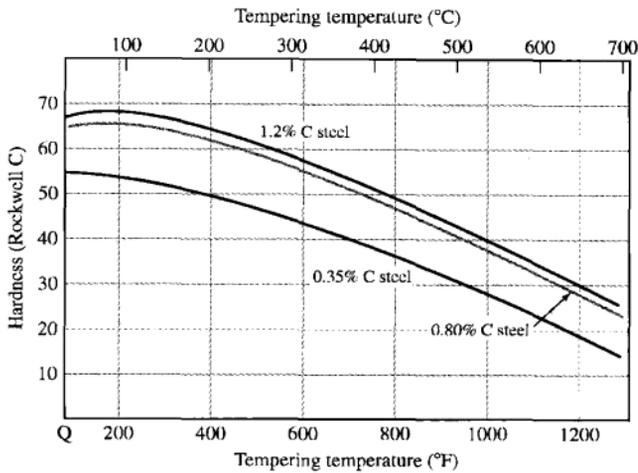


Figure 9.32
 Hardness of iron-carbon martensites (0.35 to 1.2 percent C) tempered 1 h at indicated temperatures.
 (From p. 38 in E.C. Bain and H.W. Paxton, "Alloying Elements in Steel," 2d ed., American Society for Metals, 1966. Used by permission of ASM International.)

Effect of Tempering Temperature on the Hardness of Plain-Carbon Steels
 Figure 9.32 shows the effect of increasing tempering temperature on the hardness of several martensitic plain-carbon steels. Above about 200°C, the hardness gradually decreases as the temperature is increased up to 700°C. This gradual decrease in hardness of the martensite with increasing temperature is due mainly to the diffusion of the carbon atoms from their stressed interstitial lattice sites to form second-phase iron carbide precipitates.

Martempering (Marquenching) **Martempering (marquenching)** is a modified quenching procedure used for steels to minimize distortion and cracking that may develop during uneven cooling of the heat-treated material. The martempering process consists of (1) austenitizing the steel, (2) quenching it in hot oil or molten salt at a temperature just slightly above (or slightly below) the M_s temperature, (3) holding the steel in the quenching medium until the temperature is uniform throughout and stopping this isothermal treatment before the austenite-to-bainite transformation begins, and (4) cooling at a moderate rate to room temperature to prevent large temperature differences. The steel is subsequently tempered by the conventional treatment. Figure 9.33 shows a cooling path for the martempering process.

The structure of the martempered steel is *martensite*, and that of the martempered (marquenching) steel that is subsequently tempered is *tempered martensite*. Table 9.2 lists some of the mechanical properties of a 0.95 percent C plain-carbon steel after martempering and tempering along with those obtained by conventional

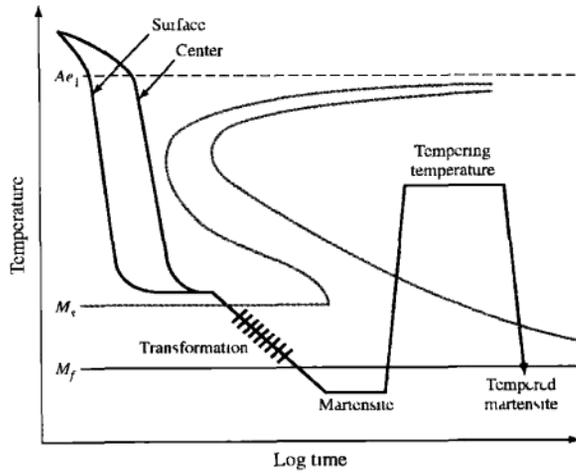


Figure 9.33

Cooling curve for martempering (marquenching) superimposed on a eutectoid plain-carbon steel IT diagram. The interrupted quench reduces the stresses developed in the metal during quenching

(From "Metals Handbook," vol 2, 8th ed., American Society for Metals, 1964, p 37 Used by permission of ASM International.)

Table 9.2 Some mechanical properties (at 20°C) of a 1095 steel developed by austempering as compared to some other heat treatments

Heat treatment	Rockwell C hardness	Impact (ft · lb)	Elongation in 1 in. (%)
Water-quench and temper	53.0	12	0
Water-quench and temper	52.5	14	0
Martemper and temper	53.0	28	0
Martemper and temper	52.8	24	0
Austemper	52.0	45	11
Austemper	52.5	40	8

Source: "Metals Handbook," vol. 2, 8th ed., American Society for Metals, 1964

quenching and tempering. The major difference in these two sets of properties is that the martempered and tempered steel has higher impact energy values. It should be noted that the term *martempering* is misleading, and a better word for the process is *marquenching*.

Austempering Austempering is an isothermal heat treatment that produces a bainite structure in some plain-carbon steels. The process provides an alternative procedure to

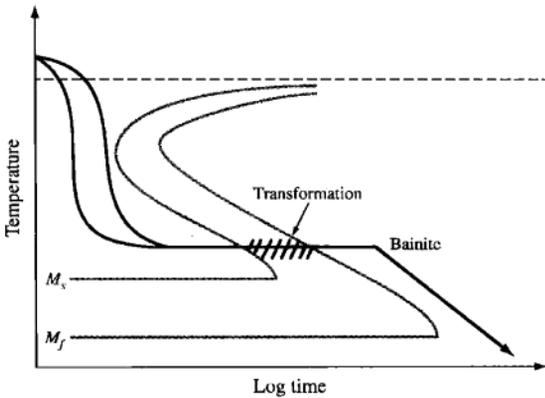


Figure 9.34

Cooling curves for austempering a eutectoid plain-carbon steel. The structure resulting from this treatment is bainite. An advantage of this heat treatment is that tempering is unnecessary. Compare with the customary quenching and tempering process shown in Fig. 9.29. M_s and M_f are the start and finish of martensitic transformation, respectively.

(From "Suiting the Heat Treatment to the Job," United States Steel Corp., 1968, p. 34. Courtesy of United States Steel Corporation.)

quenching and tempering for increasing the toughness and ductility of some steels. In the austempering process the steel is first austenitized, then quenched in a molten salt bath at a temperature just above the M_s temperature of the steel, held isothermally to allow the austenite-to-bainite transformation to take place, and then cooled to room temperature in air (Fig. 9.34). The final structure of an austempered eutectoid plain-carbon steel is *bainite*.

The advantages of austempering are (1) improved ductility and impact resistance of certain steels over those values obtained by conventional quenching and tempering (Table 9.2) and (2) decreased distortion of the quenched material. The disadvantages of austempering over quenching and tempering are (1) the need for a special molten salt bath and (2) the fact that the process can be used for only a limited number of steels.

9.3.6 Classification of Plain-Carbon Steels and Typical Mechanical Properties

Plain-carbon steels are most commonly designated by a four-digit AISI-SAE⁶ code. The first two digits are 10 and indicate that the steel is a plain-carbon steel. The last

⁶AISI stands for the American Iron and Steel Institute, and SAE for the Society for Automotive Engineers.

two digits indicate the nominal carbon content of the steel in hundredths of a percent. For example, the AISI-SAE code number 1030 for a steel indicates that the steel is a plain-carbon steel containing a nominal 0.30 percent carbon. All plain-carbon steels contain manganese as an alloying element to enhance strength. The manganese content of most plain-carbon steels ranges between 0.30 and 0.95 percent. Plain-carbon steels also contain impurities of sulfur, phosphorus, silicon, and some other elements.

Typical mechanical properties of some AISI-SAE type plain-carbon steels are listed in Table 9.3. The very-low-carbon plain-carbon steels have relatively low strengths but very high ductilities. These steels are used for sheet material for forming applications such as fenders and body panels for automobiles. As the carbon content of the plain-carbon steels is increased, the steels become stronger but less ductile. Medium-carbon steels (1020–1040) find application for shafts and gears. High-carbon steels (1060–1095) are used, for example, for springs, die blocks, cutters, and shear blades.

9.4 LOW-ALLOY STEELS

Plain-carbon steels can be used successfully if the strength and other engineering requirements are not too severe. These steels are relatively low in cost but have some limitations, which include the following:

1. Plain-carbon steels cannot be strengthened beyond about 100,000 psi (690 MPa) without a substantial loss in ductility and impact resistance.
2. Large-section thicknesses of plain-carbon steels cannot be produced with a martensitic structure throughout, i.e., they are not deep-hardenable.
3. Plain-carbon steels have low corrosion and oxidation resistance.
4. Medium-carbon plain-carbon steels must be quenched rapidly to obtain a fully martensitic structure. Rapid quenching leads to possible distortion and cracking of the heat-treated part.
5. Plain-carbon steels have poor impact resistance at low temperatures.

To overcome the deficiencies of plain-carbon steels, alloy steels have been developed that contain alloying elements to improve their properties. Alloy steels in general cost more than plain-carbon steels, but for many applications they are the only materials that can be used to meet engineering requirements. The principal alloying elements added to make alloy steels are manganese, nickel, chromium, molybdenum, and tungsten. Other elements that are sometimes added include vanadium, cobalt, boron, copper, aluminum, lead, titanium, and columbium (niobium).

9.4.1 Classification of Alloy Steels

Alloy steels may contain up to 50 percent of alloying elements and still be considered alloy steels. In this book, low-alloy steels containing from about 1 to 4 percent

Table 9.3 Typical mechanical properties and applications of plain-carbon steels

Alloy AISI-SAE number	Chemical composition (wt %)	Condition	Tensile strength		Yield strength		Elongation (%)	Typical applications
			ksi	MPa	ksi	MPa		
1010	0.10 C, 0.40 Mn	Hot-rolled	40-60	276-414	26-45	179-310	28-47	Sheet and strip for drawing; wire, rod, and nails and screws; concrete reinforcement bar
		Cold-rolled	42-58	290-400	23-38	159-262	30-45	
1020	0.20 C, 0.45 Mn	As rolled	65	448	48	331	36	Steel plate and structural sections; shafts, gears
		Annealed	57	393	43	297	36	
1040	0.40 C, 0.45 Mn	As rolled	90	621	60	414	25	Shafts, studs, high-tensile tubing, gears
		Annealed	75	517	51	352	30	
1060	0.60 C, 0.65 Mn	Tempered*	116	800	86	593	20	Spring wire, forging dies, railroad wheels
		As rolled	118	814	70	483	17	
1080	0.80 C, 0.80 Mn	Annealed	91	628	54	483	22	Music wire, helical springs, cold chisels, forging die blocks
		Tempered*	160	110	113	780	13	
1095	0.95 C, 0.40 Mn	As rolled	140	967	85	586	12	Dies, punches, taps, milling cutters, shear blades, high-tensile wire
		Annealed	89	614	54	373	25	
		Tempered*	189	1304	142	980	12	
		As rolled	140	966	83	573	9	
		Annealed	95	655	55	379	13	
		Tempered*	183	1263	118	814	10	

*Quenched and tempered at 315°C (600°F).

Table 9.4 Principal types of standard alloy steels

13xx	Manganese 1.75
40xx	Molybdenum 0.20 or 0.25; or molybdenum 0.25 and sulfur 0.042
41xx	Chromium 0.50, 0.80, or 0.95, molybdenum 0.12, 0.20, or 0.30
43xx	Nickel 1.83, chromium 0.50 or 0.80, molybdenum 0.25
44xx	Molybdenum 0.53
46xx	Nickel 0.85 or 1.83, molybdenum 0.20 or 0.25
47xx	Nickel 1.05, chromium 0.45, molybdenum 0.20 or 0.35
48xx	Nickel 3.50, molybdenum 0.25
50xx	Chromium 0.40
51xx	Chromium 0.80, 0.88, 0.93, 0.95, or 1.00
51xxx	Chromium 1.03
52xxx	Chromium 1.45
61xx	Chromium 0.60 or 0.95, vanadium 0.13 or min 0.15
86xx	Nickel 0.55, chromium 0.50, molybdenum 0.20
87xx	Nickel 0.55, chromium 0.50, molybdenum 0.25
88xx	Nickel 0.55, chromium 0.50, molybdenum 0.35
92xx	Silicon 2.00; or silicon 1.40 and chromium 0.70
50Bxx*	Chromium 0.28 or 0.50
51Bxx*	Chromium 0.80
81Bxx*	Nickel 0.30, chromium 0.45, molybdenum 0.12
94Bxx*	Nickel 0.45, chromium 0.40, molybdenum 0.12

*B denotes boron steel.

Source: "Alloy Steel: Semifinished; Hot-Rolled and Cold-Finished Bars," American Iron and Steel Institute, 1970.

of alloying elements will be considered alloy steels. These steels are mainly automotive- and construction-type steels and are commonly referred to simply as *alloy steels*.

Alloy steels in the United States are usually designated by the four-digit AISI-SAE system. The first two digits indicate the principal alloying element or groups of elements in the steel, and the last two digits indicate the hundredths of percent of carbon in the steel. Table 9.4 lists the nominal compositions of the principal types of standard alloy steels.

9.4.2 Distribution of Alloying Elements in Alloy Steels

The way in which alloy elements distribute themselves in carbon steels depends primarily on the compound- and carbide-forming tendencies of each element. Table 9.5 summarizes the approximate distribution of most of the alloying elements present in alloy steels.

Nickel dissolves in the α ferrite of the steel since it has less tendency to form carbides than iron. Silicon combines to a limited extent with the oxygen in the steel to form nonmetallic inclusions but otherwise dissolves in the ferrite. Most of the manganese added to carbon steels dissolves in the ferrite. Some of the manganese, however, will form carbides but will usually enter the cementite as $(\text{Fe}, \text{Mn})_3\text{C}$.

Table 9.5 Approximate distribution of alloying elements in alloy steels*

Element	Dissolved in ferrite	Combined in carbide	Combined as carbide	Compound	Elemental
Nickel	Ni			Ni_3Al	
Silicon	Si			$\text{SiO}_2 \cdot \text{M}_x\text{O}_y$	
Manganese	Mn \longleftrightarrow Mn		$(\text{Fe}, \text{Mn})_3\text{C}$	MnS; $\text{MnO} \cdot \text{SiO}_2$	
Chromium	Cr \longleftrightarrow Cr		$(\text{Fe}, \text{Cr}_3)\text{C}$ Cr_7C_3 Cr_{23}C_6		
Molybdenum	Mo \longleftrightarrow Mo		Mo_2C		
Tungsten	W \longleftrightarrow W		W_2C		
Vanadium	V \longleftrightarrow V		V_4C_3		
Titanium	Ti \longleftrightarrow Ti		TiC		
Columbium [†]	Cb \longleftrightarrow Cb		CbC		
Aluminum	Al			Al_2O_3 ; AlN	
Copper	Cu (small amount)				
Lead					Pb

*The arrows indicate the relative tendencies of the elements listed to dissolve in the ferrite or combine in carbides.

[†]Cb = Nb (niobium).

Source: E.C. Bain and H.W. Paxton, "Alloying Elements in Steel," 2d ed., American Society for Metals, 1966.

Chromium, which has a somewhat stronger carbide-forming tendency than iron, partitions between the ferrite and carbide phases. The distribution of chromium depends on the amount of carbon present and on whether other stronger carbide-forming elements such as titanium and columbium are absent. Tungsten and molybdenum combine with carbon to form carbides if there is sufficient carbon present and if other stronger carbide-forming elements such as titanium and columbium are absent. Vanadium, titanium, and columbium are strong carbide-forming elements and are found in steels mainly as carbides. Aluminum combines with oxygen and nitrogen to form the compounds Al_2O_3 and AlN, respectively.

9.4.3 Effects of Alloying Elements on the Eutectoid Temperature of Steels

The various alloying elements cause the eutectoid temperature of the Fe-Fe₃C phase diagram to be raised or lowered (Fig. 9.35). Manganese and nickel both lower the eutectoid temperature and act as *austenite-stabilizing elements* enlarging the austenitic region of the Fe-Fe₃C phase diagram (Fig. 9.6). In some steels with sufficient amounts of nickel or manganese, the austenitic structure may be obtained at room temperature. The carbide-forming elements such as tungsten, molybdenum, and titanium raise the eutectoid temperature of the Fe-Fe₃C phase diagram to

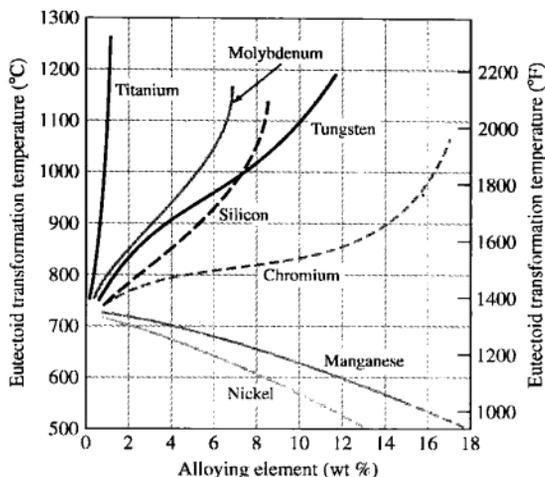


Figure 9.35

The effect of the percentage of alloying elements on the eutectoid temperature of the transformation of austenite to pearlite in the Fe-Fe₃C phase diagram.

(From "Metals Handbook," vol. 8, 8th ed., American Society for Metals, 1973, p. 191. Used by permission of ASM International.)

higher values and reduce the austenitic phase field. These elements are called *ferrite-stabilizing elements*.

9.4.4 Hardenability

The **hardenability** of a steel is defined as that property which determines the depth and distribution of hardness induced by quenching from the austenitic condition. The hardenability of a steel depends primarily on (1) the composition of the steel, (2) the austenitic grain size, and (3) the structure of the steel before quenching. Hardenability should not be confused with the *hardness* of a steel, which is its resistance to plastic deformation, usually by indentation.

In industry, hardenability is most commonly measured by the **Jominy hardenability test**. In the Jominy end-quench test, the specimen consists of a cylindrical bar with a 1 in. diameter and 4 in. length and with a $\frac{1}{16}$ in. flange at one end (Fig. 9.36a). Since prior structure has a strong effect on hardenability, the specimen is usually normalized before testing. In the Jominy test, after the sample has been austenitized, it is placed in a fixture, as shown in Fig. 9.36b, and a jet of water is quickly splashed at one end of the specimen. After cooling, two parallel flat surfaces are ground on the opposite sides of the test bar, and Rockwell C

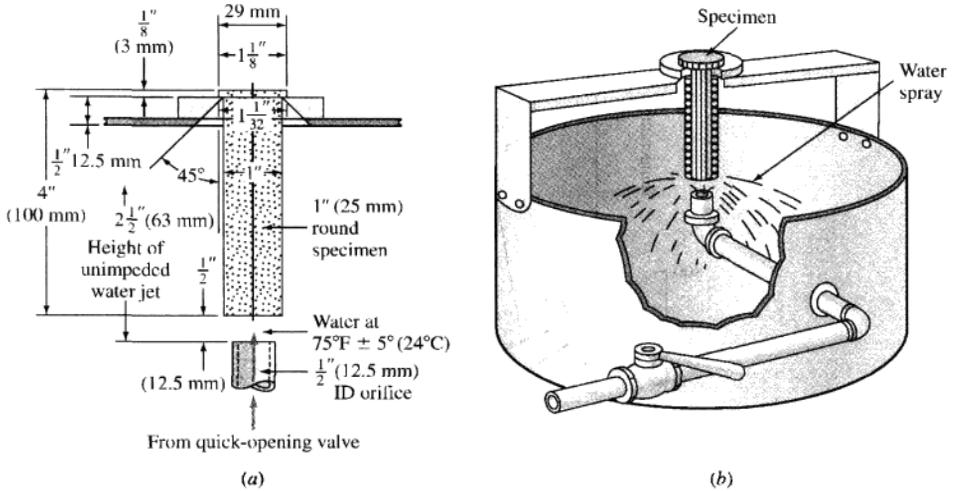


Figure 9.36

(a) Specimen and fixture for end-quench hardenability test.

(After M.A. Grossmann and E.C. Bain, "Principles of Heat Treatment," 5th ed., American Society for Metals, 1964, p. 114.)

(b) Schematic illustration of the end-quench test for hardenability.

[From H.E. McGannon (ed.), "The Making, Shaping, and Treating of Steel," 9th ed., United States Steel, 1971, p. 1099. Courtesy of United States Steel Corporation.]

hardness measurements are made along these surfaces up to 2.5 in. from the quenched end.

Figure 9.37 shows a hardenability plot of Rockwell C hardness versus distance from the quenched end for a 1080 eutectoid plain-carbon steel. This steel has relatively low hardenability since its hardness decreases from a value of RC = 65 at the quenched end of the Jominy bar to RC = 50 at just $\frac{3}{16}$ in. from the quenched end. Thus, thick sections of this steel cannot be made fully martensitic by quenching. Figure 9.37 correlates the end-quench hardenability data with the continuous transformation diagram for the 1080 steel and indicates the microstructural changes that take place along the bar at four distances A, B, C, and D from the quenched end.

Hardenability curves for some 0.40 percent C alloy steels are shown in Fig. 9.38. The 4340 alloy steel has exceptionally high hardenability and can be quenched to a hardness of RC = 40 at 2 in. from the quenched end of a Jominy bar. Alloy steels thus are able to be quenched at a slower rate and still maintain relatively high hardness values.

Alloy steels such as the 4340 steel are highly hardenable because, upon cooling from the austenitic region, the decomposition of austenite to ferrite and bainite is delayed and the decomposition of austenite to martensite can be accomplished at

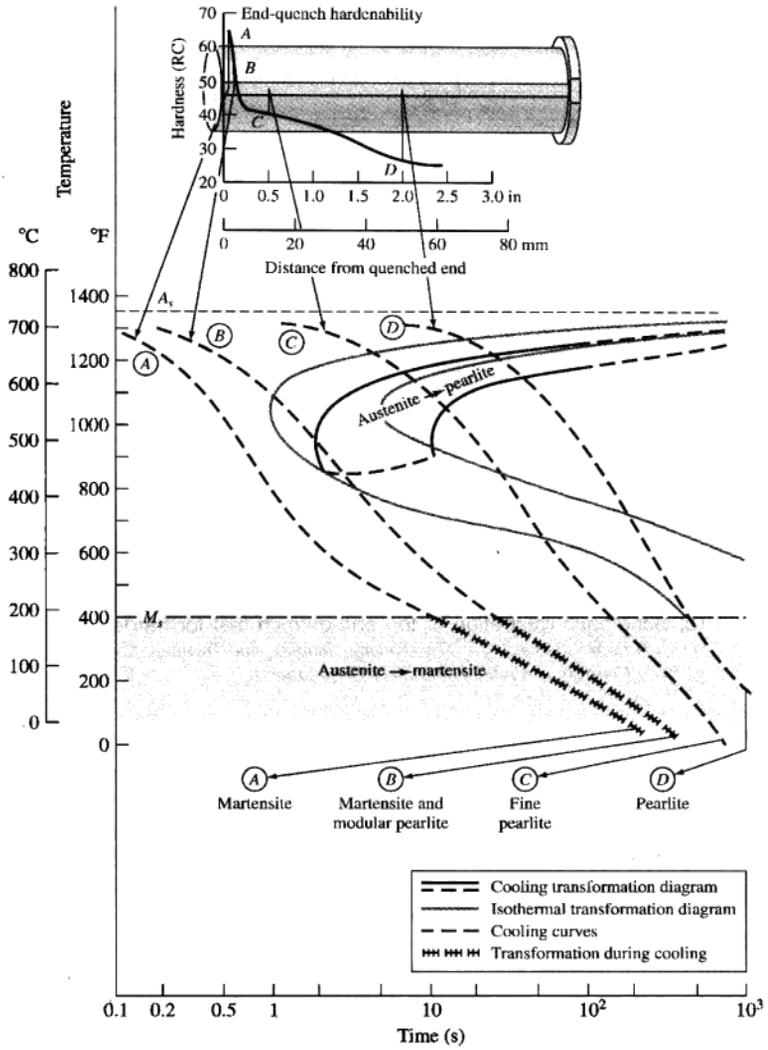


Figure 9.37 Correlation of continuous-cooling transformation diagram and end-quench hardenability test data for eutectoid carbon steel. (From "Isothermal Transformation Diagrams," United States Steel Corp., 1963, p. 181. Courtesy of United States Steel Corporation.)

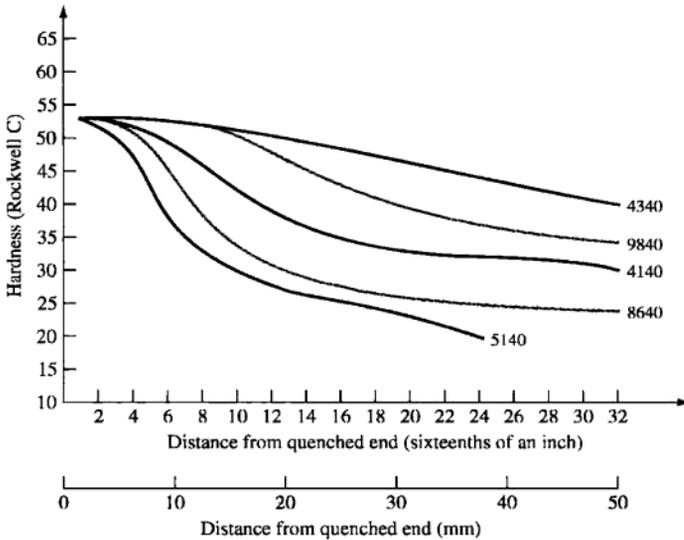


Figure 9.38

Comparative hardenability curves for 0.40 percent C alloy steel.

[From H.E. McGannon (ed.), "The Making, Shaping, and Treating of Steel," 9th ed., United States Steel Corp., 1971, p. 1139. Courtesy of United States Steel Corporation.]

slower rates. This delay of the austenite to ferrite plus bainite decomposition is quantitatively shown on the continuous-cooling transformation diagram of Fig. 9.39.

For most carbon and low-alloy steels, a standard quench produces at the same cross-section position common cooling rates along long round steel bars of the same diameter. However, the cooling rates differ (1) for different bar diameters, (2) for different positions in the cross sections of the bars, and (3) for different quenching media. Figure 9.40 shows bar diameter versus cooling rate curves for different cross-section locations within steel bars using quenches of agitated water in agitated oil. These plots can be used to determine the cooling rate and the associated distance from the quenched end of a standard quenched Jominy bar for a selected bar diameter at a particular cross-section location in the bar using a specific quenching medium. These cooling rates and their associated distances from the end of Jominy quenched bars can be used with Jominy plots of surface hardness versus distance from the quenched end for specific steels to determine the hardness of a particular steel at a specific location in the cross section of the steel bar in question. Example Problem 9.5 shows how the plots of Fig. 9.40 can be used to predict the hardness of a steel bar of a given diameter at a specific cross-section location quenched in a given medium. It should be pointed out that the Jominy hardness versus distance from the quenched-end plots are usually plotted as bands of data rather than as lines so that hardnesses obtained from the line curves are actually values in the center of a range of values.

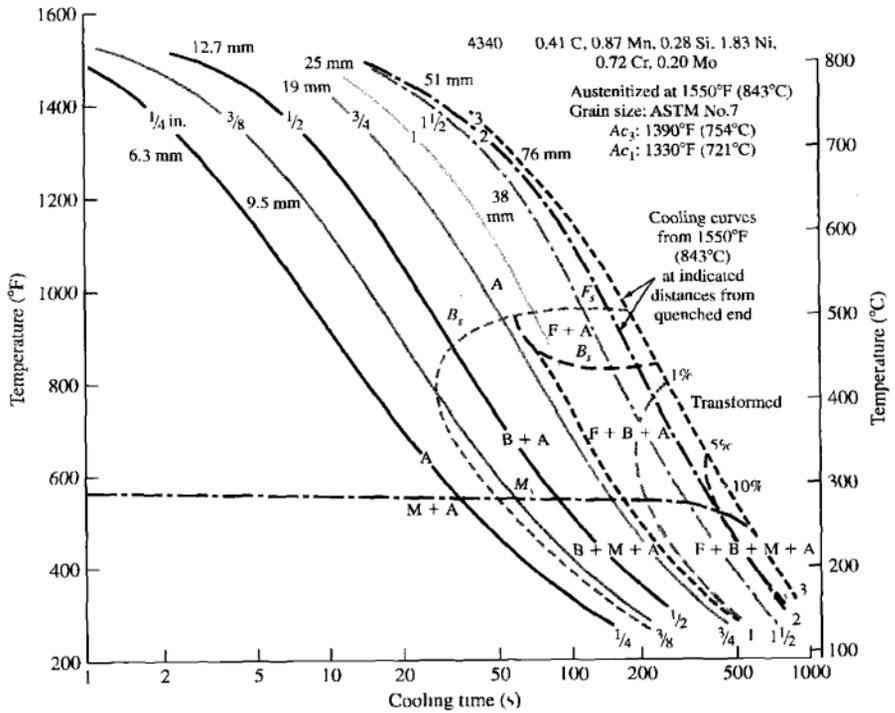


Figure 9.39

Continuous-cooling transformation diagram for AISI 4340 alloy steel. A = austenite, F = ferrite, B = bainite, M = martensite

(From "Metal Progress," September 1964, p 106 Used by permission of ASM International)

EXAMPLE PROBLEM 9.5

An austenitized 40 mm diameter 5140 alloy steel bar is quenched in agitated oil. Predict what the Rockwell C (RC) hardness of this bar will be at (a) its surface and (b) its center.

■ **Solution**

- Surface of bar. The cooling rate at the surface of the 40 mm steel bar quenched in agitated oil is found from part (ii) of Fig. 9.40 to be comparable to the cooling rate at 8 mm from the end of a standard quenched Jominy bar. Using Fig. 9.38 at 8 mm from the quenched end of the Jominy bar and the curve for the 5140 steel indicates that the hardness of the bar should be about 32 RC.
- Center of the bar. The cooling rate at the center of the 40 mm diameter bar quenched in oil is found from part (ii) of Fig. 9.40 to be associated with 13 mm from the end of a quenched Jominy bar. The corresponding hardness for this distance from the end of a quenched Jominy bar for the 5140 alloy is found by using Fig. 9.38 to be about 26 RC.

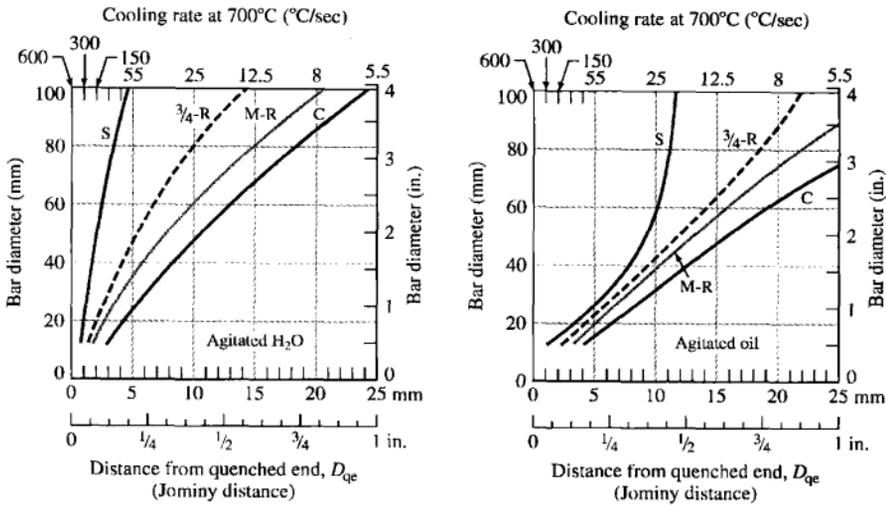


Figure 9.40

Cooling rates in long round steel bars quenched in (i) agitated water and (ii) agitated oil. Top abscissa, cooling rates at 700°C; bottom abscissa, equivalent positions on an end-quenched test bar. (C = center, M-R = midradius, S = surface, dashed line = approximate curve for $\frac{3}{4}$ -radius positions on the cross section of bars.)

(Van Vlack, L.H., "Materials for Engineering: Concepts and Applications," 1st ed., © 1982. Electronically reproduced by permission of Pearson Education, Inc., Upper Saddle River, New Jersey.)

9.4.5 Typical Mechanical Properties and Applications for Low-Alloy Steels

Table 9.6 lists some typical tensile mechanical properties and applications for some commonly used low-alloy steels. For some strength levels, low-alloy steels have better combinations of strength, toughness, and ductility than plain-carbon steels. However, low-alloy steels cost more and so are used only when necessary. Low-alloy steels are used to a great extent in the manufacture of automobiles and trucks for parts that require superior strength and toughness properties that cannot be obtained from plain-carbon steels. Some typical applications for low-alloy steels in automobiles are shafts, axles, gears, and springs. Low-alloy steels containing about 0.2 percent C are commonly carburized or surface heat-treated to produce a hard, wear-resistant surface while maintaining a tough inner core.

9.5 ALUMINUM ALLOYS

Before discussing some of the important aspects of the structure, properties, and applications of aluminum alloys, let us examine the precipitation-strengthening (hardening) process that is used to increase the strength of many aluminum and other metal alloys.

Table 9.6 Typical mechanical properties and applications of low-alloy steels

Alloy AISI-SAE number	Chemical composition (wt %)	Condition	Tensile strength		Yield strength		Elongation (%)	Typical applications
			ksi	MPa	ksi	MPa		
Manganese steels								
1340	0.40 C, 1.75 Mn	Annealed	102	704	63	435	20	High-strength bolts
		Tempered*	230	1587	206	1421	12	
Chromium steels								
5140	0.40 C, 0.80 Cr, 0.80 Mn	Annealed	83	573	43	297	29	Automobile transmission gears
		Tempered*	229	1580	210	1449	10	
5160	0.60 C, 0.80 Cr, 0.90 Mn	Annealed	105	725	40	276	17	Automobile coil and leaf springs
		Tempered*	290	2000	257	1773	9	
Chromium-molybdenum steels								
4140	0.40 C, 1.0 Cr, 0.9 Mn, 0.20 Mo	Annealed	95	655	61	421	26	Gears for aircraft gas turbine engines, transmissions
		Tempered*	225	1550	208	1433	9	
Nickel-molybdenum steels								
4620	0.20 C, 1.83 Ni, 0.55 Mn, 0.25 Mo	Annealed	75	517	54	373	31	Transmission gears, chain pins, shafts, roller bearings
		Normalized	83	573	53	366	29	
4820	0.20 C, 3.50 Ni, 0.60 Mn, 0.25 Mo	Annealed	99	683	67	462	22	Gears for steel mill equipment, paper machinery, mining machinery, earth- moving equipment
		Normalized	100	690	70	483	60	
Nickel (1.83%)-chromium-molybdenum steels								
4340 (E)	0.40 C, 1.83 Ni, 0.90 Mn, 0.80 Cr, 0.20 Mo	Annealed	108	745	68	469	22	Heavy sections, landing gears, truck parts
		Tempered*	250	1725	230	1587	10	
Nickel (0.55%)-chromium-molybdenum steels								
8620	0.20 C, 0.55 Ni, 0.50 Cr, 0.80 Mn, 0.20 Mo	Annealed	77	531	59	407	31	Transmission gears
		Normalized	92	635	52	359	26	
8650	0.50 C, 0.55 Ni, 0.50 Cr, 0.80 Mn, 0.20 Mo	Annealed	103	710	56	386	22	Small machine axles, shafts
		Tempered*	250	1725	225	1552	10	

*Tempered at 600°F (315°C).

9.5.1 Precipitation Strengthening (Hardening)

Precipitation Strengthening of a Generalized Binary Alloy The object of precipitation strengthening is to create in a heat-treated alloy a dense and fine dispersion of precipitated particles in a matrix of deformable metal. The precipitate particles act as obstacles to dislocation movement and thereby strengthen the heat-treated alloy.

The precipitation-strengthening process can be explained in a general way by referring to the binary phase diagram of metals A and B shown in Fig. 9.41. In order for an alloy system to be able to be precipitation-strengthened for certain alloy compositions, there must be a terminal solid solution that has a decreasing solid solubility as the temperature decreases. The phase diagram of Fig. 9.41 shows this type of decrease in solid solubility in terminal solid solution α in going from point a to point b along the indicated solvus.

Let us now consider the precipitation strengthening of an alloy of composition x_1 of the phase diagram of Fig. 9.41. We choose the alloy composition x_1 since there is a large decrease in the solid solubility of solid solution α in decreasing the temperature from T_2 to T_3 . The precipitation-strengthening process involves the following three basic steps:

1. *Solution heat treatment* is the *first step* in the precipitation-strengthening process. Sometimes this treatment is referred to as *solutionizing*. The alloy sample, which may be in the wrought or cast form, is heated to a temperature between the solvus and solidus temperatures and soaked there until a uniform solid-solution structure

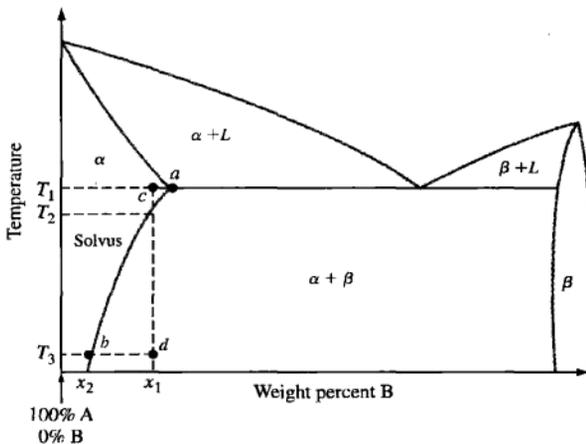


Figure 9.41

Binary phase diagram for two metals A and B having a terminal solid solution α that has a decreasing solid solubility of B in A with decreasing temperature.

is produced. Temperature T_1 at point c of Fig. 9.41 is selected for our alloy x_1 because it lies midway between the solvus and solidus phase boundaries of solid solution α .

2. *Quenching* is the *second step* in the precipitation-strengthening process. The sample is rapidly cooled to a lower temperature, usually room temperature, and the cooling medium is usually water at room temperature. The structure of the alloy sample after water quenching consists of a supersaturated solid solution. The structure of our alloy x_1 after quenching to temperature T_3 at point d of Fig. 9.41 thus consists of a supersaturated solid solution of the α phase.

3. *Aging* is the *third basic step* in the precipitation-strengthening process. Aging the solution heat-treated and quenched alloy sample is necessary so that a finely dispersed precipitate forms. The formation of a finely dispersed precipitate in the alloy is the objective of the precipitation-strengthening process. The fine precipitate in the alloy impedes dislocation movement during deformation by forcing the dislocations to either cut through the precipitated particles or go around them. By restricting dislocation movement during deformation, the alloy is strengthened.

Aging the alloy at room temperature is called *natural aging*, whereas aging at elevated temperatures is called *artificial aging*. Most alloys require artificial aging, and the aging temperature is usually between about 15 and 25 percent of the temperature difference between room temperature and the solution heat-treatment temperature.

Decomposition Products Created by the Aging of the Supersaturated Solid Solution A precipitation-hardenable alloy in the supersaturated solid-solution condition is in a high-energy state, as indicated schematically by energy level 4 of Fig. 9.42. This energy state is relatively unstable, and the alloy tends to seek a lower energy state by the spontaneous decomposition of the supersaturated solid solution into metastable phases or the equilibrium phases. The driving force for the precipitation of metastable phases or the equilibrium phase is the lowering of the energy of the system when these phases form.

When the supersaturated solid solution of the precipitation-hardenable alloy is aged at a relatively low temperature where only a small amount of activation energy is available, clusters of segregated atoms called *precipitation zones*, or *GP zones*,⁷ are formed. For the case of our alloy A-B of Fig. 9.41, the zones will be regions enriched with B atoms in a matrix primarily of A atoms. The formation of these zones in the supersaturated solid solution is indicated by the circular sketch at the lower energy level 3 of Fig. 9.42. Upon further aging and if sufficient activation energy is available (as a result of the aging temperature being high enough), the zones develop into or are replaced by a coarser (larger in size) intermediate metastable precipitate, indicated by the circular sketch at the still-lower energy

⁷Precipitation zones are sometimes referred to as GP zones, named after the two early scientists Guinier and Preston who first identified these structures by x-ray diffraction analyses.

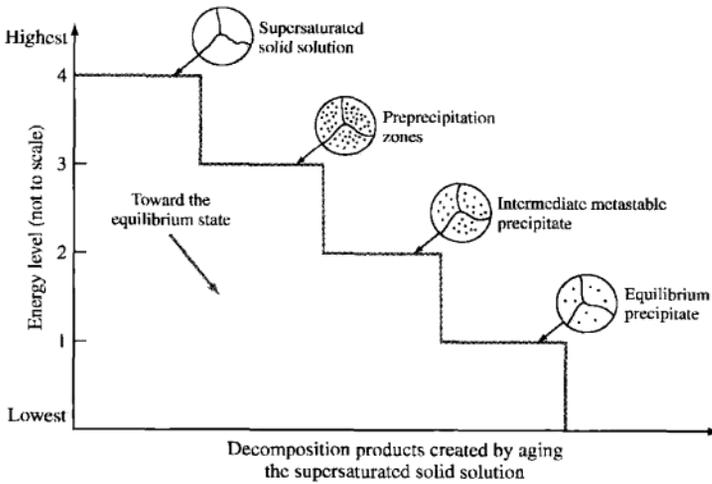


Figure 9.42

Decomposition products created by the aging of a supersaturated solid solution of a precipitation-hardenable alloy. The highest energy level is for the supersaturated solid solution, and the lowest energy level is for the equilibrium precipitate. The alloy can go spontaneously from a higher energy level to a lower one if there is sufficient activation energy for the transformation and if the kinetic conditions are favorable.

level 2. Finally, if aging is continued (usually a higher temperature is necessary) and if sufficient activation energy is available, the intermediate precipitate is replaced by the equilibrium precipitate indicated by the even-still-lower energy level 1 of Fig. 9.42.

The Effect of Aging Time on the Strength and Hardness of a Precipitation-Hardenable Alloy that Has Been Solution Heat-Treated and Quenched The effect of aging on strengthening a precipitation-hardenable alloy that has been solution heat-treated and quenched is usually presented as an *aging curve*. The aging curve is a plot of strength or hardness versus aging time (usually on a logarithmic scale) at a particular temperature. Figure 9.43 shows a schematic aging curve. At zero time, the strength of the supersaturated solid solution is indicated on the ordinate axis of the plot. As the aging time increases, preprecipitation zones form and their size increases, and the alloy becomes stronger and harder and less ductile (Fig. 9.43). A maximum strength (peak aged condition) is eventually reached if the aging temperature is sufficiently high, which is usually associated with the formation of an intermediate metastable precipitate. If aging is continued so that the intermediate precipitate coalesces and coarsens, the alloy overages and becomes weaker than in the peak aged condition (Fig. 9.43).

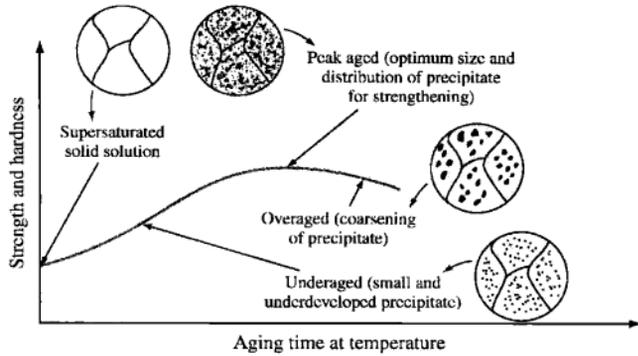


Figure 9.43

Schematic aging curve (strength or hardness versus time) at a particular temperature for a precipitation-hardenable alloy.

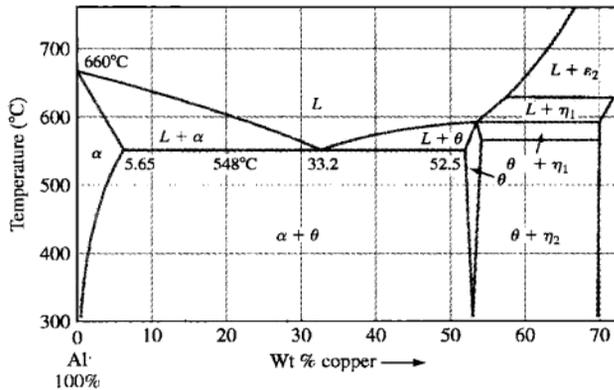


Figure 9.44

Aluminum-rich end of aluminum-copper phase diagram.

[From K.R. Van Horn (ed.), "Aluminum," vol. 1, American Society for Metals, 1967, p. 372. Used by permission of ASM International.]

Precipitation Strengthening (Hardening) of an Al-4% Cu Alloy Let us now examine the structure and hardness changes that occur during the precipitation heat treatment of an aluminum-4% copper alloy. The heat-treatment sequence for the precipitation strengthening of this alloy is:

1. Solution heat treatment: the Al-4% Cu alloy is solutionized at about 515°C (see the Al-Cu phase diagram of Fig. 9.44).
2. Quenching: the solution heat-treated alloy is rapidly cooled in water at room temperature.

3. Aging: the alloy after solution heat treatment and quenching is artificially aged in the 130°C to 190°C range.

Structures Formed During the Aging of the Al-4% Cu Alloy In the precipitation strengthening of Al-4% Cu alloys, five sequential structures can be identified: (1) supersaturated solid-solution α , (2) GP1 zones, (3) GP2 zones (also called θ'' phase), (4) θ' phase, and (5) θ phase, CuAl_2 . Not all these phases can be produced at all aging temperatures. GP1 and GP2 zones are produced at lower aging temperatures, and θ' and θ phases occur at higher temperatures.

GP1 zones. These preprecipitation zones are formed at lower aging temperatures and are created by copper atoms segregating in the supersaturated solid-solution α . GP1 zones consist of segregated regions in the shape of disks a few atoms thick (0.4 to 0.6 nm) and about 8 to 10 nm in diameter and form on the {100} cubic planes of the matrix. Since the copper atoms have a diameter of about 11 percent less than the aluminum ones, the matrix lattice around the zones is strained tetragonally. GP1 zones are said to be *coherent* with the matrix lattice since the copper atoms just replace aluminum atoms in the lattice (Fig. 9.45). GP1 zones are detected under the electron microscope by the strain fields they create (Fig. 9.46a).

GP2 zones (θ'' phase). These zones also have a tetragonal structure and are coherent with the {100} of the matrix of the Al-4% Cu alloy. Their size ranges from about 1 to 4 nm thick to 10 to 100 nm in diameter as aging proceeds (Fig. 9.46b).

θ' phase. This phase nucleates heterogeneously, especially on dislocations, and is incoherent with the matrix. (An *incoherent precipitate* is one in which the precipitated particle has a distinct crystal structure different from the matrix [Fig. 9.45a]). θ' phase has a tetragonal structure with a thickness of 10 to 150 nm (Fig. 9.46c).

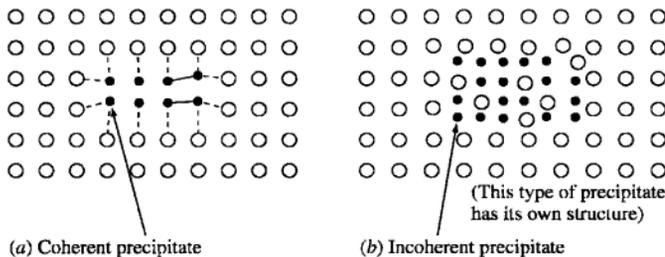
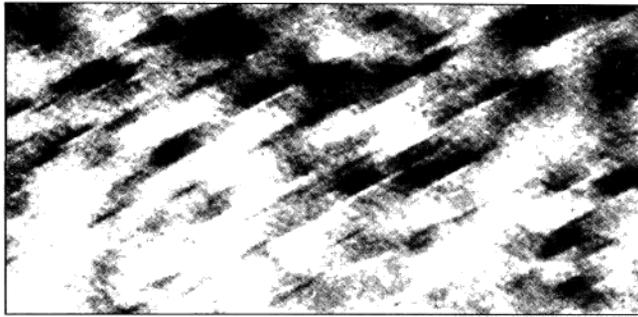


Figure 9.45

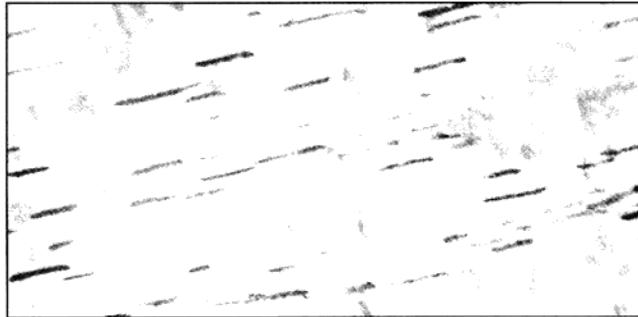
Schematic comparison of the nature of (a) a coherent precipitate and (b) an incoherent precipitate. The coherent precipitate is associated with a high strain energy and low surface energy, and the incoherent one is associated with a low strain energy and high surface energy.



(a)



(b)



(c)

Figure 9.46

Microstructures of aged Al-4% Cu alloys. (a) Al-4% Cu, heated to 540°C, water-quenched, and aged 16 h at 130°C. The GP zones have been formed as disks parallel to the {100} planes of the FCC matrix and at this stage are a few atoms thick and about 100 Å in diameter. Only disks lying on one crystallographic orientation are visible. (Electron micrograph; magnification 1,000,000 \times .) (b) Al-4% Cu, solution-treated at 540°C, quenched in water, and aged for 1 day at 130°C. This thin-foil micrograph shows strain fields due to coherent GP2 zones. The dark regions surrounding the zones are caused by strain fields. (Electron micrograph; magnification 800,000 \times .) (c) Al-4% Cu alloy solution heat-treated at 540°C, quenched in water, and aged for 3 days at 200°C. This thin-foil micrograph shows the incoherent and metastable phase θ' that forms by heterogeneous nucleation and growth. (Electron micrograph; magnification 25,000 \times .)

(After J. Nutting and R.G. Baker, "The Microstructure of Metals," Institute of Metals, 1965, pp. 65 and 67.)

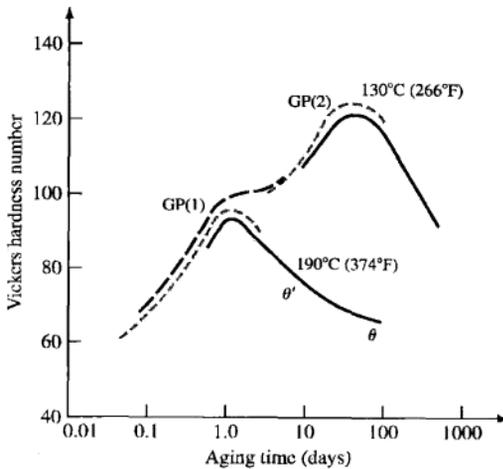


Figure 9.47

Correlation of structures and hardness of Al-4% Cu alloy aged at 130°C and 190°C.

[From J.M. Silcock, T.J. Heal, and H.K. Hardy as presented in K.R. Van Horn (ed.), "Aluminum," vol. 1, American Society for Metals, 1967, p. 123. Used by permission of ASM International.]

θ phase. The equilibrium phase θ is incoherent and has the composition CuAl_2 . This phase has a BCT structure ($a = 0.607$ nm and $c = 0.487$ nm) and forms from θ' or directly from the matrix.

The general sequence of precipitation in binary aluminum-copper alloys can be represented by

Supersaturated solid solution \rightarrow GP1 zones \rightarrow
 GP2 zones (θ'' phase) \rightarrow θ' \rightarrow θ (CuAl_2)

Correlation of Structures and Hardness in an Al-4% Cu Alloy The hardness versus aging time curves for an Al-4% Cu alloy aged at 130°C and 190°C are shown in Fig. 9.47. At 130°C, GP1 zones are formed and increase the hardness of the alloy by impeding dislocation movement. Further aging at 130°C creates GP2 zones that increase the hardness still more by making dislocation movement still more difficult. A maximum in hardness is reached with still more aging time at 130°C as θ' forms. Aging beyond the hardness peak dissolves the GP2 zones and coarsens the θ' phase, causing the decrease in the hardness of the alloy. GP1 zones do not form during aging at 190°C in the Al-4% Cu alloy since this temperature is above the GP1 solvus. With long aging times at 190°C, the equilibrium θ phase forms.

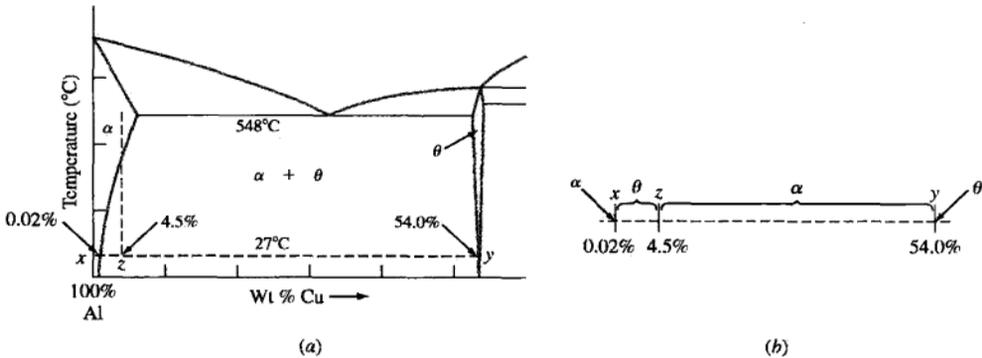
**EXAMPLE
PROBLEM 9.6**

Calculate the theoretical weight percent of the θ phase that could be formed at 27°C (room temperature) when a sample of Al–4.50 wt % Cu alloy is very slowly cooled from 548°C. Assume the solid solubility of Cu in Al at 27°C is 0.02 wt % and that the θ phase contains 54.0 wt % Cu.

■ Solution

First, we draw a tie line xy on the Al–Cu phase diagram at 27°C between the α and θ phases, as shown in Fig. EP9.6a. Next, we indicate the 4.5 percent Cu composition point at z . The ratio xz divided by the whole tie line xy (Fig. EP9.6b) gives the weight fraction of the θ phase. Thus,

$$\theta \text{ wt \%} = \frac{4.50 - 0.02}{54.0 - 0.02} (100\%) = \frac{4.48}{53.98} (100\%) = 8.3\% \blacktriangleleft$$

**Figure EP9.6**

- (a) Al–Cu phase diagram with tie line xy indicated on it at 27°C and point z located at 4.5% Cu.
 (b) Isolated tie line xy indicating segment xz as representing the weight fraction of the θ phase.

9.5.2 General Properties of Aluminum and Its Production

Engineering Properties of Aluminum Aluminum possesses a combination of properties that make it an extremely useful engineering material. Aluminum has a low density (2.70 g/cm^3), making it particularly useful for transportation manufactured products. Aluminum also has good corrosion resistance in most natural environments due to the tenacious oxide film that forms on its surface. Although pure aluminum has low strength, it can be alloyed to a strength of about 100 ksi (690 MPa). Aluminum is nontoxic and is used extensively for food containers and packaging. The good electrical properties of aluminum make it suitable for many applications in the electrical industry. The relatively low price of aluminum (96¢/lb in 1989) along with its many useful properties make this metal very important industrially.

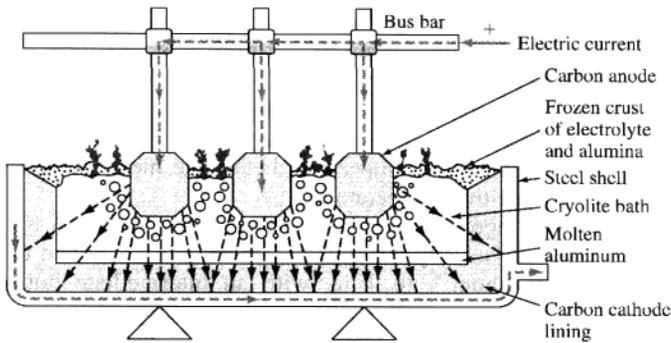


Figure 9.48
Electrolytic cell used to produce aluminum.
(Courtesy of Aluminum Company of America.)



Production of Aluminum Aluminum is the most abundant metallic element in the earth's crust and always occurs in the combined state with other elements such as iron, oxygen, and silicon. Bauxite, which consists mainly of hydrated aluminum oxides, is the chief commercial mineral used for the production of aluminum. In the Bayer process, bauxite is reacted with hot sodium hydroxide to convert the aluminum in the ore to sodium aluminate. After separation of the insoluble material, aluminum hydroxide is precipitated from the aluminate solution. The aluminum hydroxide is then thickened and calcined to aluminum oxide, Al_2O_3 .

The aluminum oxide is dissolved in a molten bath of cryolite (Na_3AlF_6) and electrolyzed in an electrolytic cell (Fig. 9.48) by using carbon anodes and cathodes. In the electrolysis process, metallic aluminum forms in the liquid state and sinks to the bottom of the cell and is periodically tapped off. The cell-tapped aluminum usually contains from 99.5 to 99.9 percent aluminum with iron and silicon being the major impurities.

Aluminum from the electrolytic cells is taken to large refractory-lined furnaces where it is refined before casting. Alloying elements and alloying-element master ingots may also be melted and mixed in with the furnace charge. In the refining operation, the liquid metal is usually purged with chlorine gas to remove dissolved hydrogen gas, which is followed by a skimming of the liquid-metal surface to remove oxidized metal. After the metal has been degassed and skimmed, it is screened and cast into ingot shapes for remelting or into primary ingot shapes such as sheet or extrusion ingots for further fabrication.

9.5.3 Wrought Aluminum Alloys

Primary Fabrication Ingot shapes such as sheet and extrusion ingots are usually semicontinuously cast by the *direct-chill method*. Figure 4.8 shows schematically how an aluminum ingot is cast by this method, and Fig. 4.1 is a photograph of a large semicontinuously cast ingot being removed from the casting pit.

In the case of sheet ingots, about $\frac{1}{2}$ in. of metal is removed from the ingot surfaces that will make contact with the hot-rolling-mill rolls. This operation is called *scalping* and is done to ensure a clean, smooth surface for the fabricated sheet or plate. Next the ingots are *preheated* or *homogenized* at a high temperature for about 10 to 24 h to allow atomic diffusion to make the composition of the ingot uniform. The preheating must be done at a temperature below the melting point of the constituent with the lowest melting temperature.

After reheating, the ingots are *hot-rolled* by using a four-high reversing hot-rolling mill. The ingots are usually hot-rolled to about 3 in. thick and then reheated and hot-rolled down to about $\frac{3}{4}$ to 1 in. with an intermediate hot-rolling mill (Fig. 6.1). Further reduction is usually carried out on a series of tandem hot-rolling mills to produce metal about 0.1 in. thick. Figure 6.8 shows a typical cold-rolling operation. More than one intermediate anneal is usually required if thin sheet is to be produced.

Classification of Wrought Aluminum Alloys Aluminum alloys produced in the wrought form (i.e., sheet, plate, extrusions, rod, and wire) are classified according to the major alloying elements they contain. A four-digit numerical designation is used to identify aluminum wrought alloys. The first digit indicates the alloy group that contains specific alloying elements. The last two digits identify the aluminum alloy or indicate the aluminum purity. The second digit indicates modification of the original alloy or impurity limits. Table 9.7 lists the wrought aluminum alloy groups.

Temper Designations Temper designations for wrought aluminum alloys follow the alloy designation and are separated by a hyphen (for example, 1100-0). Subdivisions of a basic temper are indicated by one or more digits and follow the letter of the basic designation (for example, 1100-H14).

Basic Temper Designations

F—As fabricated. No control over the amount of strain hardening; no mechanical property limits.

O—Annealed and recrystallized. Temper with the lowest strength and highest ductility.

Table 9.7 Wrought aluminum alloy groups

Aluminum, 99.00% minimum and greater	1xxx
Aluminum alloys grouped by major alloying elements:	
Copper	2xxx
Manganese	3xxx
Silicon	4xxx
Magnesium	5xxx
Magnesium and silicon	6xxx
Zinc	7xxx
Other element	8xxx
Unused series	9xxx

H—Strain-hardened (see subsequent subsection for subdivisions):

T—Heat-treated to produce stable tempers other than F or O (see subsequent subsection for subdivisions).

Strain-Hardened Subdivisions

H1—Strain-hardened only. The degree of strain hardening is indicated by the second digit and varies from quarter-hard (H12) to full-hard (H18), which is produced with approximately 75 percent reduction in area.

H2—Strain-hardened and partially annealed. Tempers ranging from quarter-hard to full-hard obtained by partial annealing of cold-worked materials with strengths initially greater than desired. Tempers are H22, H24, H26, and H28.

H3—Strain-hardened and stabilized. Tempers for age-softening aluminum-magnesium alloys that are strain-hardened and then heated at a low temperature to increase ductility and stabilize mechanical properties. Tempers are H32, H34, H36, and H38.

Heat-Treated Subdivisions

T1—Naturally aged. Product is cooled from an elevated-temperature shaping process and naturally aged to a substantially stable condition.

T3—Solution heat-treated, cold-worked, and naturally aged to a substantially stable condition.

T4—Solution heat-treated and naturally aged to a substantially stable condition.

T5—Cooled from an elevated-temperature shaping process and then artificially aged.

T6—Solution heat-treated and then artificially aged.

T7—Solution heat-treated and stabilized.

T8—Solution heat-treated, cold-worked, and then artificially aged.

Non-Heat-Treatable Wrought Aluminum Alloys Wrought aluminum alloys can conveniently be divided into two groups: *non-heat-treatable* and *heat-treatable alloys*. Non-heat-treatable aluminum alloys cannot be precipitation-strengthened but can only be cold-worked to increase their strength. The three main groups of non-heat-treatable wrought aluminum alloys are the 1xxx, 3xxx, and 5xxx groups. Table 9.8 lists the chemical composition, typical mechanical properties, and applications for some selected industrially important wrought aluminum alloys.

1xxx alloys. These alloys have a minimum of 99.0 percent aluminum with iron and silicon being the major impurities (alloying elements). An addition of 0.12 percent copper is added for extra strength. The 1100 alloy has a tensile strength of about 13 ksi (90 MPa) in the annealed condition and is used mainly for sheet metal work applications.

3xxx alloys. *Manganese* is the principal alloying element of this group and strengthens aluminum mainly by solid-solution strengthening. The most important alloy of this group is 3003, which is essentially an 1100 alloy

Table 9.8 Typical mechanical properties and applications for aluminum alloys

Alloy number*	Chemical composition (wt %) [†]	Condition [‡]	Tensile strength		Yield strength		Elongation (%)	Typical applications
			ksi	MPa	ksi	MPa		
Wrought alloys								
1100	99.0 min Al, 0.12 Cu	Annealed (-O) Half-hard (-H14)	13 18	89 (av) 124 (av)	3.5 14	24 (av) 97 (av)	25 4	Sheet metal work, fin stock
3003	1.2 Mn	Annealed (-O) Half-hard (-H14)	17 23	117 (av) 159 (av)	5 23	34 (av) 159 (av)	23 17	Pressure vessels, chemical equipment, sheet metal work
5052	2.5 Mg, 0.25 Cr	Annealed (-O) Half-hard (-H34)	28 38	193 (av) 262 (av)	9.5 26	65 (av) 179 (av)	18 4	Bus, truck, and marine uses, hydraulic tubes
2024	4.4 Cu, 1.5 Mg, 0.6 Mn	Annealed (-O) Heat-treated (-T6)	32 64	220 (max) 442 (min)	14 50	97 (max) 345 (min)	12 5	Aircraft structures
6061	1.0 Mg, 0.6 Si, 0.27 Cu, 0.2 Cr	Annealed (-O) Heat-treated (-T6)	22 42	152 (max) 290 (min)	12 35	82 (max) 241 (min)	16 10	Truck and marine structures, pipelines, railings
7075	5.6 Zn, 2.5 Mg, 1.6 Cu, 0.23 Cr	Annealed (-O) Heat-treated (-T6)	40 73	276 (max) 504 (min)	21 62	145 (max) 428 (min)	10 8	Aircraft and other structures
Casting alloys								
355.0	5 Si, 1.2 Cu, 0.5 Mg	Sand cast (-T6) Permanent mold (-T6)	32 37	220 (min) 285 (min)	20 ...	138 (min) ...	2.0 1.5	Pump housings, aircraft fittings, crankcases
356.0	7 Si, 0.3 Mg	Sand cast (-T6) Permanent mold (-T6)	30 33	207 (min) 229 (min)	20 22	138 (min) 152 (min)	3 3	Transmission cases, truck axle housings, truck wheels
332.0	9.5 Si, 3 Cu, 1.0 Mg	Permanent mold (-T5)	31	214 (min)				Automotive pistons
413.0	12 Si, 2 Fe	Die casting	43	297	21	145 (min)	2.5	Large, intricate castings

*Aluminum Association number.

[†]Balance aluminum.[‡]O = annealed and recrystallized; H14 = strain-hardened only; H34 = strain-hardened and stabilized; T5 = cooled from elevated-temperature shaping process, then artificially aged; T6 = solution heat-treated, then artificially aged.

with the addition of about 1.25 percent manganese. The 3003 alloy has a tensile strength of about 16 ksi (110 MPa) in the annealed condition and is used as a general-purpose alloy where good workability is required.

5xxx alloys. *Magnesium* is the principal alloying element of this group and is added for solid-solution strengthening in amounts up to about 5 percent. One of the most industrially important alloys of this group is 5052, which contains about 2.5 percent magnesium (Mg) and 0.2 percent chromium (Cr). In the annealed condition, alloy 5052 has a tensile strength of about 28 ksi (193 MPa). This alloy is also used for sheet metal work, particularly for bus, truck, and marine applications.

Heat-Treatable Wrought Aluminum Alloys Some aluminum alloys can be precipitation-strengthened by heat treatment (see pages 420 to 424). Heat-treatable wrought aluminum alloys of the 2xxx, 6xxx, and 7xxx groups are all precipitation-strengthened by similar mechanisms as described in Sec. 9.5 for aluminum-copper alloys. Table 9.8 lists the chemical compositions, typical mechanical properties, and applications of some of the industrially important wrought heat-treatable aluminum alloys.

2xxx alloys. The principal alloying element of this group is *copper*, but *magnesium* is also added to most of these alloys. Small amounts of other elements are also added. One of the most important alloys of this group is 2024, which contains about 4.5 percent copper (Cu), 1.5 percent Mg, and 0.6 percent Mn. This alloy is strengthened mainly by solid-solution and precipitation strengthening. An intermetallic compound of the approximate composition of Al_2CuMg is the main strengthening precipitate. Alloy 2024 in the T6 condition has a tensile strength of about 64 ksi (442 MPa) and is used, for example, for aircraft structurals.

6xxx alloys. The principal alloying elements for the 6xxx group are *magnesium* and *silicon*, which combine together to form an intermetallic compound, Mg_2Si , which in precipitate form strengthens this group of alloys. Alloy 6061 is one of the most important alloys of this group and has an approximate composition of 1.0 percent Mg, 0.6 percent Si, 0.3 percent Cu, and 0.2 percent Cr. This alloy in the T6 heat-treated condition has a tensile strength of about 42 ksi (290 MPa) and is used for general-purpose structurals.

7xxx alloys. The principal alloying elements for the 7xxx group of aluminum alloys are zinc, magnesium, and copper. Zinc and magnesium combine to form an intermetallic compound, $MgZn_2$, which is the basic precipitate that strengthens these alloys when they are heat-treated. The relatively high solubility of zinc and magnesium in aluminum makes it possible to create a high density of precipitates and hence to produce very great increases in strength. Alloy 7075 is one of the most important alloys of this group and has an approximate composition of 5.6 percent Zn, 2.5 percent Mg, 1.6 percent Cu, and 0.25 percent Cr. Alloy 7075, when heat-treated to the T6 temper, has a tensile strength of about 73 ksi (504 MPa) and is used mainly for aircraft structurals.

9.5.4 Aluminum Casting Alloys

Casting Processes Aluminum alloys are normally cast by one of three main processes: sand casting, permanent-mold, and die casting.

Sand casting is the simplest and most versatile of the aluminum casting processes. Figure 9.49 shows how a simple sand mold for producing sand castings is constructed. The sand-casting process is usually chosen for the production of (1) small quantities of identical castings, (2) complex castings with intricate cores, (3) large castings, and (4) structural castings.

In *permanent-mold casting* the molten metal is poured into a permanent metal mold under gravity, low pressure, or centrifugal pressure only. Figure 6.2 shows an open permanent mold, while Fig. 6.3a shows the permanent-mold casting of two aluminum alloy automobile pistons. Castings of the same alloy and shape produced by a permanent mold have a finer grain structure and higher strength than those cast by sand molds. The faster cooling rate of permanent-mold casting produces a finer grain structure. Also, permanent-mold castings usually have less shrinkage and gas porosity than sand castings. However, permanent molds have size limitations, and complex parts may be difficult or impossible to cast with a permanent mold.

In *die casting*, identical parts are cast at maximum production rates by forcing molten metal under considerable pressure into metal molds. Two metal die halves are securely locked together to withstand high pressure. The molten aluminum is forced into the cavities in the dies. When the metal has solidified, the dies are unlocked and opened to eject the hot casting. The die halves are locked together again, and the casting cycle is repeated. Some of the advantages of die casting are (1) parts die cast are almost completely finished and can be produced at high rates, (2) dimensional tolerances of each cast part can be more closely held than with any other major casting process, (3) smooth surfaces on the casting are obtainable, (4) rapid cooling of the casting produces a fine-grain structure, and (5) the process can be automated easily.

Aluminum Casting Alloy Compositions Aluminum casting alloys have been developed for casting qualities such as fluidity and feeding ability as well as for properties such as strength, ductility, and corrosion resistance. As a result, their chemical compositions differ greatly from those of the wrought aluminum alloys. Table 9.8 lists the chemical compositions, mechanical properties, and applications for some selected aluminum casting alloys. These alloys are classified in the United States according to the Aluminum Association system. In this system, aluminum casting alloys are grouped by the major alloying elements they contain by using a four-digit number with a period between the last two digits, as listed in Table 9.9.

Silicon in the range of about 5 to 12 percent is the most important alloying element in aluminum casting alloys since it increases the fluidity of the molten metal and its feeding ability in the mold as well as strengthens the aluminum. Magnesium in the range of about 0.3 to 1 percent is added to increase strength, mainly by precipitation strengthening through heat treatment. Copper in the range of about 1 to 4 percent is also added to some aluminum casting alloys to increase strength, par-

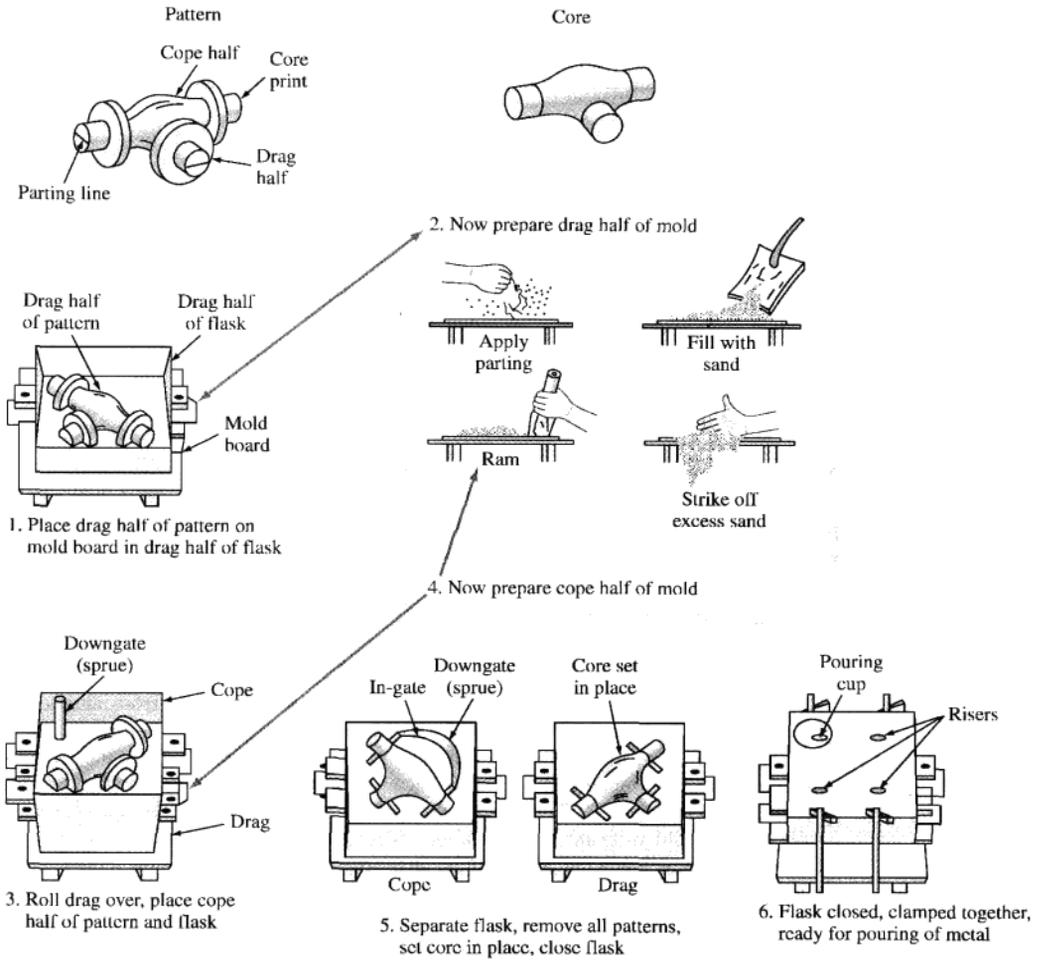


Figure 9.49
 Steps in the construction of a simple sand mold for making a sand casting.
 (After H.F. Taylor, M.C. Flemings, and J. Wulff, "Foundry Engineering," Wiley, 1959, p. 20.)

ticularly at elevated temperatures. Other alloying elements such as zinc, tin, titanium, and chromium are also added to some aluminum casting alloys.

In some cases, if the cooling rate of the solidified casting in the mold is sufficiently rapid, a heat-treatable alloy can be produced in the supersaturated solid condition. Thus, the solution heat-treatment and quenching steps can be omitted for precipitation strengthening the casting, and only subsequent aging of the casting after it has been

Table 9.9 Cast aluminum alloy groups

Aluminum, 99.00% minimum and greater	1xx.x
Aluminum alloys grouped by major alloying elements:	
Copper	2xx.x
Silicon, with added copper and/or magnesium	3xx.x
Silicon	4xx.x
Magnesium	5xx.x
Zinc	7xx.x
Tin	8xx.x
Other element	9xx.x
Unused series	6xx.x

removed from the mold is required. A good example of the application of this type of heat treatment is in the production of precipitation-strengthened automobile pistons. The pistons shown in Fig. 6.3a, after being removed from the mold, only require an aging treatment to be precipitation-strengthened. This heat-treatment temper is called T5.

9.6 SUMMARY

Engineering alloys can be conveniently subdivided into two types: ferrous and nonferrous. Ferrous alloys have iron as their principal alloying metal, whereas nonferrous alloys have a principal alloying metal other than iron. The steels, which are ferrous alloys, are by far the most important metal alloys, mainly because of their relatively low cost and wide range of mechanical properties. The mechanical properties of carbon steels can be varied considerably by cold working and annealing. When the carbon content of steels is increased to above about 0.3 percent, they can be heat-treated by quenching and tempering to produce high strength with reasonable ductility. Alloying elements such as nickel, chromium, and molybdenum are added to plain-carbon steels to produce low-alloy steels. Low-alloy steels have good combinations of high strength and toughness and are used extensively in the automotive industry for applications such as gears, shafts, and axles.

Aluminum alloys are the most important of the nonferrous alloys mainly because of their lightness, workability, corrosion resistance, and relatively low cost. Unalloyed copper is used extensively because of its high electrical conductivity, corrosion resistance, workability, and relatively low cost. Copper is alloyed with zinc to form a series of brass alloys that have higher strength than unalloyed copper.

Stainless steels are important ferrous alloys because of their high corrosion resistance in oxidizing environments. To make a stainless steel "stainless," it must contain at least 12 percent Cr.

Cast irons are still another industrially important family of ferrous alloys. They are low in cost and have special properties such as good castability, wear resistance, and durability. Gray cast iron has high machinability and vibration-damping capacity due to the graphite flakes in its structure.

Other nonferrous alloys briefly discussed in this chapter are magnesium, titanium, and nickel alloys. Magnesium alloys are exceptionally light and have aerospace applications,

and they are also used for materials-handling equipment. Titanium alloys are expensive but have a combination of strength and lightness not available from any other metal alloy system; they are used extensively for aircraft structural parts. Nickel alloys have high corrosion and oxidation resistance and are therefore commonly used in the oil and chemical process industries. Nickel when alloyed with chromium and cobalt forms the basis for the nickel-base superalloys needed in gas turbines for jet aircraft and some electric-power generating equipment.

In this chapter, we have discussed to a limited extent the structure, properties, and applications of some of the important engineering alloys. We have also introduced special purpose alloys that are growing in importance and application in various industries. Of particular importance is the use of intermetallics, amorphous metals, and advanced superalloys in various fields. These materials have superior properties to conventional alloys.

9.7 DEFINITIONS

Sec. 9.2

Cementite: the intermetallic compound Fe_3C ; a hard and brittle substance.

α ferrite (α phase in the Fe- Fe_3C phase diagram): an interstitial solid solution of carbon in BCC iron; maximum solid solubility of carbon in BCC iron is 0.02 percent.

Eutectoid (plain-carbon steel): a steel with 0.8 percent C.

Hypoeutectoid (plain-carbon steel): a steel with less than 0.8 percent C.

Hypereutectoid (plain-carbon steel): a steel with 0.8 to 2.0 percent C.

Austenite (γ phase in Fe- Fe_3C phase diagram): an interstitial solid solution of carbon in FCC iron; the maximum solid solubility of carbon in austenite is 2.0 percent.

Austenitizing: heating a steel into the austenite temperature range so that its structure becomes austenite. The austenitizing temperature will vary depending on the composition of the steel.

Pearlite: a mixture of α ferrite and cementite (Fe_3C) phases in parallel plates (lamellar structure) produced by the eutectoid decomposition of austenite.

Proeutectoid α ferrite: α ferrite that forms by the decomposition of austenite at temperatures above the eutectoid temperature.

Eutectoid α ferrite: α ferrite that forms during the eutectoid decomposition of austenite; the α ferrite in pearlite.

Proeutectoid cementite (Fe_3C): cementite that forms by the decomposition of austenite at temperatures above the eutectoid temperature.

Eutectoid cementite (Fe_3C): cementite that forms during the eutectoid decomposition of austenite; the cementite in pearlite.

Sec. 9.3

Martensite: a supersaturated interstitial solid solution of carbon in body-centered tetragonal iron.

Isothermal transformation (IT) diagram: a time-temperature-transformation diagram that indicates the time for a phase to decompose into other phases isothermally at different temperatures.

Bainite: a mixture of α ferrite and very small particles of Fe_3C particles produced by the decomposition of austenite; a nonlamellar eutectoid decomposition product of austenite.

Continuous-cooling transformation (CCT) diagram: a time-temperature-transformation diagram that indicates the time for a phase to decompose into other phases continuously at different rates of cooling.

Tempering (of a steel): the process of reheating a quenched steel to increase its toughness and ductility. In this process martensite is transformed into tempered martensite.

Plain-carbon steel: an iron-carbon alloy with 0.02 to 2 percent C. All commercial plain-carbon steels contain about 0.3 to 0.9 percent manganese along with sulfur, phosphorus, and silicon impurities.

Spheroidite: a mixture of particles of cementite (Fe_3C) in an α ferrite matrix.

Martempering (marquenching): a quenching process whereby a steel in the austenitic condition is hot-quenched in a liquid (salt) bath at above the M_s temperature, held for a time interval short enough to prevent the austenite from transforming, and then allowed to cool slowly to room temperature. After this treatment, the steel will be in the martensitic condition, but the interrupted quench allows stresses in the steel to be relieved.

Austempering: a quenching process whereby a steel in the austenitic condition is quenched in a hot liquid (salt) bath at a temperature just above the M_s of the steel, held in the bath until the austenite of the steel is fully transformed, and then cooled to room temperature. With this process, a plain-carbon eutectoid steel can be produced in the fully bainitic condition.

M_s : the temperature at which the austenite in a steel starts to transform to martensite.

M_f : the temperature at which the austenite in a steel finishes transforming to martensite.

Sec. 9.4

Hardenability: the ease of forming martensite in a steel upon quenching from the austenitic condition. A highly hardenable steel is one that will form martensite throughout in thick sections. Hardenability should not be confused with hardness. Hardness is the resistance of a material to penetration. The hardenability of a steel is mainly a function of its composition and grain size.

Jominy hardenability test: a test in which a 1 in. (2.54 cm) diameter bar 4 in. (10.2 cm) long is austenitized and then water-quenched at one end. Hardness is measured along the side of the bar up to about 2.5 in. (6.35 cm) from the quenched end. A plot called the *Jominy hardenability curve* is made by plotting the hardness of the bar against the distance from the quenched end.

9.8 PROBLEMS

Answers to problems marked with an asterisk are given at the end of the book.

Knowledge and Comprehension Problems

- 9.1 (a) How is raw pig iron extracted from iron oxide ores? (b) Write a typical chemical reaction for the reduction of iron oxide (Fe_2O_3) by carbon monoxide to produce iron. (c) Describe the basic oxygen process for converting pig iron into steel.
- 9.2 (a) Why is the Fe- Fe_3C phase diagram a metastable phase diagram instead of a true equilibrium phase diagram? (b) Define the following phases that exist in the Fe- Fe_3C phase diagram: (i) austenite, (ii) α ferrite, (iii) cementite, (iv) δ ferrite. (c) Write the reactions for the three invariant reactions that take place in the Fe- Fe_3C phase diagram.
- 9.3 (a) What is the structure of pearlite? (b) Draw a schematic showing all the appropriate phases.
- 9.4 Distinguish between the following three types of plain-carbon steels: (a) eutectoid, (b) hypoeutectoid, and (c) hypereutectoid.
- 9.5 Distinguish between proeutectoid ferrite and eutectoid ferrite.
- 9.6 Define an Fe-C martensite. (b) Describe the following types of Fe-C martensites that occur in plain-carbon steels: (i) lath martensite, (ii) plate martensite. (c)

Describe some of the characteristics of the Fe-C martensite transformation that occurs in plain-carbon steels. (d) What causes the tetragonality to develop in the BCC iron lattice when the carbon content of Fe-C martensites exceeds about 0.2 percent? (e) What causes the high hardness and strength to be developed in Fe-C martensites of plain-carbon steels when their carbon content is high?

- 9.7 (a) What is an isothermal transformation in the solid state? (b) Draw an isothermal transformation diagram for a plain-carbon eutectoid steel and indicate the various decomposition products on it. How can such a diagram be constructed by a series of experiments?
- 9.8 How does the isothermal transformation diagram for a hypoeutectoid plain-carbon steel differ from that of a eutectoid one?
- 9.9 Draw a continuous-cooling transformation diagram for a eutectoid plain-carbon steel. How does it differ from a eutectoid isothermal transformation diagram for a plain-carbon steel?
- 9.10 (a) Describe the full-annealing heat treatment for a plain-carbon steel. (b) What types of microstructures are produced by full annealing (i) a eutectoid steel and (ii) a hypoeutectoid steel?
- 9.11 Describe the process-annealing heat treatment for a plain-carbon hypoeutectoid steel with less than 0.3 percent C.
- 9.12 What is the normalizing heat treatment for steel and what are some of its purposes?
- 9.13 Describe the tempering process for a plain-carbon steel.
- 9.14 (a) Describe the martempering (marquenching) process for a plain-carbon steel. (b) Draw a cooling curve for a martempered (marquenched) austenitized eutectoid plain-carbon steel by using an IT diagram. (c) What type of microstructure is produced after martempering this steel? (d) What are the advantages of martempering? (e) What type of microstructure is produced after tempering a martempered steel? (f) Why is the term *martempering* a misnomer? Suggest an improved term.
- 9.15 (a) Describe the austempering process for a plain-carbon steel. Draw a cooling curve for an austempered austenitized eutectoid plain-carbon steel by using an IT diagram. (b) What is the microstructure produced after austempering a eutectoid plain-carbon steel? (c) Does an austempered steel need to be tempered (explain)? (d) What are the advantages of the austempering process? (e) Disadvantages?
- 9.16 (a) Explain the numbering system used by the AISI and SAE for plain-carbon steels? (b) What is the AISI-SAE system for designating low-alloy steels?
- 9.17 (a) What are some of the limitations of plain-carbon steels for engineering designs? (b) What are the principal alloying elements added to plain-carbon steels to make low-alloy steels? (c) What elements dissolve primarily in the ferrite of carbon steels? (d) List in order of increasing carbide-forming tendency the following elements: titanium, chromium, molybdenum, vanadium, and tungsten.
- 9.18 (a) What compounds does aluminum form in steels? (b) Name two austenite-stabilizing elements in steels. (c) Name four ferrite-stabilizing elements in steels.
- 9.19 Which elements raise the eutectoid temperature of the Fe-Fe₃C phase diagram? Which elements lower it?
- 9.20 (a) Define the hardenability of a steel. (b) Define the hardness of a steel. (c) Describe the Jominy hardenability test. (d) Explain how the data for the plotting of the Jominy hardenability curve are obtained and how the curve is constructed. (e) Of what industrial use are Jominy hardenability curves?

- 9.21 (a) Explain how a precipitation-hardenable alloy is strengthened by heat treatment. (b) What type of phase diagram is necessary for a binary alloy to be precipitation-hardenable? (c) What are the three basic heat-treatment steps to strengthen a precipitation-hardenable alloy? (d) In what temperature range must a binary precipitation-hardenable alloy be heated for the solution heat-treatment step? (e) Why is a precipitation-hardenable alloy relatively weak just after solution heat treatment and quenching?
- 9.22 (a) Distinguish between natural aging and artificial aging for a precipitation-hardenable alloy. (b) What is the driving force for the decomposition of a supersaturated solid solution of a precipitation-hardenable alloy? (c) What is the first decomposition product of a precipitation-hardenable alloy in the supersaturated solid-solution condition after aging at a low temperature? (d) What are GP zones?
- 9.23 (a) What is an aging curve for a precipitation-hardenable alloy? (b) What types of precipitates are developed in an alloy that is considerably underaged at low temperatures? (c) What types are developed upon overaging?
- 9.24 What is the difference between a coherent precipitate and an incoherent one?
- 9.25 Describe the four decomposition structures that can be developed when a supersaturated solid solution of an Al-4% Cu alloy is aged.
- 9.26 (a) What are some of the properties that make aluminum an extremely useful engineering material? (b) How is aluminum oxide extracted from bauxite ores? (c) How is aluminum extracted from pure aluminum oxide? (d) How are aluminum wrought alloys classified? (e) What are the basic temper designations for aluminum alloys?
- 9.27 (a) Which series of aluminum wrought alloys are non-heat-treatable? (b) Which are heat-treatable? (c) What are the basic strengthening precipitates for the wrought heat-treatable aluminum alloys?
- 9.28 (a) Describe the three principal casting processes used for aluminum alloys. (b) How are aluminum casting alloys classified? (c) What is the most important alloying element for aluminum casting alloys? Why?
- 9.29 (a) What are some of the important properties of unalloyed copper that make it an important industrial metal? (b) How is copper extracted from copper sulfide ore concentrates? (c) How are copper alloys classified by the Copper Development Association system?
- 9.30 Why can't electrolytic tough-pitch copper be used for applications in which it is heated above 400°C in a hydrogen-containing atmosphere?
- 9.31 How can the hydrogen embrittlement of ETP copper be avoided? (Give two methods.)
- 9.32 (a) What alloying element and how much of it (weight percent) is necessary to make a stainless steel "stainless"? (b) What type of surface film protects stainless steels? (c) What are the four basic types of stainless steels?
- 9.33 (a) What is the gamma loop in the Fe-Cr phase diagram? (b) Is chromium an austenite or ferrite-stabilizing element for iron? Explain the reason for your answer.
- 9.34 (a) What is the basic composition of ferritic stainless steels? (b) Why are ferritic stainless steels considered non-heat-treatable? (c) What are some applications for ferritic steels?
- 9.35 (a) What is the basic composition of martensitic stainless steels? (b) Why are these steels heat-treatable? (c) What are some applications for martensitic

stainless steels?

- 9.36** (a) What are the cast irons? (b) What is their basic range of composition? (c) What are some of the properties of cast irons that make them important engineering materials? (d) What are some of their applications? (e) What are the four basic types of cast irons?
- 9.37** (a) Describe the as-cast microstructure of unalloyed white cast iron at 100 \times . (b) Why does the fractured surface of white cast iron appear "white"?
- 9.38** (a) Describe the microstructure of a class 30 gray cast iron in the as-cast condition at 100 \times . (b) Why does the fractured surface of a gray cast iron appear gray? (c) What are some of the applications for gray cast irons?
- 9.39** (a) What are the composition ranges for the carbon and silicon in gray cast iron? (b) Why do gray cast irons have relatively high amounts of silicon? (c) What casting conditions favor the formation of gray cast iron?
- 9.40** How can a fully ferritic matrix be produced in an as-cast gray iron after it has been cast?
- 9.41** (a) What are the composition ranges for the carbon and silicon in ductile cast irons? (b) Describe the microstructure of an as-cast grade 80-55-06 ductile cast iron at 100 \times . (c) What causes the bull's-eye structure? (d) Why are ductile cast irons in general more ductile than gray cast irons? (e) What are some applications for ductile cast irons?
- 9.42** Why does the graphite form spherical nodules in ductile cast irons instead of graphite flakes as in gray cast irons?
- 9.43** (a) What are the composition ranges of carbon and silicon in malleable cast irons? (b) Describe the microstructure of a ferritic malleable cast iron (grade M3210) at 100 \times . (c) How are malleable cast irons produced? (d) What are some of the property advantages of malleable cast irons? (e) What are some applications for malleable cast irons?
- 9.44** (a) What advantages do magnesium alloys have as engineering materials? (b) How are magnesium alloys designated? (c) What alloying elements are added to magnesium for solid-solution strengthening? (d) Why is it difficult to cold-work magnesium alloys? (e) What alloying elements are added to magnesium to provide better high-temperature strengths?
- 9.45** Explain what the following magnesium alloy designations indicate:
(a) ZE63A-T6, (b) ZK51A-T5, and (c) AZ31B-H24.
- 9.46** (a) Why are titanium and its alloys of special engineering importance for aerospace applications? (b) Why is titanium metal so expensive? (c) What crystal-structure change takes place in titanium at 883°C? (d) What are two alpha phase stabilizing elements for titanium? (e) What are two beta phase stabilizing elements for titanium? (f) What is the most important titanium alloy? (g) What are some applications for titanium and its alloys?
- 9.47** (a) Why is nickel an important engineering metal? (b) What are its advantages? (c) Disadvantages?
- 9.48** (a) What are the Monel alloys? (b) What are some of their applications? (c) What type of precipitates are used to strengthen the precipitation-hardenable alloy Monel K500?
- 9.49** (a) In what respect are the nickel-base superalloys "super"? (b) What is the basic

- composition of most nickel-base superalloys? (c) What are the three main phases present in nickel-base superalloys?
- 9.50 (a) What are intermetallics (give some examples)? (b) Name some applications for intermetallics? (c) What are the advantages of intermetallics over other high-temperature alloys? (d) Disadvantages? (e) What is the role of aluminum in intermetallics such as nickel aluminides and titanium aluminides?
- 9.51 (a) What are shape memory alloys (SMAs)? (b) Name some applications for SMAs and give some examples of SMAs. (c) How are SMAs produced? (d) Explain using schematics how SMAs work.
- 9.52 (a) What is an amorphous metal? (b) How are amorphous metals produced? (c) What are some special characteristics and applications? (d) Explain using schematics how SMA works?

Application and Analysis Problems

- 9.53 Describe the structural changes that take place when a plain-carbon eutectoid steel is slowly cooled from the austenitic region just above the eutectoid temperature.
- 9.54 Describe the structural changes that take place when a 0.4 percent C plain-carbon steel is slowly cooled from the austenitic region just above the upper transformation temperature.
- *9.55 If a thin sample of a eutectoid plain-carbon steel is hot-quenched from the austenitic region and held at 700°C until transformation is complete, what will be its microstructure?
- 9.56 If a thin sample of a eutectoid plain-carbon steel is water-quenched from the austenitic region to room temperature, what will be its microstructure?
- 9.57 (a) What types of microstructures are produced by tempering a plain-carbon steel with more than 0.2 percent carbon in the temperature ranges (i) 20 to 250°C, (ii) 250 to 350°C, and (iii) 400 to 600°C? (b) What causes the decrease in hardness during the tempering of a plain-carbon steel?
- *9.58 A 0.65 percent C hypoeutectoid plain-carbon steel is slowly cooled from about 950°C to a temperature just slightly above 723°C. Calculate the weight percent austenite and weight percent proeutectoid ferrite in this steel.
- 9.59 A 0.25 percent C hypoeutectoid plain-carbon steel is slowly cooled from 950°C to a temperature just slightly below 723°C.
- (a) Calculate the weight percent proeutectoid ferrite in the steel.
- (b) Calculate the weight percent eutectoid ferrite and weight percent eutectoid cementite in the steel.
- 9.60 A plain-carbon steel contains 93 wt % ferrite–7 wt % Fe₃C. What is its average carbon content in weight percent?
- 9.61 A plain-carbon steel contains 45 wt % proeutectoid ferrite. What is its average carbon content in weight percent?
- 9.62 A plain-carbon steel contains 5.9 wt % hypoeutectoid ferrite. What is its average carbon content?
- 9.63 A 0.90 percent C hypereutectoid plain-carbon steel is slowly cooled from 900°C to a temperature just slightly above 723°C. Calculate the weight percent proeutectoid

cementite and weight percent austenite present in the steel.

- 9.64** A 1.10 percent C hypereutectoid plain-carbon steel is slowly cooled from 900°C to a temperature just slightly below 723°C.
- Calculate the weight percent proeutectoid cementite present in the steel.
 - Calculate the weight percent eutectoid cementite and the weight percent eutectoid ferrite present in the steel.
- *9.65** If a hypereutectoid plain-carbon steel contains 4.7 wt % proeutectoid cementite, what is its average carbon content?
- 9.66** A hypereutectoid plain carbon steel contains 10.7 wt % eutectoid Fe₃C. What is its average carbon content in weight percent?
- 9.67** A plain-carbon steel contains 20.0 wt % proeutectoid ferrite. What is its average carbon content?
- 9.68** A 0.55 percent C hypoeutectoid plain-carbon steel is slowly cooled from 950°C to a temperature just slightly below 723°C.
- Calculate the weight percent proeutectoid ferrite in the steel.
 - Calculate the weight percent eutectoid ferrite and eutectoid cementite in the steel.
- 9.69** A hypoeutectoid steel contains 44.0 wt % eutectoid ferrite. What is its average carbon content?
- 9.70** A hypoeutectoid steel contains 24.0 wt % eutectoid ferrite. What is its average carbon content?
- *9.71** A 1.10 percent C hypereutectoid plain-carbon steel is slowly cooled from 900°C to a temperature just slightly below 723°C.
- Calculate the weight percent proeutectoid cementite present in the steel.
 - Calculate the weight percent eutectoid cementite and the weight percent eutectoid ferrite present in the steel.
- 9.72** Draw time-temperature cooling paths for a 1080 steel on an isothermal transformation diagram that will produce the following microstructures. Start with the steels in the austenitic condition at time = 0 and temperature = 850°C. (a) 100 percent martensite, (b) 50 percent martensite and 50 percent coarse pearlite, (c) 100 percent fine pearlite, (d) 50 percent martensite and 50 percent upper bainite, (e) 100 percent upper bainite, and (f) 100 percent lower bainite.
- 9.73** Draw time-temperature cooling paths for a 1080 steel on a continuous-cooling transformation diagram that will produce the following microstructures. Start with the steels in the austenitic condition at time = 0 and temperature = 850°C. (a) 100 percent martensite, (b) 50 percent fine pearlite and 50 percent martensite, (c) 100 percent coarse pearlite, and (d) 100 percent fine pearlite.
- *9.74** Thin pieces of 0.3 mm thick hot-rolled strips of 1080 steel are heat-treated in the following ways. Use the IT diagram of Fig. 9.23 and other knowledge to determine the microstructure of the steel samples after each heat treatment.
- Heat 1 h at 860°C; water-quench.
 - Heat 1 h at 860°C; water-quench; reheat 1 h at 350°C. What is the name of this heat treatment?
 - Heat 1 h at 860°C; quench in molten salt bath at 700°C and hold 2 h; water quench.
 - Heat 1 h at 860°C; quench in molten salt bath at 260°C and hold 1 min; air-

- cool. What is the name of this heat treatment?
- (e) Heat 1 h at 860°C; quench in molten salt bath at 350°C; hold 1 h; and air-cool. What is the name of this heat treatment?
- (f) Heat 1 h at 860°C; water-quench; and reheat 1 h at 700°C.
- *9.75** An austenitized 55-mm diameter steel bar of a 9840 steel is quenched in agitated oil. Predict the Rockwell C hardness at $\frac{3}{4}$ R from (a) the center of the bar, and (b) at the center of the bar.
- 9.76** An austenitized 60-mm diameter 4140 long steel bar is quenched in agitated water. Predict the Rockwell C hardness at (a) its surface and (b) center.
- 9.77** An austenitized 50-mm diameter 5140 steel bar is quenched in agitated oil. Predict what the Rockwell C hardness of the bar will be at (a) its surface and (b) midway between its surface and center (midradius).
- 9.78** An austenitized 80-mm diameter 4340 steel bar is quenched in agitated water. Predict what the Rockwell C hardness of the bar will be at (a) its surface and (b) its center.
- 9.79** An austenitized 50-mm diameter 5140 steel bar is quenched in agitated oil. Predict what the Rockwell C hardness of the bar will be at (a) $\frac{3}{4}$ R and (b) the center.
- *9.80** An austenitized and quenched 4140 steel bar has a Rockwell C hardness of 40 at a point on its surface. What cooling rate did the bar experience at this point?
- 9.81** An austenitized and quenched 8640 steel bar has a Rockwell C hardness of 35 at a point on its surface. What cooling rate did the bar experience at this point?
- 9.82** An austenitized and quenched 5140 steel bar has a Rockwell C hardness of 35 at a point on its surface. What cooling rate did the bar experience at this point?
- 9.83** An austenitized 40-mm diameter 4340 steel bar is quenched in agitated water. Plot the Rockwell C hardness of the bar versus distance from one surface of the bar to the other across the diameter of the bar at the following points: surface, $\frac{3}{4}$ R, $\frac{1}{2}$ R (mid-radius), and center. This type of plot is called a hardness profile across the diameter of the bar. Assume the hardness profile is symmetrical about the center of the bar.
- 9.84** An austenitized 50-mm diameter bar of 9840 steel is quenched in agitated oil. Repeat the hardness profile of Prob. 9.75 for this steel.
- 9.85** An austenitized 60-mm diameter 8640 steel bar is quenched in agitated oil. Repeat the hardness profile of Prob. 9.75 for this steel.
- 9.86** An austenitized 60-mm diameter 8640 steel bar is quenched in agitated water. Repeat the hardness profile of Prob. 9.75 for this steel.
- *9.87** An austenitized 4340 standard steel bar is cooled at a rate of 5°C/s (51-mm from the quenched end of a Jominy bar). What will be the constituents in the microstructure of the bar at 200°C? See Fig. 9.39.
- 9.88** An austenitized 4340 standard steel bar is cooled at a rate of 8°C/s (19.0-mm from the quenched end of a Jominy bar). What will be the constituents in the microstructure of the bar at 200°C? See Fig. 9.39.
- 9.89** An austenitized 4340 standard steel bar is cooled at a rate of 50°C/s (9.5-mm from the quenched end of a Jominy bar). What will be the constituents in the microstructure of the bar at 200°C? See Fig. 9.39.
- 9.90** Describe the microstructures of the following Cu-Zn brasses at 75×: (a) 70% Cu–30% Zn (cartridge brass) in the annealed condition and (b) 60% Cu–40% Zn (Muntz metal) in the hot-rolled condition.

- *9.91** Calculate the wt % θ in an Al–5.0% Cu alloy that is slowly cooled from 548°C to 27°C. Assume the solid solubility of Cu in Al at 27°C is 0.02 wt % and that the θ phase contains 54.0 wt % Cu.
- 9.92** A binary Al–8.5 wt % Cu alloy is slowly cooled from 700°C to just below 548°C (the eutectic temperature)
- Calculate the wt % proeutectic α present just above 548°C
 - Calculate the wt % eutectic α present just below 548°C.
 - Calculate the wt % θ phase present just below 548°C.

Synthesis and Evaluation Problems

- 9.93** (a) For a plain carbon steel with 1 wt % carbon content at 900°C, on average, how many carbon atoms can you find in 100 unit cells? (b) If this alloy is cooled to just below 723°C, on average, how many carbon atoms can you find in 100 unit cells in the ferrite phase, α ? (c) If at room temperature, the carbon content of ferrite drops to 0.005 wt %, on average, how many unit cells would you have to search to find one carbon atom? Can you explain the differences in the three answers?
- 9.94** In Fig. 9.19, consider a plain carbon steel with carbon 1.2 wt % carbon. At this carbon content, find, using the figure, the hardness of martensitic steel, pearlitic steel, and spheroidized steels. What is the reason for the drastic difference in hardness when they all have the same composition? Explain in detail.
- 9.95** For eutectoid steel, Fig. 9.24, the upper bainite microstructure (produced at isothermal transformation temperature of 350°C to 550°C) has larger Fe_3C regions than lower bainite (produced at isothermal transformation temperature of 250°C to 350°C). Can you explain why?
- 9.96** According to Fig. 9.25, it is impossible to form 100% martensitic steel from a hypoeutectoid steel (0.47 wt % carbon). Explain why.
- 9.97** How would the schematic of the Isothermal Transformation Diagram for a plain carbon steel of 1.1 wt % carbon be generally different than that of a eutectoid steel depicted in Fig. 9.23? Show the differences schematically.
- 9.98** The microstructure of a cast plain carbon steel (0.4 wt % carbon) component is observed to be too coarse, nonhomogenous, and soft. How would you refine the grain structure of the component without significantly decreasing its ductility?
- 9.99** As the tempering temperature of martensitic plain carbon steels increases, the hardness gradually decreases (see Fig. 9.32). Explain why from an atomic scale point of view.
- 9.100** In Fig. 9.33, if the cooling curve for the center of the specimen, only, is shifted to the right, from its current position, so it intersects a small section of the S curve, how will the microstructure within the specimen change?
- 9.101** Alloy steel 4340 is highly hardenable because the decomposition of austenite to ferrite and bainite is delayed. Explain, in terms of the cooling curve, how this affects hardenability. Use Fig. 9.39 to answer the question.
- 9.102** Estimate the cooling rate between 400°C and 600°C at (a) a distance of 6.3 mm from the quenched end, (b) 19 mm from the quenched end, and (c) 51 mm from the quenched end. What does the comparison of these rates tell you about the outcome?

10

CHAPTER

Polymeric Materials



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Microfibers are man-made fibers that are significantly smaller than a human hair (finer than silk fiber) and are split many times into v-shapes (see middle figure above). Conventional fibers are significantly thicker and have a solid circular cross-section. Microfibers can be produced from a variety of polymers including polyester, nylon, and acrylic. Fabrics made of microfiber possess significantly higher surface area due to smaller fiber and v-shaped crevices that can trap liquid and dirt. The water and dirt are actually trapped in v-shaped crevices of the fiber as opposed to being simply pushed away by conventional solid circular fibers. Thus, microfiber fabrics are softer and have a silky feeling (important in the clothing industry), and absorb water and dirt at significantly higher amounts (important to the cleaning industry). The above characteristics make microfiber cloths highly popular in sports garment and cleaning industries. The two main microfiber materials are polyester (scrubbing material) and polyamide (absorbing material). ■

LEARNING OBJECTIVES

By the end of this chapter, students will be able to . . .

1. Define and classify polymers including thermosets, thermoplastics, and elastomers.
2. Describe various polymerization reactions and steps.
3. Describe terms such as functionality, vinyl, vinylidene, homopolymer, and copolymer.
4. Describe various industrial polymerization methods.
5. Describe the structure of polymers and compare with metals.
6. Describe the glass transition temperature and the changes to the structure and properties of polymeric materials around this temperature.
7. Describe various manufacturing processes used to manufacture thermosetting and thermoplastic components.
8. Be able to name a reasonable number of general purpose thermoplastics, thermosets, elastomers, and their applications.
9. Be able to explain the deformation, strengthening, stress-relaxation, and fracture mechanisms in polymers.
10. Describe biopolymers and their use in biomedical applications.

10.1 INTRODUCTION

The word *polymer* literally means “many parts.” A polymeric solid material may be considered to be one that contains many chemically bonded parts or units that themselves are bonded together to form a solid. In this chapter, we shall study some aspects of the structure, properties, processing, and applications of two industrially important polymeric materials: *plastics* and *elastomers*. *Plastics*¹ are a large and varied group of synthetic materials that are processed by forming or molding into shape. Just as we have many types of metals such as aluminum and copper, we have many types of plastics such as polyethylene and nylon. Plastics can be divided into two classes, **thermoplastics** and **thermosetting plastics**, depending on how they are structurally chemically bonded. *Elastomers* or rubbers can be elastically deformed a large amount when a force is applied to them and can return to their original shape (or almost) when the force is released.

¹The word *plastic* has many meanings. As a noun, plastic refers to a class of materials that can be molded or formed into shape. As an adjective, plastic can mean capable of being molded. Another use of plastic as an adjective is to describe the continuous permanent deformation of a metal without rupture, as in the “plastic deformation of metals.”

10.1.1 Thermoplastics

Thermoplastics require heat to make them formable and after cooling, retain the shape they were formed into. These materials can be reheated and reformed into new shapes a number of times without significant change in their properties. Most thermoplastics consist of very long main chains of carbon atoms covalently bonded together. Sometimes nitrogen, oxygen, or sulfur atoms are also covalently bonded in the main molecular chain. Pendant atoms or groups of atoms are covalently bonded to the main-chain atoms. In thermoplastics, the long molecular chains are bonded to each other by secondary bonds.

10.1.2 Thermosetting Plastics (Thermosets)

Thermosetting plastics formed into a permanent shape and cured or “set” by a chemical reaction cannot be remelted and reformed into another shape but degrade or decompose upon being heated to too high a temperature. Thus, thermosetting plastics cannot be recycled. The term *thermosetting* implies that heat (the Greek word for heat is *thermē*) is required to permanently set the plastic. There are, however, many so-called thermosetting plastics that set or cure at room temperature by a chemical reaction only. Most thermosetting plastics consist of a network of carbon atoms covalently bonded to form a rigid solid. Sometimes nitrogen, oxygen, sulfur, or other atoms are also covalently bonded into a thermoset network structure.

Plastics are important engineering materials for many reasons. They have a wide range of properties, some of which are unattainable from any other materials, and in most cases they are relatively low in cost. The use of plastics for mechanical engineering designs offers many advantages, which include elimination of parts through engineering design with plastics, elimination of many finishing operations, simplified assembly, weight savings, noise reduction, and in some cases elimination of the need for lubrication of some parts. Plastics are also very useful for many electrical engineering designs mainly because of their excellent insulative properties. Electrical-electronic applications for plastic materials include connectors, switches, relays, TV tuner components, coil forms, integrated circuit boards, and computer components. Figure 10.1 shows some examples of the use of plastic materials in engineering designs.

The amount of plastic materials used by industry has increased markedly. A good example of the increased industrial use of plastics is in the manufacture of automobiles. Engineers designing the 1959 Cadillac were amazed to find that they had put as much as 25 lb of plastics in that vehicle. In 1980, there was an average of about 200 lb of plastic used per car. The use of plastics in the 1990 car was about 300 lb per car. Certainly not all industries have increased their usage of plastics like the auto industry, but there has been an overall increased usage of plastics in industry in recent decades. Let us now look into the details of the structure, properties, and applications of plastics and elastomers.

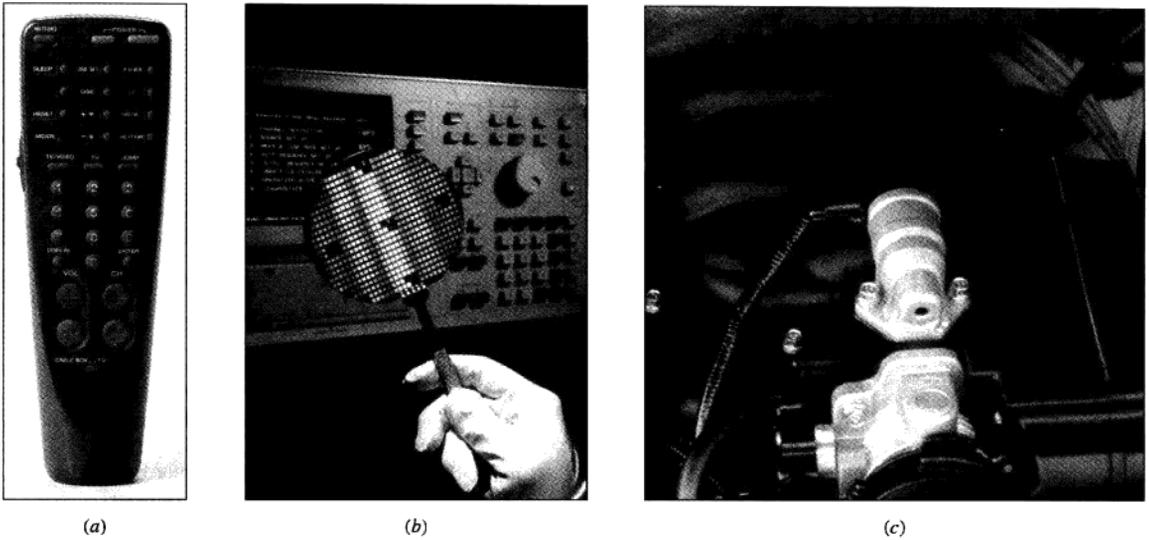


Figure 10.1

Some applications for engineering plastics. (a) TV remote control casing using advanced styrenic resin to meet requirements for gloss, toughness, and crack resistance. (b) Semiconductor wafer wands made of Vitrex PEEK (polyetheretherketone) thermoplastic. (c) Nylon thermoplastic reinforced with 30 percent glass fiber to replace aluminum in the air intake manifold of the turbodiesel engine for the Ford Transit. (DSM Engineering Plastics, The Netherlands.)

[(a) © CORBIS/RF. (b) © CORBIS/RF. (c) © Tom Pantages.]

10.2 POLYMERIZATION REACTIONS

Most thermoplastics are synthesized by the process of *chain-growth polymerization*. In this process, many (there may be thousands) small molecules are covalently bonded together to form very long molecular chains. The simple molecules that are covalently bonded into long chains are called **monomers** (from the Greek words *mono*, meaning “one,” and *meros*, meaning “part”). The long-chain molecule formed from the monomer units is called a **polymer** (from the Greek words *polys*, meaning “many,” and *meros*, meaning “part”).

10.2.1 Covalent Bonding Structure of an Ethylene Molecule

The ethylene molecule, C_2H_4 , is chemically bonded by a double covalent bond between the carbon atoms and by four single covalent bonds between the carbon and hydrogen atoms (Fig. 10.2). A carbon-containing molecule that has one or more

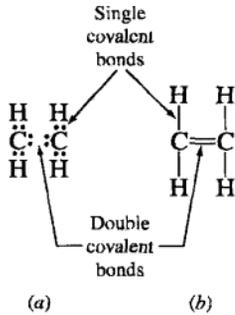


Figure 10.2
Covalent bonding in the ethylene molecule illustrated by (a) electron-dot (dots represent valence electrons) and (b) straight-line notation. There is one double carbon-carbon covalent bond and four single carbon-hydrogen covalent bonds in the ethylene molecule. The double bond is chemically more reactive than the single bonds.

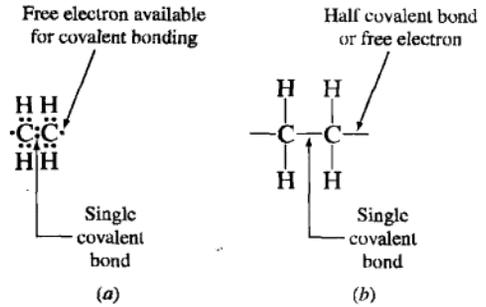


Figure 10.3
Covalent bonding structure of an activated ethylene molecule. (a) Electron-dot notation (where dots represent valence electrons). Free electrons are created at each end of the molecule that can be covalently bonded with free electrons from other molecules. Note that the double covalent bond between the carbon atoms has been reduced to a single bond. (b) Straight-line notation. The free electrons created at the ends of the molecule are indicated by half bonds that are only attached to one carbon atom.

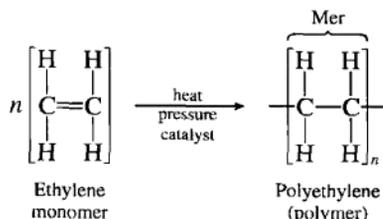
carbon-carbon double bonds is said to be an *unsaturated molecule*. Thus, ethylene is an unsaturated carbon-containing molecule since it contains one carbon-carbon double bond.

10.2.2 Covalent Bonding Structure of an Activated Ethylene Molecule

When the ethylene molecule is activated so that the double bond between the two carbon atoms is "opened up," the double covalent bond is replaced by a single covalent bond, as shown in Fig. 10.3. As a result of the activation, each carbon atom of the former ethylene molecule has a free electron for covalent bonding with another free electron from another molecule. In the following discussion, we shall see how the ethylene molecule can be activated and, as a result, how many ethylene monomer units can be covalently bonded together to form a polymer. This is the process of **chain polymerization**. The polymer produced by the polymerization of ethylene is called *polyethylene*.

10.2.3 General Reaction for the Polymerization of Polyethylene and the Degree of Polymerization

The general reaction for the chain polymerization of ethylene monomer into polyethylene may be written as



The repeating subunit in the polymer chain is called a **mer**. The mer for polyethylene is $\text{---CH}_2\text{---CH}_2\text{---}$ and is indicated in the preceding equation. The n in the equation is known as the **degree of polymerization (DP)** of the polymer chain and is equal to the number of subunits or mers in the polymer molecular chain. The average DP for polyethylene ranges from about 3500 to 25,000, corresponding to average molecular masses ranging from about 100,000 to 700,000 g/mol.

If a particular type of polyethylene has a molecular mass of 150,000 g/mol, what is its degree of polymerization?

EXAMPLE PROBLEM 10.1

■ Solution

The repeating unit or mer for polyethylene is $\text{---CH}_2\text{---CH}_2\text{---}$. This mer has a mass of 4 atoms \times 1 g = 4 g for the hydrogen atoms plus a mass of 2 atoms \times 12 g = 24 g for the carbon atoms, making a total of 28 g for each polyethylene mer.

$$\begin{aligned}
 \text{DP} &= \frac{\text{molecular mass of polymer (g/mol)}}{\text{mass of a mer (g/mer)}} & (10.1) \\
 &= \frac{150,000 \text{ g/mol}}{28 \text{ g/mer}} = 5357 \text{ mers/mol} \blacktriangleleft
 \end{aligned}$$

10.2.4 Chain Polymerization Steps

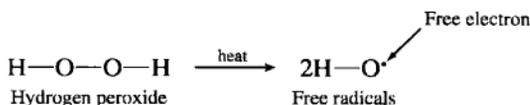
The reactions for the chain polymerization of monomers like ethylene into linear polymers like polyethylene can be divided into the following steps: (1) initiation, (2) propagation, and (3) termination.

Initiation For the chain polymerization of ethylene, one of many types of catalysts can be used. In this discussion, we shall consider the use of organic peroxides that act as free-radical formers. A *free radical* can be defined as an atom, often part of a larger group, that has an unpaired electron (free electron) that can covalently bond to an unpaired electron (free electron) of another atom or molecule.

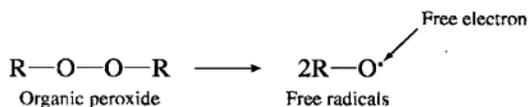
Let us first consider how a molecule of hydrogen peroxide, H_2O_2 , can decompose into two free radicals, as shown by the following equations. Using electron-dot notation for the covalent bonds,



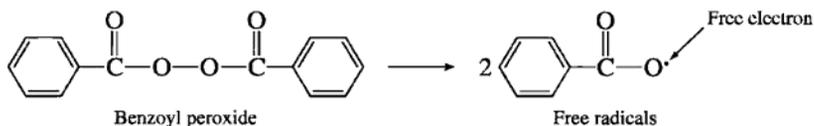
Using straight-line notation for the covalent bonds,



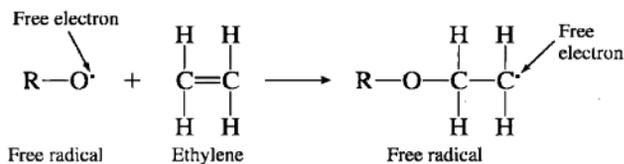
In the free-radical chain polymerization of ethylene, an organic peroxide can decompose in the same way as hydrogen peroxide. If $\text{R}-\text{O}-\text{O}-\text{R}$ represents an organic peroxide, where R is a chemical group, then upon heating, this peroxide can decompose into two free radicals in a manner similar to that of hydrogen peroxide, as



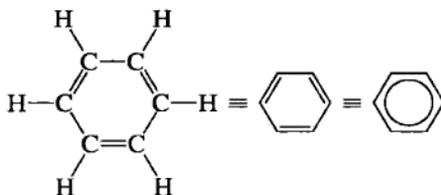
Benzoyl peroxide is an organic peroxide used to initiate some chain polymerization reactions. It decomposes into free radicals as it follows:²



One of the free radicals created by the decomposition of the organic peroxide can react with an ethylene molecule to form a new longer-chain free radical, as shown by the reaction



²The hexagonal ring represents the benzene structure, as indicated below. Also see Sec. 2.6.



The organic free radical in this way acts as an initiator catalyst for the polymerization of ethylene.

Propagation The process of extending the polymer chain by the successive addition of monomer units is called *propagation*. The double bond at the end of an ethylene monomer unit can be "opened up" by the extended free radical and be covalently bonded to it. Thus, the polymer chain is further extended by the reaction



The polymer chains in chain polymerization keep growing spontaneously because the energy of the chemical system is lowered by the chain polymerization process. That is, the sum of the energies of the produced polymers is lower than the sum of the energies of the monomers that produced the polymers. The degrees of polymerization of the polymers produced by chain polymerization vary within the polymeric material. Also, the average DP varies among polymeric materials. For commercial polyethylene, the DP usually averages in the range from 3500 to 25,000.

Termination *Termination* can occur by the addition of a terminator free radical or when two chains combine. Another possibility is that trace amounts of impurities may terminate the polymer chain. Termination by the coupling of two chains can be represented by the reaction



10.2.5 Average Molecular Weight for Thermoplastics

Thermoplastics consist of chains of polymers of many different lengths, each of which has its own molecular weight and degree of polymerization. Thus, one must speak of an average molecular weight when referring to the molecular mass of a thermoplastic material.

The average molecular weight of a thermoplastic can be determined by using special physical-chemical techniques. One method commonly used for this analysis is to determine the weight fractions of molecular weight ranges. The average molecular weight of the thermoplastic is then the sum of the weight fractions times their mean molecular weight for each particular range divided by the sum of the weight fractions. Thus,

$$\bar{M}_m = \frac{\sum f_i M_i}{\sum f_i} \quad (10.2)$$

where \bar{M}_m = average molecular weight for a thermoplastic

M_i = mean molecular weight for each molecular weight range selected

f_i = weight fraction of the material having molecular weights of a selected molecular weight range

**EXAMPLE
PROBLEM 10.2**

Calculate the average molecular weight \bar{M}_m for a thermoplastic material that has the mean molecular weight fractions f_i for the molecular weight ranges listed in the following table:

Molecular weight range, g/mol	M_i	f_i	$f_i M_i$
5000–10,000	7500	0.11	825
10,000–15,000	12,500	0.17	2125
15,000–20,000	17,500	0.26	4550
20,000–25,000	22,500	0.22	4950
25,000–30,000	27,500	0.14	3850
30,000–35,000	32,500	0.10	3250
		$\Sigma = 1.00$	$\Sigma = 19,550$

■ Solution

First determine the mean values for the molecular weight ranges and then list these values, as in the column under M_i shown in the table. Then multiply f_i by M_i to obtain the $f_i M_i$ values. The average molecular weight for this thermoplastic is

$$\bar{M}_m = \frac{\sum f_i M_i}{\sum f_i} = \frac{19,550}{1.00} = 19,550 \text{ g/mol} \blacktriangleleft$$

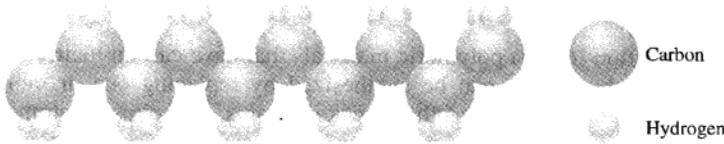
10.2.6 Functionality of a Monomer

In order for a monomer to polymerize, it must have at least two active chemical bonds. When a monomer has two active bonds, it can react with two other monomers, and by repetition of the bonding, other monomers of the same type can form a long-chain or linear polymer. When a monomer has more than two active bonds, polymerization can take place in more than two directions, and thus three-dimensional network molecules can be built up.

The number of active bonds a monomer has is called the **functionality** of the monomer. A monomer that uses two active bonds for the polymerization of long chains is called *bifunctional*. Thus, ethylene is an example of a bifunctional monomer. A monomer that uses three active bonds to form a network polymeric material is called *trifunctional*. Phenol, C_6H_5OH , is an example of a trifunctional monomer and is used in the polymerization of phenol and formaldehyde, which will be discussed later.

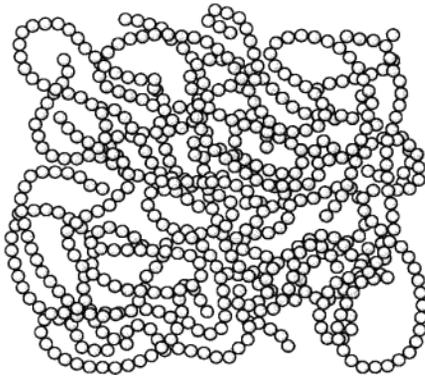
10.2.7 Structure of Noncrystalline Linear Polymers

If we microscopically examine a short length of a polyethylene chain, we find that it takes on a zigzag configuration (Fig. 10.4) because the covalent bonding angle between single carbon-carbon covalent bonds is about 109° . However, on a larger scale, the polymer chains in noncrystalline polyethylene are randomly entangled like spaghetti thrown into a bowl. This entanglement of a linear polymer is illustrated in Fig. 10.5. For some polymeric materials, of which polyethylene is one, there can be

**Figure 10.4**

The molecular structure of a short length of a polyethylene chain. The carbon atoms have a zigzag arrangement because all carbon-carbon covalent bonds are directed at about 109° to each other.

(From W.G. Moffatt, G.W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. 1: "Structure," Wiley, 1965, p. 65.)

**Figure 10.5**

A schematic representation of a polymer. The spheres represent the repeating units of the polymer chain, not specific atoms.

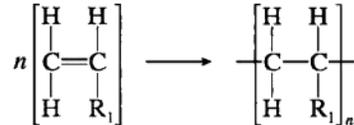
(From W.G. Moffatt, G.W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. 1: "Structure," Wiley, 1965, p. 104.)

both crystalline and noncrystalline regions. This subject will be discussed in more detail in Sec. 10.4.

The bonding between the long molecular chains in polyethylene consists of weak, permanent dipole secondary bonds. However, the physical entanglement of the long molecular chains also adds to the strength of this type of polymeric material. Side branches also can be formed that cause loose packing of the molecular chains and favor a noncrystalline structure. Branching of linear polymers thus weakens secondary bonds between the chains and lowers the tensile strength of the bulk polymeric material.

10.2.8 Vinyl and Vinylidene Polymers

Many useful addition (chain) polymeric materials that have carbon main-chain structures similar to polyethylene can be synthesized by replacing one or more of the hydrogen atoms of ethylene with other types of atoms or groups of atoms. If only one hydrogen atom of the ethylene monomer is replaced with another atom or group of atoms, the polymerized polymer is called a *vinyl polymer*. Examples of vinyl polymers are polyvinyl chloride, polypropylene, polystyrene, acrylonitrile, and polyvinyl acetate. The general reaction for the polymerization of the vinyl polymers is



where R_1 can be another type of atom or group of atoms. Figure 10.6 shows the structural bonding of some vinyl polymers.

If both hydrogen atoms on one of the carbon atoms of the ethylene monomer are replaced by other atoms or groups of atoms, the polymerized polymer is called a *vinylidene polymer*. The general reaction for the polymerization of vinylidene polymers is

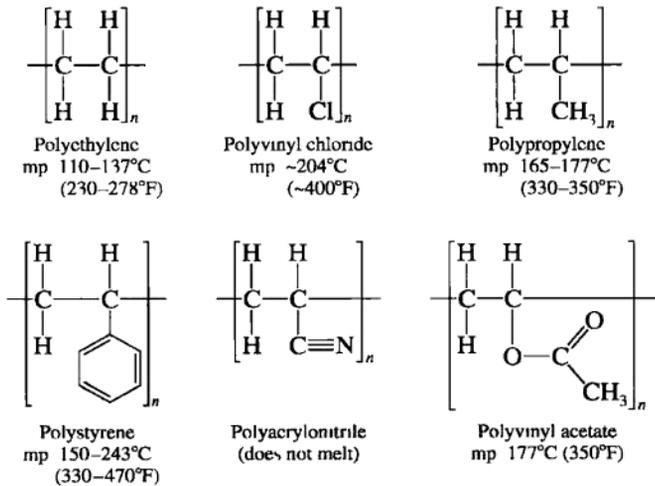
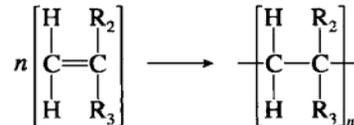


Figure 10.6
Structural formulas for some vinyl polymers

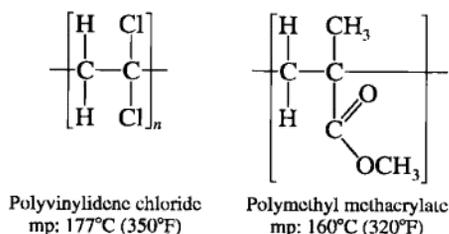


Figure 10.7
Structural formulas for some vinylidene polymers.

where R_2 and R_3 can be other types of atoms or atomic groups. Figure 10.7 shows the structural bonding for two vinylidene polymers.

10.2.9 Homopolymers and Copolymers

Homopolymers are polymeric materials that consist of polymer chains made up of single repeating units. That is, if A is a repeating unit, a homopolymer chain will have a sequence of AAAAAAA ... in the polymer molecular chain. **Copolymers**, in contrast, consist of polymer chains made up of two or more chemically different repeating units that can be in different sequences.

Although the monomers in most copolymers are randomly arranged, four distinct types of copolymers have been identified: random, alternating, block, and graft (Fig. 10.8).

Random copolymers. Different monomers are randomly arranged within the polymer chains. If A and B are different monomers, then an arrangement might be (Fig. 10.8a)



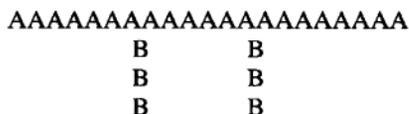
Alternating copolymers. Different monomers show a definite ordered alternation as (Fig. 10.8b)

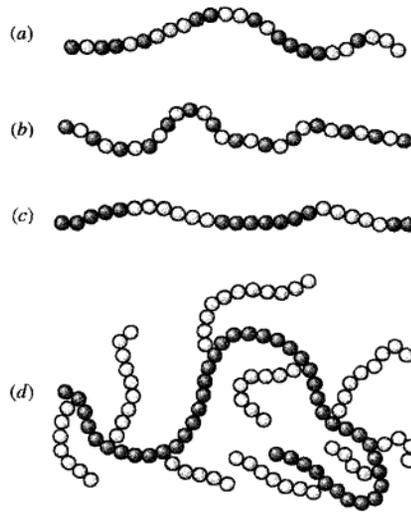


Block copolymers. Different monomers in the chain are arranged in relatively long blocks of each monomer as (Fig. 10.8c)



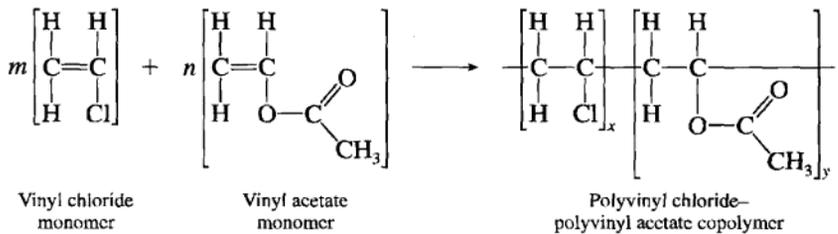
Graft copolymers. Appendages of one type of monomer are grafted to the long chain of another as (Fig. 10.8d)



**Figure 10.8**

Copolymer arrangements. (a) A copolymer in which the different units are randomly distributed along the chain. (b) A copolymer in which the units alternate regularly. (c) A block copolymer. (d) A graft copolymer.

(From W.G. Moffatt, G.W. Pearsall, and J. Wulff, "The Structure and Properties of Materials," vol. 1: "Structure," Wiley, 1965, p. 108.)

**Figure 10.9**

Generalized polymerization reaction of vinyl chloride and vinyl acetate monomers to produce a copolymer of polyvinyl chloride–polyvinyl acetate.

Chain-reaction polymerization can take place between two or more different monomers if they can enter the growing chains at the same relative energy level and rates. An example of an industrially important copolymer is one formed with polyvinyl chloride and polyvinyl acetate, which is used as coating material for cables, pools, and cans. A generalized polymerization reaction for the production of this copolymer is given in Fig. 10.9.

A copolymer consists of 15 wt % polyvinyl acetate (PVA) and 85 wt % polyvinyl chloride (PVC). Determine the mole fraction of each component.

**EXAMPLE
PROBLEM 10.3**

■ **Solution**

Let the basis be 100 g of copolymer; therefore, we have 15 g of PVA and 85 g of PVC. First we determine the number of moles of each component that we have, and then we calculate the mole fractions of each.

Moles of polyvinyl acetate. The molecular weight of the PVA mer is obtained by adding up the atomic masses of the atoms in the structural formula for the PVA mer (Fig. EP10.3a):

$$4 \text{ C atoms} \times 12 \text{ g/mol} + 6 \text{ H atoms} \times 1 \text{ g/mol} + 2 \text{ O atoms} \times 16 \text{ g/mol} = 86 \text{ g/mol}$$

$$\text{No. of moles of PVA in 100 g of copolymer} = \frac{15 \text{ g}}{86 \text{ g/mol}} = 0.174$$

Moles of polyvinyl chloride. The molecular weight of the PVC mer is obtained from Fig. EP10.3b.

$$2 \text{ C atoms} \times 12 \text{ g/mol} + 3 \text{ H atoms} \times 1 \text{ g/mol} + 1 \text{ Cl atom} \times 35.5 \text{ g/mol} = 62.5 \text{ g/mol}$$

$$\text{No. of moles of PVC in 100 g of copolymer} = \frac{85 \text{ g}}{62.5 \text{ g/mol}} = 1.36$$

$$\text{Mole fraction of PVA} = \frac{0.174}{0.174 + 1.36} = 0.113$$

$$\text{Mole fraction of PVC} = \frac{1.36}{0.174 + 1.36} = 0.887$$

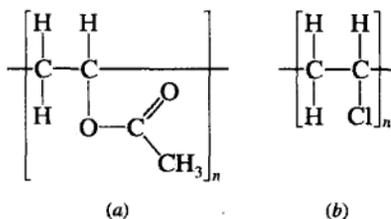


Figure EP10.3
Structural formulas for the mers of
(a) polyvinyl acetate and (b) polyvinyl
chloride.

**EXAMPLE
PROBLEM 10.4**

Determine the mole fractions of vinyl chloride and vinyl acetate in a copolymer having a molecular weight of 10,520 g/mol and a degree of polymerization of 160.

■ Solution

From Example Problem 10.3, the molecular weight of the PVC mer is 62.5 g/mol and that of the PVA mer is 86 g/mol.

Since the sum of the mole fractions of polyvinyl chloride, f_{vc} , and polyvinyl acetate, $f_{va} = 1$, $f_{va} = 1 - f_{vc}$. Thus, the average molecular weight of the copolymer mer is

$$MW_{av}(\text{mer}) = f_{vc}MW_{vc} + f_{va}MW_{va} = f_{vc}MW_{vc} + (1 - f_{vc})MW_{va}$$

The average molecular weight of the copolymer mer is also

$$MW_{av}(\text{mer}) = \frac{MW_{av}(\text{polymer})}{DP} = \frac{10,520 \text{ g/mol}}{160 \text{ mers}} = 65.75 \text{ g/(mol} \cdot \text{mer)}$$

The value of f_{vc} can be obtained by equating the two equations of $MW_{av}(\text{mer})$.

$$f_{vc}(62.5) + (1 - f_{vc})(86) = 65.75 \quad \text{or} \quad f_{vc} = 0.86$$

$$f_{va} = (1 - f_{vc}) = 1 - 0.86 = 0.14$$

**EXAMPLE
PROBLEM 10.5**

If a vinyl chloride–vinyl acetate copolymer has a ratio of 10:1 vinyl chloride to vinyl acetate mers and a molecular weight of 16,000 g/mol, what is its degree of polymerization?

■ Solution

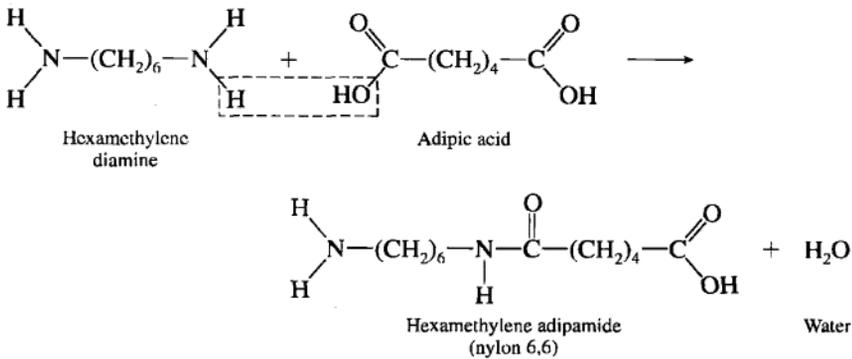
$$MW_{av}(\text{mer}) = \frac{10}{11}MV_{vc} + \frac{1}{11}MW_{va} = \frac{10}{11}(62.5) + \frac{1}{11}(86) = 64.6 \text{ g/(mol} \cdot \text{mer)}$$

$$DP = \frac{16,000 \text{ g/mol (polymer)}}{64.6 \text{ g/(mol} \cdot \text{mer)}} = 248 \text{ mers}$$

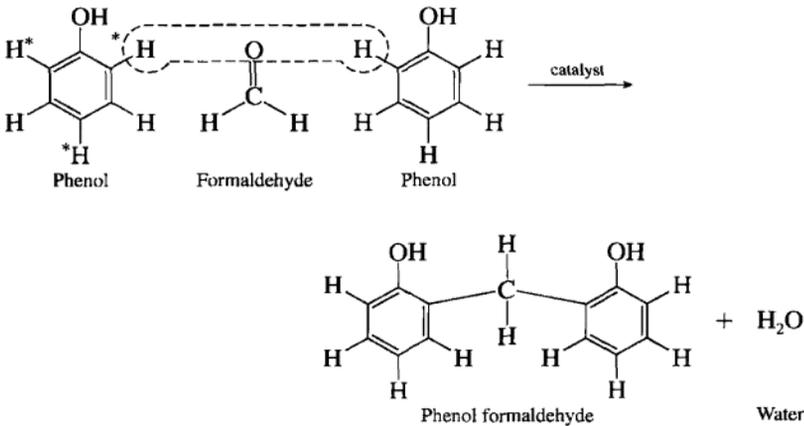
10.2.10 Other Methods of Polymerization

Stepwise Polymerization In **stepwise polymerization**, monomers chemically react with each other to produce linear polymers. The reactivity of the functional groups at the ends of a monomer in stepwise polymerization is usually assumed to be about the same for a polymer of any size. Thus, monomer units can react with each other or with produced polymers of any size. In many stepwise polymerization reactions, a small molecule is produced as a by-product, so these types of reactions are sometimes called *condensation polymerization reactions*. An example of a stepwise polymerization reaction is the reaction of hexamethylene diamine with adipic acid to produce nylon 6,6 and water as a by-product, as shown in Fig. 10.10 for the reaction of one molecule of hexamethylene diamine with another of adipic acid.

Network Polymerization For some polymerization reactions that involve a chemical reactant with more than two reaction sites, a three-dimensional network plastic

**Figure 10.10**

Polymerization reaction of hexamethylene diamine with adipic acid to produce a unit of nylon 6,6.

**Figure 10.11**

Polymerization reaction of phenol (asterisks represent reaction sites) with formaldehyde to produce a phenolic resin unit linkage.

material can be produced. This type of polymerization occurs in the curing of thermosetting plastics such as the phenolics, epoxies, and some polyesters. The polymerization reaction of two phenol molecules and one formaldehyde molecule is shown in Fig. 10.11. Note that a molecule of water is formed as a by-product of the reaction. The phenol molecule is trifunctional, and in the presence of a suitable catalyst and sufficient heat and pressure, it can be polymerized with formaldehyde into a network thermosetting phenolic plastic material that is sometimes referred to by the trade name *Bakelite*.

10.3 INDUSTRIAL POLYMERIZATION METHODS

At this stage, one must certainly be wondering how plastic materials are produced industrially. The answer to this question is not simple since many different processes are used and new ones are constantly being developed. To start with, basic raw materials such as *natural gas*, *petroleum*, and *coal* are used to produce the basic chemicals for the polymerization processes. These chemicals are then polymerized by many different processes into plastic materials such as granules, pellets, powders, or liquids that are further processed into finished products. The chemical polymerization processes used to produce plastic materials are complex and diverse. The chemical engineer plays a major role in their development and industrial utilization. Some of the most important polymerization methods are outlined in the following paragraphs and illustrated in Figs. 10.12 and 10.13.

Bulk polymerization (Fig. 10.12*a*). The monomer and activator are mixed in a reactor that is heated and cooled as required. This process is used extensively for condensation polymerization where one monomer may be charged into the reactor and another added slowly. The bulk process can be

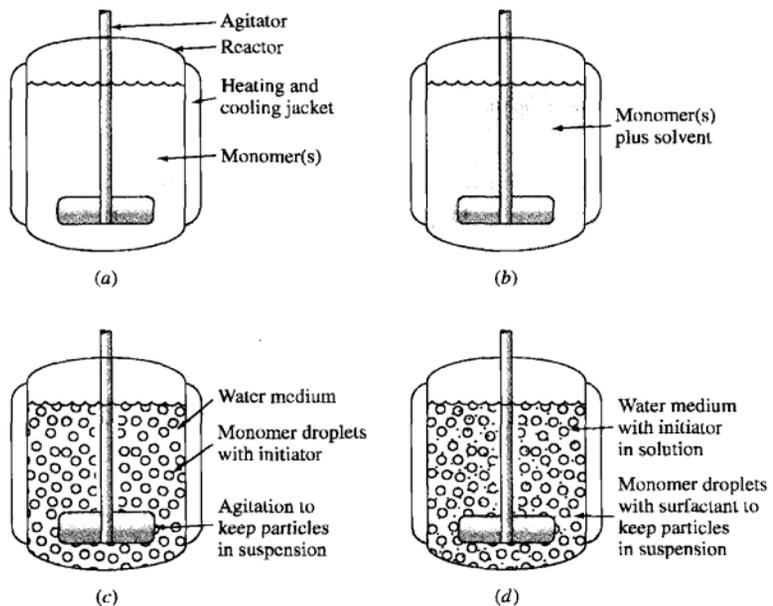


Figure 10.12

Schematic illustration of some commonly used industrial polymerization methods: (a) bulk, (b) solution, (c) suspension, and (d) emulsion.

(From W.E. Driver, "Plastics Chemistry and Technology," Van Nostrand Reinhold, 1979, p. 19.)

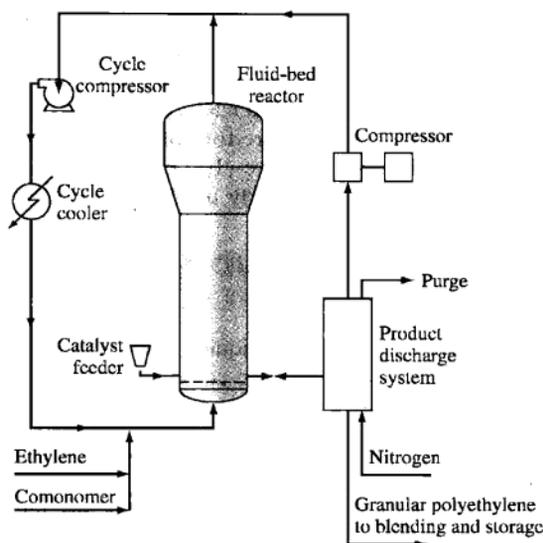


Figure 10.13

Gas-phase polymerization process for low-density polyethylene. Flow diagram outlining the basic steps of the process.

(After *Chemical Engineering*, Dec. 3, 1979, pp. 81, 83.)

used for many condensation polymerization reactions because of their low heats of reaction.

Solution polymerization (Fig. 10.12*b*). The monomer is dissolved in a non-reactive solvent that contains a catalyst. The heat released by the reaction is absorbed by the solvent, and so the reaction rate is reduced.

Suspension polymerization (Fig. 10.12*c*). The monomer is mixed with a catalyst and then dispersed as a suspension in water. In this process, the heat released by the reaction is absorbed by the water. After polymerization, the polymerized product is separated and dried. This process is commonly used to produce many of the vinyl-type polymers such as polyvinyl chloride, polystyrene, polyacrylonitrile, and polymethyl methacrylate.

Emulsion polymerization (Fig. 10.12*d*). This polymerization process is similar to the suspension process since it is carried out in water. However, an emulsifier is added to disperse the monomer into very small particles.

In addition to the batch polymerization processes just described, many types of mass continuous polymerization processes have been developed, and research and

development in this area continues. One very important process³ is Union Carbide's gas-phase Unipol process for producing low-density polyethylene. In this process, gaseous ethylene monomer along with some comonomer are fed continuously into a fluidized-bed reactor into which a special catalyst is added (Fig. 10.13). The advantages of this process are lower temperature for polymerization (100°C instead of the older process's 300°C) and lower pressure (100 psi instead of 300 psi for the older process). Many industrial plants are already using the Unipol process.

10.4 CRYSTALLINITY AND STEREOISOMERISM IN SOME THERMOPLASTICS

A thermoplastic, when solidified from the liquid state, forms either a noncrystalline or a partly crystalline solid. Let us investigate some of the solidification and structural characteristics of these materials.

10.4.1 Solidification of Noncrystalline Thermoplastics

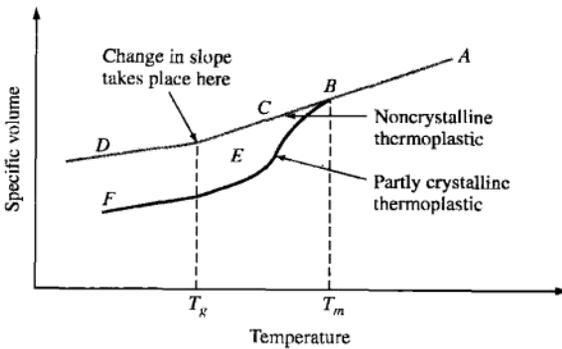
Let us consider the solidification and slow cooling to low temperatures of a noncrystalline thermoplastic. When noncrystalline thermoplastics solidify, there is no sudden decrease in specific volume (volume per unit mass) as the temperature is lowered (Fig. 10.14). The liquid, upon solidification, changes to a supercooled liquid that is in the solid state and shows a gradual decrease in specific volume with decreasing temperature, as indicated along the line *ABC* in Fig. 10.14.

Upon cooling this material to lower temperatures, a change in slope of the specific volume versus temperature curve occurs, as indicated by *C* and *D* of curve *ABCD* of Fig. 10.14. The average temperature within the narrow temperature range over which the slope in the curve changes is called the **glass transition temperature** T_g . Above T_g , noncrystalline thermoplastics show viscous (rubbery or flexible leathery) behavior, and below T_g , these materials show glass-brittle behavior. In some ways, T_g might be considered a ductile-brittle transition temperature. Below T_g , the material is glass-brittle because molecular chain motion is very restricted. Figure 10.15 shows an experimental plot of specific volume versus temperature for noncrystalline polypropylene that indicates a slope change for the T_g of this material at -12°C . Table 10.1 lists T_g values for some thermoplastics.

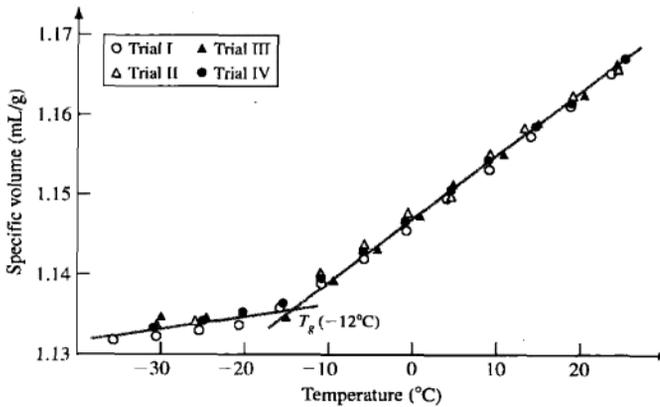
10.4.2 Solidification of Partly Crystalline Thermoplastics

Let us now consider the solidification and cooling to low temperatures of a partly crystalline thermoplastic. When this material solidifies and cools, a sudden decrease in specific volume occurs, as indicated by the line *BE* in Fig. 10.14. This decrease in specific volume is caused by the more-efficient packing of the polymer chains into crystalline regions. The structure of the partly crystalline thermoplastic at *E* will thus be that of crystalline regions in a supercooled liquid (viscous solid) noncrystalline

³Chemical Engineering, Dec. 3, 1979, p. 80.

**Figure 10.14**

Solidification and cooling of noncrystalline and partly crystalline thermoplastics showing change in specific volume with temperature (schematic). T_g is the glass transition temperature and T_m is the melting temperature. Noncrystalline thermoplastic cools along line $ABCD$, where A = liquid, B = highly viscous liquid, C = supercooled liquid (rubbery), and D = glassy solid (hard and brittle). Partly crystalline thermoplastic cools along line $ABEF$, where E = solid crystalline regions in supercooled liquid matrix and F = solid crystalline regions in glassy matrix.

**Figure 10.15**

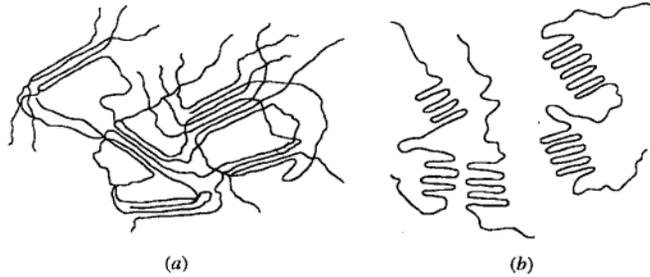
Experimental data of specific volume versus temperature for the determination of the glass transition temperature of atactic polypropylene. T_g is at -12°C .

[After D.L. Beck, A.A. Hiltz and J.R. Knox, *Soc. Plast. Eng. Trans.*, 3:279(1963). Used by permission.]

Table 10.1 Glass transition temperature T_g^* (°C) for some thermoplastics

Polyethylene	-110	(nominal)
Polypropylene	-18	(nominal)
Polyvinyl acetate	29	
Polyvinyl chloride	82	
Polystyrene	75-100	
Polymethyl methacrylate	72	

*Note that the T_g of a thermoplastic is not a physical constant like the melting temperature of a crystalline solid but depends to some extent on variables such as degree of crystallinity, average molecular weight of the polymer chains, and rate of cooling of the thermoplastic.

**Figure 10.16**

Two suggested crystallite arrangements for partly crystalline thermoplastic materials: (a) fringed-micelle model and (b) folded-chain model.

(Copyright 1982 from F. Rodriguez, "Principles of Polymer Systems," 2d ed., p. 42. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.)

matrix. As cooling is continued, the glass transition is encountered, as indicated by the slope change of specific volume versus temperature in Fig. 10.14 between E and F . In going through the glass transition, the supercooled liquid matrix transforms to the glassy state, and thus the structure of the thermoplastic at F consists of crystalline regions in a glassy noncrystalline matrix. An example of a thermoplastic that solidifies to form a partly crystalline structure is polyethylene.

10.4.3 Structure of Partly Crystalline Thermoplastic Materials

The exact way in which polymer molecules are arranged in a crystalline structure is still in doubt, and more research is needed in this area. The longest dimension of crystalline regions or crystallites in polycrystalline polymeric materials is usually about 5 to 50 nm, which is a small percentage of the length of a fully extended polymer molecule that may be about 5000 nm. An early model called the *fringed-micelle model* pictured long polymer chains of about 5000 nm wandering successively through a series of disordered and ordered regions along the length of the polymer molecule (Fig. 10.16a). A newer model called the *folded-chain model* pictures

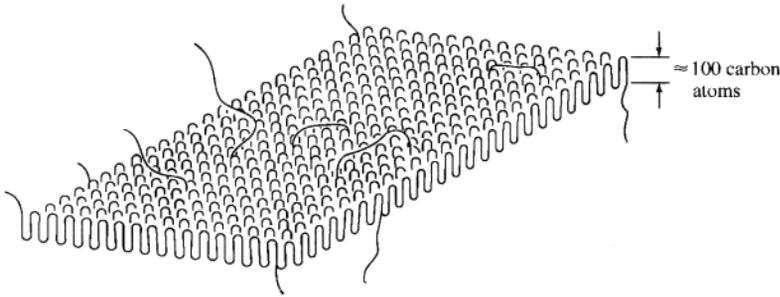


Figure 10.17

Schematic folded-chain structure of a lamella of low-density polyethylene.

[From R.L. Boysen, "Olefin Polymers (High-Pressure Polyethylene)," in "Kirk-Othmer, Encyclopedia of Chemical Technology," vol. 16, Wiley, 1981, p. 405. Reprinted by permission of John Wiley & Sons, Inc.]

sections of the molecular chains folding on themselves so that a transition from crystalline to noncrystalline regions can be formed (Fig. 10.16b).

There has been an intensive study over the past years on partly crystalline thermoplastics, especially polyethylene. Polyethylene is believed to crystallize in a folded-chain structure with an orthorhombic cell, as shown in Fig. 10.17. Each length of chain between folds is about 100 carbon atoms, with each single layer of the folded-chain structure being referred to as a *lamella*. Under laboratory conditions, low-density polyethylene crystallizes in a spherulitic-type structure, which is shown in Fig. 10.18. The spherulitic regions, which consist of crystalline lamellae, are the dark areas, and the regions between the spherulitic structures are noncrystalline white areas. The spherulitic structure shown in Fig. 10.18 grows only under carefully controlled stress-free laboratory conditions.

The degree of crystallinity in partly crystalline linear polymeric materials ranges from about 5 to 95 percent of their total volume. Complete crystallization is not attainable even with polymeric materials that are highly crystallizable because of molecular entanglements and crossovers. The amount of crystalline material within a thermoplastic affects its tensile strength. In general as the degree of crystallinity increases, the strength of the material increases.

10.4.4 Stereoisomerism in Thermoplastics

Stereoisomers are molecular compounds that have the same chemical compositions but different structural arrangements. Some thermoplastics such as polypropylene can exist in three different stereoisomeric forms:

1. **Atactic stereoisomer.** The pendant methyl group of polypropylene is randomly arranged on either side of the main-carbon chain (Fig. 10.19a).
2. **Isotactic stereoisomer.** The pendant methyl group is always on the same side of the main-carbon chain (Fig. 10.19b).
3. **Syndiotactic stereoisomer.** The pendant group regularly alternates from one side of the main chain to the other side (Fig. 10.19c).

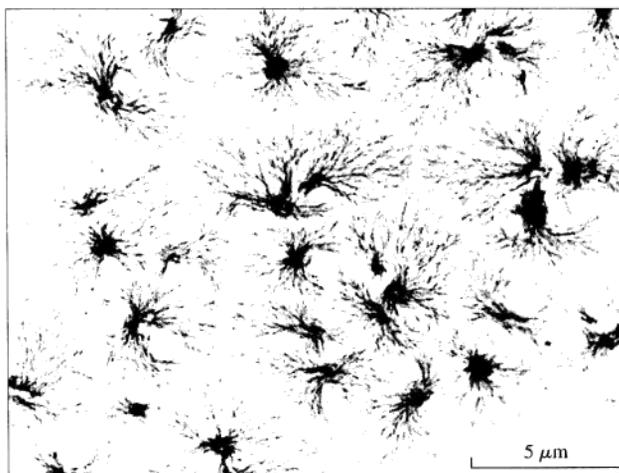


Figure 10.18

Cast-film spherulitic structure of low-density polyethylene, density 0.92 g/cm^3 .

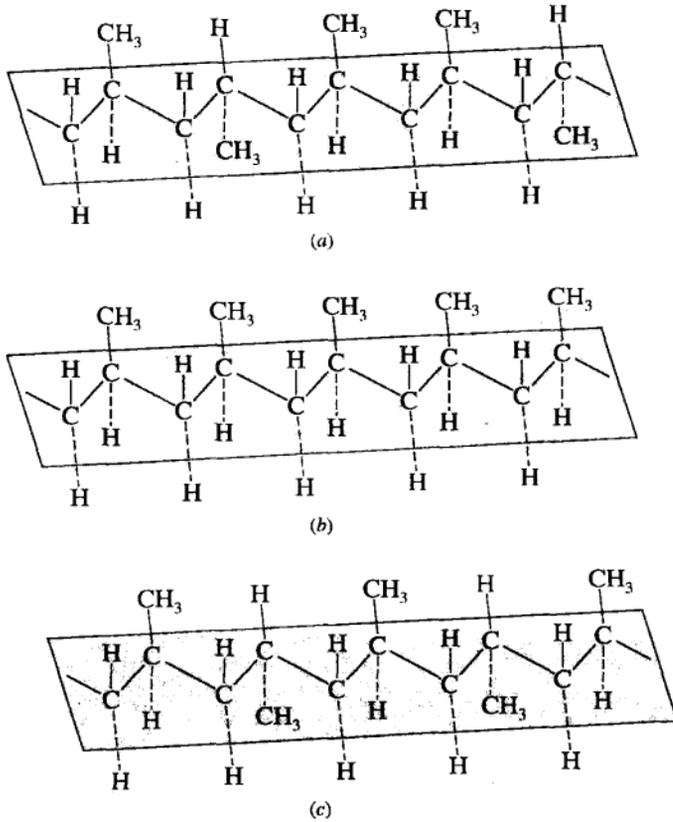
[From R.L. Boysen, "Olefin Polymers (High-Pressure Polyethylene)," in "Kirk-Othmer, Encyclopedia of Chemical Technology," vol. 16, Wiley, 1981, p. 406. Reprinted with permission of John Wiley & Sons, Inc.]

The discovery of a catalyst that made possible the industrial polymerization of isotactic linear-type polymers was a great breakthrough for the plastics industry. With a **stereospecific catalyst**, isotactic polypropylene could be produced on a commercial scale. Isotactic polypropylene is a highly crystalline polymeric material with a melting point of 165°C to 175°C . Because of its high crystallinity, isotactic propylene has higher strengths and higher heat-deflection temperatures than atactic polypropylene.

10.4.5 Ziegler and Natta Catalysts

Karl Ziegler and Giulio Natta were awarded the 1963 Nobel Prize (jointly)⁴ for their work on linear polyethylenes and stereoisomers of polypropylene. Many books have been written on this subject, and the details are beyond the scope of this book, but references are given for those who wish to pursue this subject. Briefly, metallocene catalysts are used in conjunction with the product. Thus, the metallocenes are not true catalysts in the sense that they *do* take part in the reactions and are consumed to a small extent by the reactions. Therefore, metallocene catalysts have opened a new era for polyolefin polymerization.

⁴1963 Nobel laureates in Chemistry were Karl Ziegler and Giulio Natta for their work on the controlled polymerization of hydrocarbons through the use of novel organometallic catalysts.

**Figure 10.19**

Polypropylene stereoisomers. (a) Atactic isomer in which the pendant CH₃ groups are randomly arranged on either side of main-chain carbons. (b) Isotactic isomer in which the pendant CH₃ groups are all on the same side of the main-chain carbons. (c) Syndiotactic isomer in which the pendant CH₃ groups are regularly alternating from one side to the other of main-chain carbons.

[From G. Crespi and L. Luciani, "Olefin Polymers (Polyethylene)," in "Kirk-Othmer Encyclopedia of Chemical Technology," vol. 16, Wiley, 1982, p. 454. Reprinted with permission of John Wiley & Sons, Inc.]

10.5 PROCESSING OF PLASTIC MATERIALS

Many different processes are used to transform plastic granules and pellets into shaped products such as sheet, rods, extruded sections, pipe, or finished molded parts. The process used depends to a certain extent on whether the plastic is a thermoplastic or thermosetting one. Thermoplastics are usually heated to a soft condition and then

reshaped before cooling. On the other hand, thermosetting materials, not having been completely polymerized before processing to the finished shape, use a process by which a chemical reaction occurs to cross-link polymer chains into a network polymeric material. The final polymerization can take place by the application of heat and pressure or by catalytic action at room temperature or higher temperatures.

In this section, we shall discuss some of the most important processes used for thermoplastic and thermosetting materials.

10.5.1 Processes Used for Thermoplastic Materials

Injection Molding Injection molding is one of the most important processing methods used for forming thermoplastic materials. The modern injection-molding machine uses a reciprocating-screw mechanism for melting the plastic and injecting it into a mold (Figs. 10.20 and 10.21). Older-type injection-molding machines use a plunger for melt injection. One of the main advantages of the reciprocating-screw method over the plunger type is that the screw drive delivers a more homogeneous melt for injection.

In the injection-molding process, plastic granules from a hopper are fed through an opening in the injection cylinder onto the surface of a rotating screw drive, which carries them forward toward the mold (Fig. 10.22a). The rotation of the screw forces

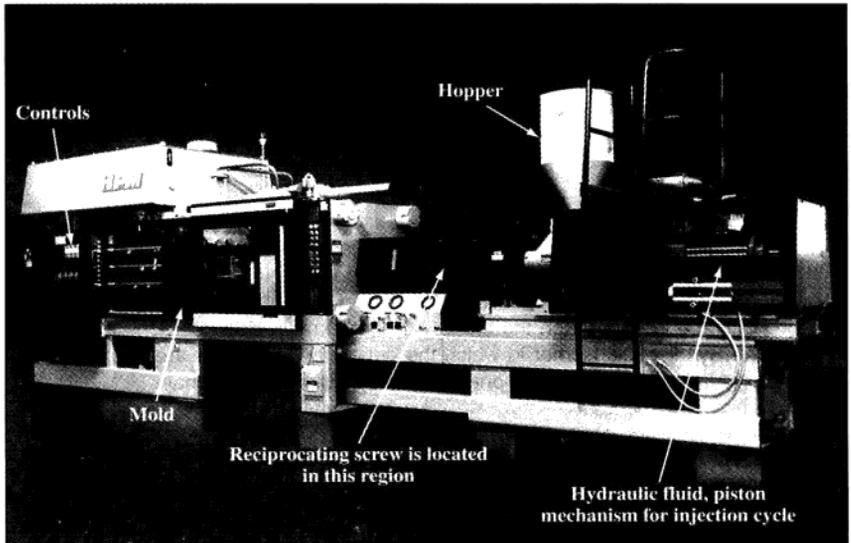


Figure 10.20

Front view of a 500-ton reciprocating-screw injection-molding machine for plastic materials.

(Courtesy of HPM Corporation.)

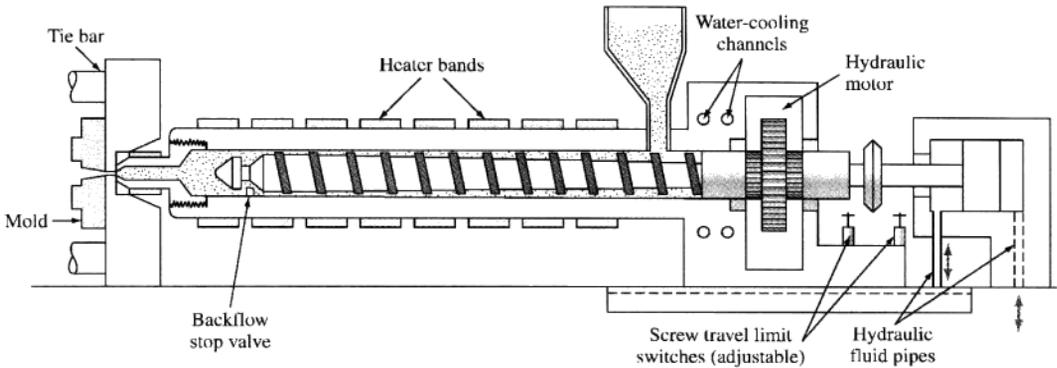


Figure 10.21

Cross section of reciprocating-screw injection-molding machine for plastic materials. (From J. Bown, "Injection Molding of Plastic Components," McGraw-Hill, 1979, p. 28.)

the granules against the heated walls of the cylinder, causing them to melt due to the heat of compression, friction, and the hot walls of the cylinder (Fig. 10.22*b*). When sufficient plastic material is melted at the mold end of the screw, the screw stops and by plungerlike motion injects a "shot" of melted plastic through a runner-gate system and then into the closed mold cavities (Fig. 10.22*c*). The screw shaft maintains pressure on the plastic material fed into the mold for a short time to allow it to become solid and then is retracted. The mold is water-cooled to rapidly cool the plastic part. Finally, the mold is opened and the part is ejected from the mold with air or by spring-loaded ejector pins (Fig. 10.22*d*). The mold is then closed and ready for another cycle.

The main advantages of injection molding are:

1. High-quality parts can be produced at a high production rate.
2. The process has relatively low labor costs.
3. Good surface finishes can be produced on the molded part.
4. The process can be highly automated.
5. Intricate shapes can be produced.

The main disadvantages of injection molding are:

1. High cost of the machine means that a large volume of parts must be made to pay for the machine.
2. The process must be closely controlled to produce a quality product.

Extrusion **Extrusion** is another of the important processing methods used for thermoplastics. Some of the products manufactured by the extrusion process are pipe, rod, film, sheet, and shapes of all kinds. The extrusion machine is also used for

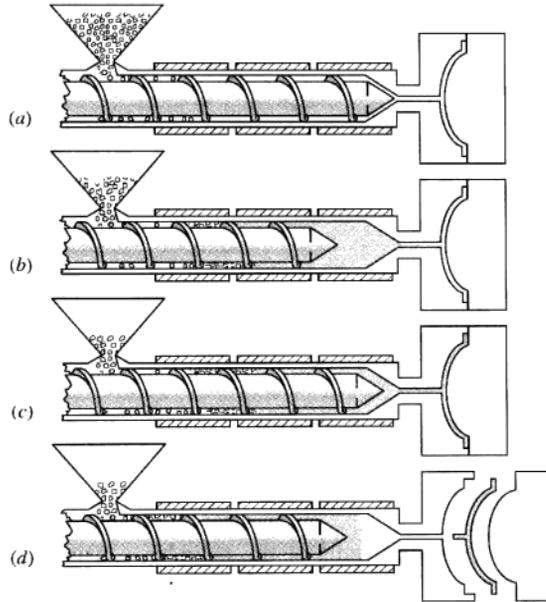


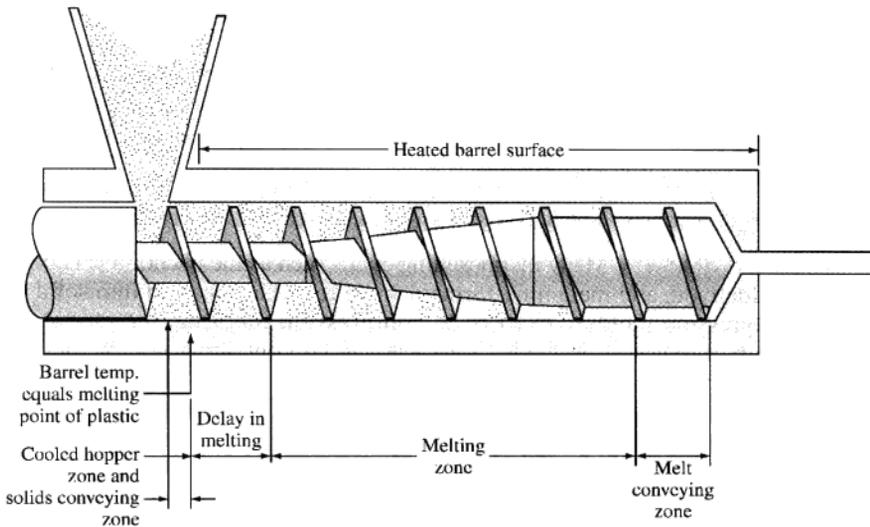
Figure 10.22

Sequence of operations for the reciprocating-screw injection-molding process for plastic materials. (a) Plastic granules are delivered by a revolving-screw barrel. (b) Plastic granules are melted as they travel along the revolving screw, and when sufficient material is melted at the end of the screw, the screw stops rotating. (c) The screw barrel is then driven forward with a plungerlike motion and injects the melted plastic through an opening into a runner and gate system and then into a closed-mold cavity. (d) The screw barrel is retracted and the finished plastic part ejected.

making compounded plastic materials for the production of raw shapes such as pellets and for the reclamation of scrap thermoplastic materials.

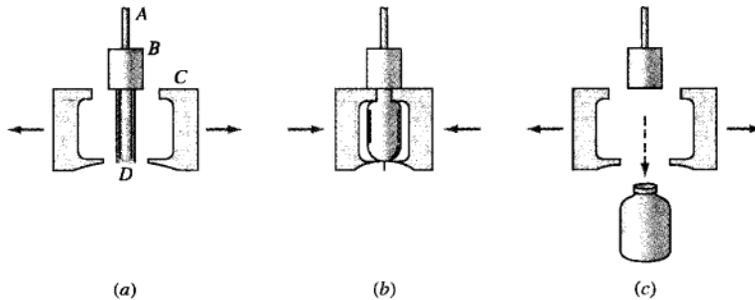
In the extrusion process, thermoplastic resin is fed into a heated cylinder, and the melted plastic is forced by a rotating screw through an opening (or openings) in an accurately machined die to form continuous shapes (Fig. 10.23). After exiting from the die, the extruded part must be cooled below its glass transition temperature to ensure dimensional stability. The cooling is usually done with an air-blast or water-cooling system.

Blow Molding and Thermoforming Other important processing methods for thermoplastics are blow molding and thermoforming of sheet. In **blow molding**, a cylinder or tube of heated plastic called a *parison* is placed between the jaws of a mold (Fig. 10.24a). The mold is closed to pinch off the ends of the cylinder (Fig. 10.24b),

**Figure 10.23**

Schematic drawing of an extruder, showing the various functional zones: hopper, solids-conveying zone, delay in melting start, melting zone, and melt-pumping zone.

[H.S. Kaufman and J.J. Falchetta (eds.), "Introduction to Polymer Science and Technology," Society of Plastic Engineers, Wiley, 1977, p. 462. Reprinted by permission of Dr. Herman S. Kaufman.]

**Figure 10.24**

Sequence of steps for the blow molding of a plastic bottle. (a) A section of tube is introduced into the mold. (b) The mold is closed, and the bottom of the tube is pinched together by the mold. (c) Air pressure is fed through the mold into the tube, which expands to fill the mold, and the part is cooled as it is held under air pressure. A = air line, B = die, C = mold, D = tube section.

(From P.N. Richardson, "Plastics Processing," in "Kirk-Othmer, Encyclopedia of Chemical Technology," vol. 18, Wiley, 1982, p. 198. Reprinted with permission of John Wiley & Sons, Inc.)

and compressed air is blown in, forcing the plastic against the walls of the mold (Fig. 10.24c).

In **thermoforming**, a heated plastic sheet is forced into the contours of a mold by pressure. Mechanical pressure may be used with mating dies, or a vacuum may be used to pull the heated sheet into an open die. Air pressure may also be used to force a heated sheet into an open die.

10.5.2 Processes Used for Thermosetting Materials

Compression Molding Many thermosetting resins such as the phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde resins are formed into solid parts by the compression-molding process. In **compression molding**, the plastic resin, which may be preheated, is loaded into a hot mold containing one or more cavities (Fig. 10.25a). The upper part of the mold is forced down on the plastic resin, and the applied pressure and heat melts the resin and forces the liquefied plastic to fill the cavity or cavities (Fig. 10.25b). Continued heating (usually a minute or two) is required to complete the cross-linking of the thermosetting resin, and then the part is ejected from the mold. The excess flash is trimmed later from the part.

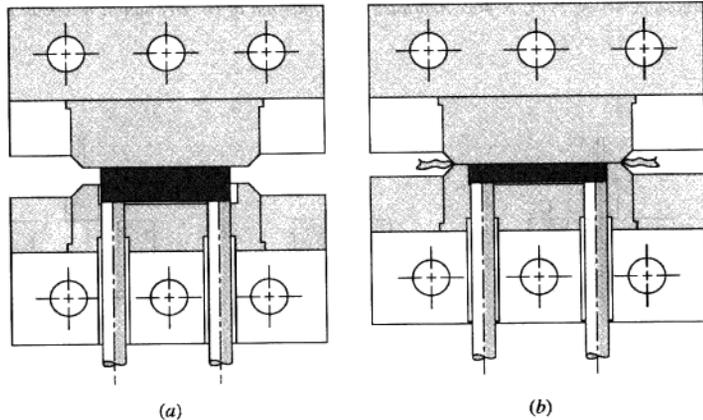


Figure 10.25

Compression molding. (a) Cross section of open mold containing preformed powdered shape in mold cavity. (b) Cross section of closed mold showing molded specimen and excess flash.

(From R.B. Seymour, "Plastics Technology" in "Kirk-Othmer, Encyclopedia of Chemical Technology," vol. 15, Interscience, 1968, p. 802. Reprinted with permission of John Wiley & Sons, Inc.)

The advantages of compression molding are:

1. Because of the relative simplicity of the molds, initial mold costs are low.
2. The relatively short flow of material reduces wear and abrasion on molds.
3. Production of large parts is more feasible.
4. More-compact molds are possible because of the simplicity of the mold.
5. Expelled gases from the curing reaction can escape during the molding process.

The disadvantages of compression molding are:

1. Complicated part configurations are difficult to make with this process.
2. Inserts may be difficult to hold to close tolerances.
3. Flash must be trimmed from the molded parts.

Transfer Molding **Transfer molding** is also used for molding thermosetting plastics such as the phenolics, ureas, melamines, and alkyd resins. Transfer molding differs from compression molding in how the material is introduced into the mold cavities. In transfer molding, the plastic resin is not fed directly into the mold cavity but into a chamber outside the mold cavities (Fig. 10.26a). In transfer molding, when the mold is closed, a plunger forces the plastic resin (which is usually preheated) from the outside chamber through a system of runners and gates into the

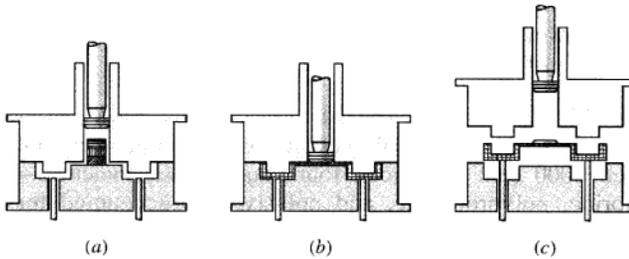


Figure 10.26

Transfer molding. (a) Preformed plastic shape is forced into a preclosed mold by a plunger. (b) Pressure on plastic shape is applied, and plastic is forced through a system of runners and gates into the mold cavities. (c) After the plastic has cured, the plunger is removed and the mold cavity is opened. The part is then ejected.

mold cavities (Fig. 10.26*b*). After the molded material has had time to cure so that a rigid network polymeric material is formed, the molded part is ejected from the mold (Fig. 10.26*c*).

The advantages of transfer molding are:

1. Transfer molding has the advantage over compression molding in that no flash is formed during molding, and thus the molded part requires less finishing.
2. Many parts can be made at the same time by using a runner system.
3. Transfer molding is especially useful for making small, intricate parts that would be difficult to make by compression molding.

Injection Molding Using modern technology, some thermosetting compounds can be injection molded by reciprocating-screw injection-molding machines. Special heating and cooling jackets have been added to the standard-type injection-molding machines so that the resin can be cured in the process. Good venting of the mold cavities is required for some thermosetting resins that give off reaction products during curing. In the future, injection molding will probably become more important for producing thermosetting parts because of the efficiency of this process.

10.6 GENERAL-PURPOSE THERMOPLASTICS

In this section some important aspects of the structure, chemical processing, properties, and applications of the following thermoplastics will be discussed: polyethylene, polyvinyl chloride, polypropylene, polystyrene, ABS, polymethyl methacrylate, cellulose acetate and related materials, and polytetrafluoroethylene.

Let us first, however, examine the sales tonnages, list prices, and some of the important properties of these materials.

Global Sales Tonnages and Bulk List Prices for Some General-Purpose Thermoplastics Based on the global sales tonnages of certain thermoplastics in 1998, along with their 2000 bulk list prices, four major plastic materials—polyethylene, polyvinyl chloride, polypropylene, and polystyrene—accounted for most of the plastic materials sold. These materials have a relatively low cost of about 50¢/lb (2000 prices), which undoubtedly accounts for part of the reason for their extensive usage in industry and for many engineering applications. However, when special properties are required that are unobtainable with the cheaper thermoplastics, more costly plastic materials are used. For example, polytetrafluoroethylene (Teflon), which has special high-temperature and lubrication properties, cost about five to nine dollars per pound in 2000.

Some Basic Properties of Selected General-Purpose Thermoplastics Table 10.2 lists the densities, tensile strengths, impact strengths, dielectric strengths, and maximum-use temperatures for some selected general-purpose thermoplastics. One of the most important advantages of many plastic materials for many engineering applications is

Table 10.2 Some properties of selected general-purpose thermoplastics

Material	Density (g/cm ³)	Tensile strength (×1000 psi)*	Impact strength, Izod (ft · lb/in)†	Dielectric strength (V/mil)‡	Max-use temp. (no load)	
					°F	°C
Polyethylene:						
Low-density	0.92–0.93	0.9–2.5		480	180–212	82–100
High-density	0.95–0.96	2.9–5.4	0.4–14	480	175–250	80–120
Rigid, chlorinated PVC	1.49–1.58	7.5–9	1.0–5.6		230	110
Polypropylene, general-purpose	0.90–0.91	4.8–5.5	0.4–2.2	650	225–300	107–150
Styrene-acrylonitrile (SAN)	1.08	10–12	0.4–0.5	1775	140–220	60–104
ABS, general-purpose	1.05–1.07	5.9	6	385	160–200	71–93
Acrylic, general- purpose	1.11–1.19	11.0	2.3	450–500	130–230	54–110
Cellulosics, acetate	1.2–1.3	3–8	1.1–6.8	250–600	140–220	60–104
Polytetrafluoroethylene	2.1–2.3	1–4	2.5–4.0	400–500	550	288

*1000 psi = 6.9 MPa.

†Notched Izod test: 1 ft · lb/in = 53.38 J/m.

‡1 V/mil = 39.4 V/mm.

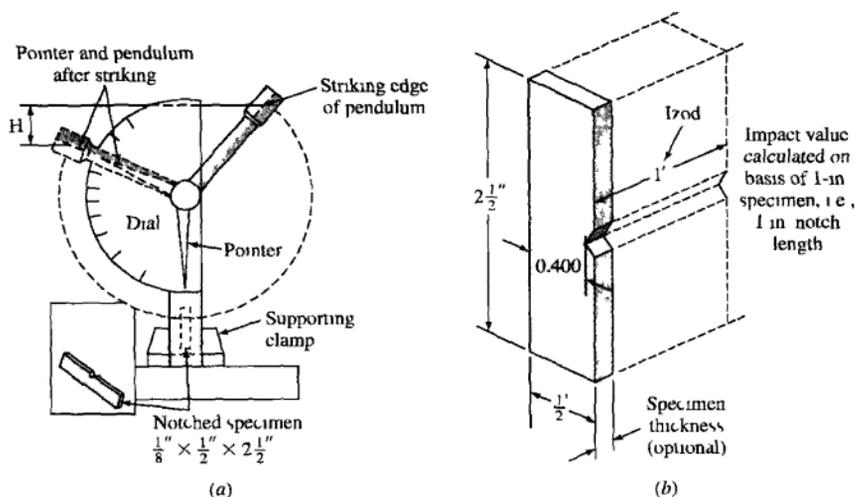
Source: *Materials Engineering*, May 1972.

their relatively low densities. Most general-purpose plastics have densities of about 1 g/cm³ compared to 7.8 g/cm³ for iron.

The tensile strengths of plastic materials are relatively low, and as a result this property can be a disadvantage for some engineering designs. Most plastic materials have a tensile strength of less than 10,000 psi (69 MPa) (Table 10.2). The tensile test for plastic materials is carried out with the same equipment used for metals (Fig. 6.18).

The impact test that is usually used for plastic materials is the notched Izod test. In this test, a $\frac{1}{8} \times \frac{1}{2} \times 2\frac{1}{2}$ in. sample (Fig. 10.27) is normally used and is clamped to the base of a pendulum testing machine. The amount of energy absorbed per unit length of the notch when the pendulum strikes the sample is measured and is called the *notched impact strength* of the material. This energy is usually reported in foot pounds per inch (ft · lb/in) or joules per meter (J/m). The notched impact strengths of general-purpose plastic materials in Table 10.2 range from 0.4 to 14 ft · lb/in.

Plastic materials are generally good electrical insulative materials. The electrical insulative strength of plastic materials is usually measured by their *dielectric strength*, which may be defined as the voltage gradient that produces electrical breakdown through the material. Dielectric strength is usually measured in volts per mil or volts per millimeter. The dielectric strengths of the plastic materials of Table 10.2 vary from 385 to 1775 V/mil.

**Figure 10.27**

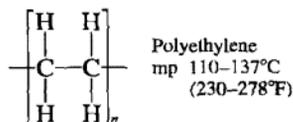
(a) Izod impact test (b) Sample used for plastic materials for the Izod impact test.
 (From WE Driver, 'Plastics Chemistry and Technology,' Van Nostrand Reinhold, 1979, pp. 196-197)

The maximum-use temperature for most plastic materials is relatively low and varies from 130°F to 300°F (54°C to 149°C) for most thermoplastic materials. However, some thermoplastics have higher maximum-use temperatures. For example, polytetrafluoroethylene can withstand temperatures up to 550°F (288°C).

10.6.1 Polyethylene

Polyethylene (PE) is a clear-to-whitish, translucent thermoplastic material and is often fabricated into clear thin films. Thick sections are translucent and have a waxy appearance. With the use of colorants, a wide variety of colored products is obtained.

Repeating Chemical Structural Unit



Types of Polyethylene In general there are two types of polyethylene: *low-density (LDPE)* and *high-density (HDPE)*. Low-density has a branched-chain structure (Fig. 10.28b), whereas high-density polyethylene has essentially a straight-chain structure (Fig. 10.28a).

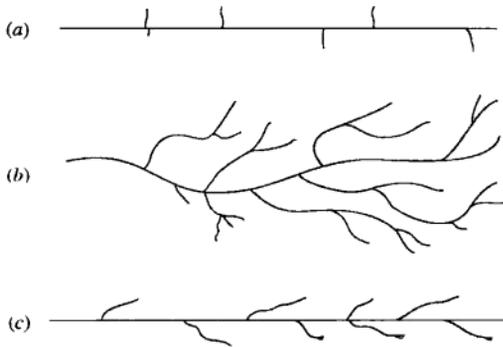


Figure 10.28
Chain structure of different types of polyethylene
(a) high-density, (b) low-density, and (c) linear-
low-density

Low-density polyethylene was first commercially produced in the United Kingdom in 1939 by using autoclave (or tubular) reactors requiring pressures in excess of 14,500 psi (100 MPa) and a temperature of about 300°C. High-density polyethylene was first produced commercially by the Phillips and Ziegler processes by using special catalysts in 1956–1957. In these processes, the pressure and temperature for the reaction to convert ethylene to polyethylene were considerably lowered. For example, the Phillips process operates at 100°C to 150°C and 290 to 580 psi (2 to 4 MPa) pressure.

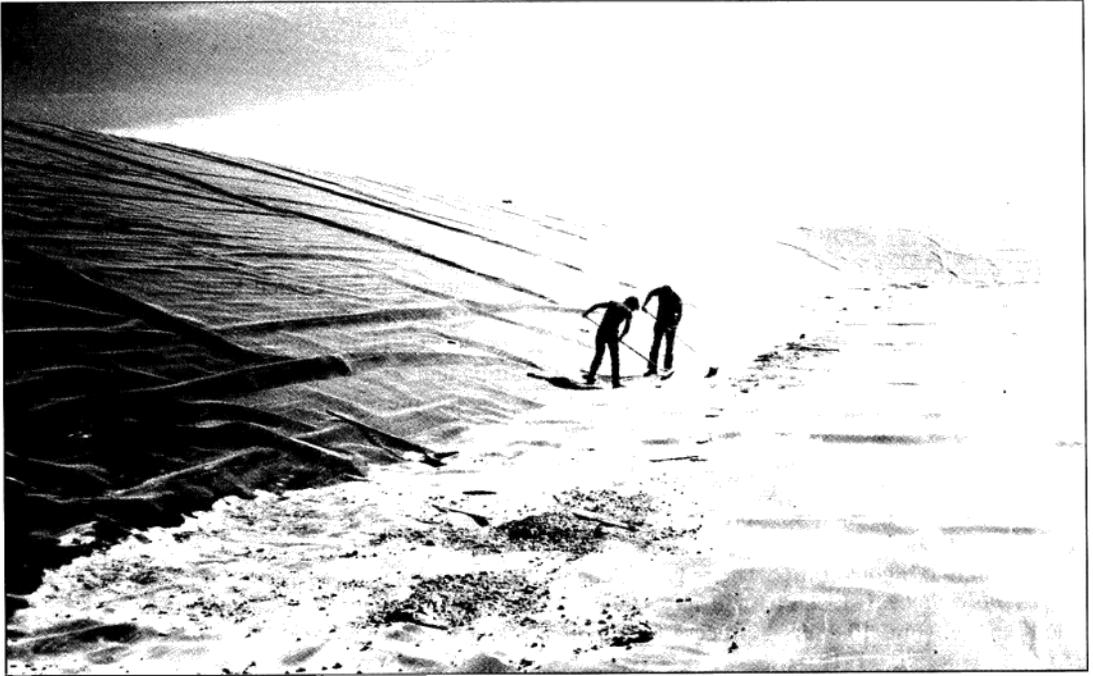
In about 1976 a new low-pressure simplified process for producing polyethylene was developed that uses a pressure of about 100 to 300 psi (0.7 to 2 MPa) and a temperature of about 100°C. The polyethylene produced is described as *linear-low-density polyethylene* (LLDPE) and has a linear-chain structure with short, slanting side branches (Fig. 10.28c). A process for producing LLDPE has been described in Sec. 10.3 (see Fig. 10.13).

Structure and Properties The chain structures of low- and high-density polyethylenes are shown in Fig. 10.28. Low-density polyethylene has a branched-chain structure that lowers its degree of crystallinity and its density (Table 10.2). The branched-chain structure also lowers the strength of low-density polyethylene because it reduces intermolecular bonding forces. High-density polyethylene, in contrast, has very little branching on the main chains, and so the chains can pack more closely together to increase crystallinity and strength (Table 10.3).

Polyethylene is by far the most extensively used plastic material. The main reason for its prime position is that it is low in cost and has many industrially important properties, which include toughness at room temperature and at low temperatures with sufficient strength for many product applications, good flexibility over

Table 10.3 Some properties of low- and high-density polyethylenes

Property	Low-density polyethylene	Linear-low-density polyethylene	High-density polyethylene
Density (g/cm^3)	0.92–0.93	0.922–0.926	0.95–0.96
Tensile strength ($\times 1000$ psi)	0.9–2.5	1.8–2.9	2.9–5.4
Elongation (%)	550–600	600–800	20–120
Crystallinity (%)	65	...	95

**Figure 10.29**

High-density polyethylene film pond liner dwarfs workers installing it. Individual sheets can be half an acre in area and weigh up to 5 tons.

(Courtesy of Schlegel Lining Technology, Inc.)

a wide range of temperatures even down to -73°C , excellent corrosion resistance, excellent insulating properties, odorlessness and tastelessness, and low water-vapor transmission.

Applications Applications for polyethylene include containers, electrical insulation, chemical tubing, housewares, and blow-molded bottles. Uses for polyethylene films include films for packaging and materials handling and water-pond liners (Fig. 10.29).