Ductile (Nodular) Iron. In the ductile-iron structure, graphite is in a **nodular** or **spheroid** form (Fig. 4.11b), which permits the material to be somewhat ductile and shock resistant. The shape of graphite flakes can be changed into nodules (spheres), by small additions of magnesium and/or cerium to the molten metal prior to pouring. Ductile iron can be made ferritic or pearlitic by heat treatment; it can also be heat treated to obtain a structure of tempered martensite (Section 4.7).

White Cast Iron. *White cast iron* is obtained either by cooling gray iron rapidly or by adjusting the composition by keeping the carbon and silicon content low; it is also called *white iron* because of the white crystalline appearance of the fracture surface. The white cast iron structure is very hard, wear resistant, and brittle, because of the presence of large amounts of iron carbide (instead of graphite).

Malleable Iron. *Malleable iron* is obtained by annealing white cast iron in an atmosphere of carbon monoxide and carbon dioxide, at between 800°C and 900°C for up to several hours, depending on the size of the part. During this process, the cementite decomposes (*dissociates*) into iron and graphite. The graphite exists as *clusters* or *rosettes* (Fig. 4. 11c) in a ferrite or pearlite matrix; consequently, malleable iron has a structure similar to that of nodular iron. This structure promotes good ductility, strength, and shock resistance—hence, the term *malleable* (from the Latin *malleus* meaning "it can be hammered").

Compacted-graphite Iron. The graphite in this structure is in the form of short, thick, interconnected flakes having undulating surfaces and rounded extremities. The mechanical and physical properties of this cast iron are intermediate between those of flake-graphite and nodular-graphite cast irons.

4.7 Heat Treatment of Ferrous Alloys

The various microstructures described thus far can be modified by **heat-treatment** techniques—that is, by controlled heating and cooling of the alloys at various rates. These treatments induce **phase transformations**, which greatly influence such mechanical properties as strength, hardness, ductility, toughness, and wear resistance. The effects of thermal treatment depend on the particular alloy, its composition and microstructure, the degree of prior cold work, and the rates of heating and cooling during heat treatment.

This section focuses on the microstructural changes in the iron–carbon system. Because of their technological significance, the structures considered are pearlite, spheroidite, bainite, martensite, and tempered martensite. The heat-treatment processes described are annealing, quenching, and tempering.

Pearlite. If the ferrite and cementite lamellae in the pearlite structure of the eutectoid steel, shown in Fig. 4.9, are thin and closely packed, the microstructure is called **fine pearlite**; if they are thick and widely spaced, it is called **coarse pearlite**. The difference between the two depends on the rate of cooling through the eutectoid temperature, which is the site of a reaction in which austenite is transformed into pearlite. If the rate of cooling is relatively high (as in air), fine pearlite is produced; if cooling is slow (as in a furnace), coarse pearlite is produced.

QR Code 4.1 Hardening chains with induction heating. (*Source:* Courtesy of GH Induction Atmospheres)

Spheroidite. When pearlite is heated to just below the eutectoid temperature and then held at that temperature for a period of time, such as at 700°C for a

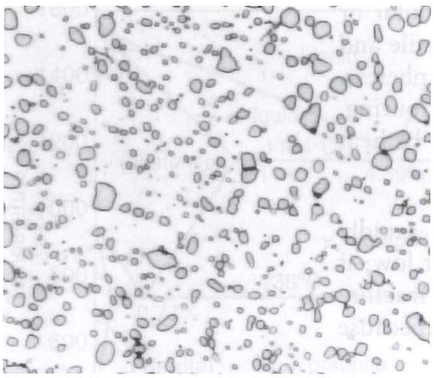


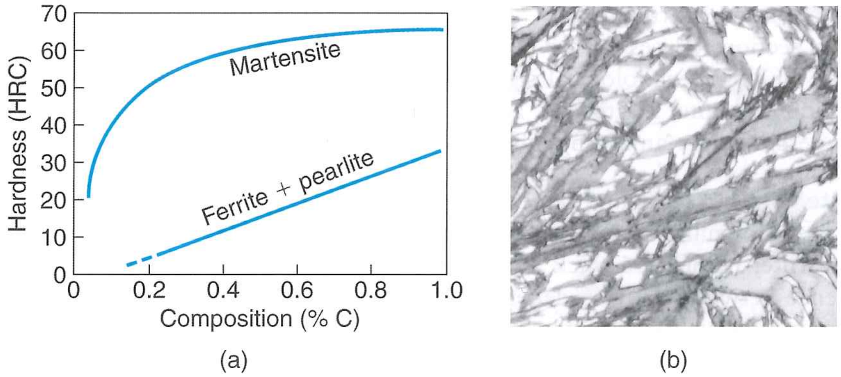
FIGURE 4.12 Microstructure of eutectoid steel. Spheroidite is formed by tempering the steel at 700°C. Magnification: 1000×.

day, the cementite lamellae transform to roughly spherical shapes (Fig. 4.12). Unlike the lamellar shapes of cementite, which act as stress raisers, **spheroidites** (spherical particles) have smaller stress concentrations because of their rounded shapes. Consequently, this structure has higher toughness and lower hardness than the pearlite structure. It can be cold worked, because the ductile ferrite has high toughness and the spheroidal carbide particles prevent the initiation of cracks within the material.

Bainite. Visible only through electron microscopy, *bainite* is a very fine microstructure, consisting of ferrite and cementite, similar to pearlite, but having a different morphology. Bainite can be produced in steels with alloying elements and at cooling rates that are higher than those required for pearlite. This structure, called **bainitic steel** (after the American metallurgist E.C. Bain, 1891–1971), is generally stronger and more ductile than pearlitic steels at the same hardness level.

Martensite. When austenite is cooled at a high rate, such as by quenching in water, its fcc structure is transformed into a **body-centered tetragonal** (bct) structure, which can be described as a body-centered rectangular prism that is slightly elongated along one of its principal axes (see Fig. 4.7d). This microstructure is called *martensite* (after the German metallurgist A. Martens, 1850–1914). Because martensite does not have as many slip systems as a bcc structure, and the carbon is in interstitial positions, it is extremely hard and brittle (Fig. 4.13). Martensite transformation takes place almost instantaneously, because it involves not the diffusion process but a slip mechanism and thus involves plastic deformation. This is a time-dependent phenomenon that is the mechanism in other transformations as well.

Retained Austenite. If the temperature to which the alloy is quenched is not sufficiently low, only a portion of the structure is transformed to martensite. The rest is *retained austenite*, which is visible as white areas in the structure, along with the dark, needlelike martensite. Retained austenite can cause dimensional instability and cracking, and lower the hardness and strength of the alloy.



(a)

(b)

FIGURE 4.13 (a) Hardness of martensite as a function of carbon content. (b) Micrograph of martensite containing 0.8% carbon. The gray platelike regions are martensite; they have the same composition as the original austenite (white regions). Magnification: 1000×.

Tempered Martensite. Martensite is tempered in order to improve its mechanical properties. *Tempering* is a heating process by which hardness is reduced and toughness is increased. The body-centered tetragonal martensite is heated to an intermediate temperature, typically 150°–650°C, where it decomposes to a two-phase microstructure, consisting of bcc alpha ferrite and small particles of cementite.

With increasing tempering time and temperature, the hardness of tempered martensite decreases (Fig. 4.14). The reason is that the cementite particles coalesce and grow, and the distance between the particles in the soft ferrite matrix increases as the less stable and smaller carbide particles dissolve.

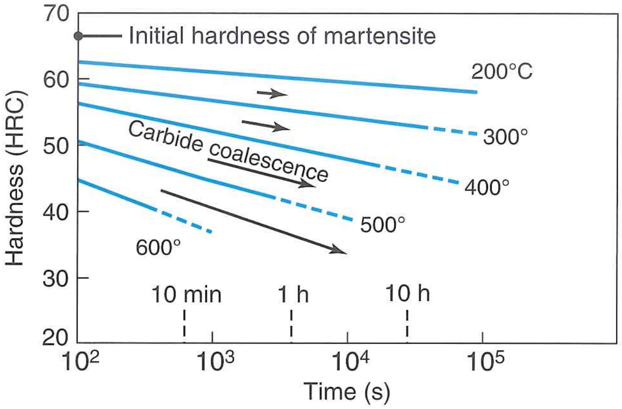


FIGURE 4.14 Hardness of tempered martensite as a function of tempering time for 1080 steel quenched to 65 HRC. Hardness decreases because the carbide particles coalesce and grow in size, thereby increasing the interparticle distance of the softer ferrite.

4.7.1 Time-temperature-transformation Diagrams

The percentage of austenite transformed into pearlite is a function of temperature and time (Fig. 4.15a). This transformation is best illustrated by Figs. 4.15b and c in diagrams called **isothermal transformation (IT) diagrams**, or *time–temperature–transformation* (TTT) *diagrams*, constructed from the data given in Fig. 4.15a. The higher the temperature or the longer the time, the more austenite is transformed into pearlite. Note that, for each temperature, there is a minimum time for the transformation to begin. This time period defines the critical cooling rate; with longer times, austenite begins to transform into pearlite, as can be traced in Figs. 4.15b and c.

The TTT diagrams shown allow the design of heat-treatment schedules to obtain desirable microstructures. For example, consider the TTT curves shown in Fig. 4.15c; the steel can be raised to a very high temperature (above the eutectic temperature) to start with a state of austenite. If the material is cooled rapidly, it can follow the 140°C/s cooling rate trajectory shown, resulting in complete martensite. On the other hand, it can be more slowly cooled (in a molten salt bath) to develop pearlite- or bainite-containing steels. If tempered martensite is desired, the heat treat and quench stages is followed by a tempering process.

The differences in hardness and toughness of the various structures obtained are shown in Fig. 4.16. Fine pearlite is harder and less ductile than coarse pearlite. The effects of various percentages of carbon, cementite, and pearlite on other mechanical properties of steels are shown in Fig. 4.17.

4.8 Hardenability of Ferrous Alloys

The capability of an alloy to be hardened by heat treatment is called its **hardenability**, and is a measure of the *depth* of hardness that can be obtained by heating and subsequent quenching. The term "hardenability" should not be confused with "hardness," which is the resistance of a material to indentation or scratching (Section 2.6). From the discussion thus far, it can be seen that hardenability of ferrous alloys depends on the (a) carbon content, (b) grain size of the austenite, (c) alloying elements present in the material, and (d) cooling rate.

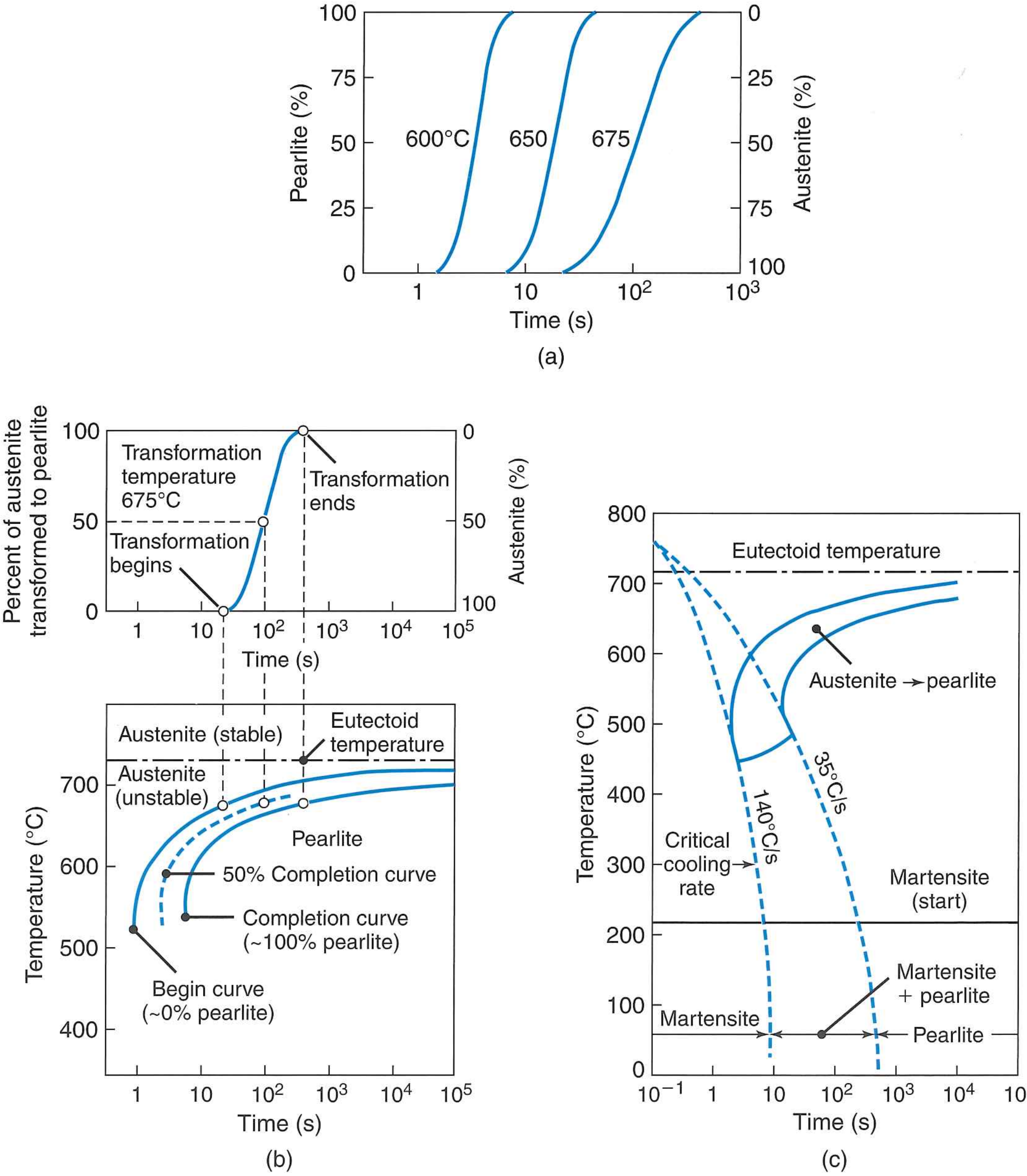


FIGURE 4.15 (a) Austenite-to-pearlite transformation of iron–carbon alloy as a function of time and temperature. (b) Isothermal transformation diagram obtained from (a) for a transformation temperature of 675°C. (c) Microstructures obtained for a eutectoid iron–carbon alloy as a function of cooling rate.

4.8.1 The End-quench Hardenability Test

In this commonly used **Jominy test** (after the American metallurgist W.E. Jominy, 1893–1976), a round test bar 100 mm long, made from a particular alloy, is **austenitized**—that is, heated to the proper temperature to form 100% austenite. It is then quenched directly at one end (Fig. 4.18a) with a stream of water at 24°C. The cooling rate thus varies throughout the length of the bar, the rate being

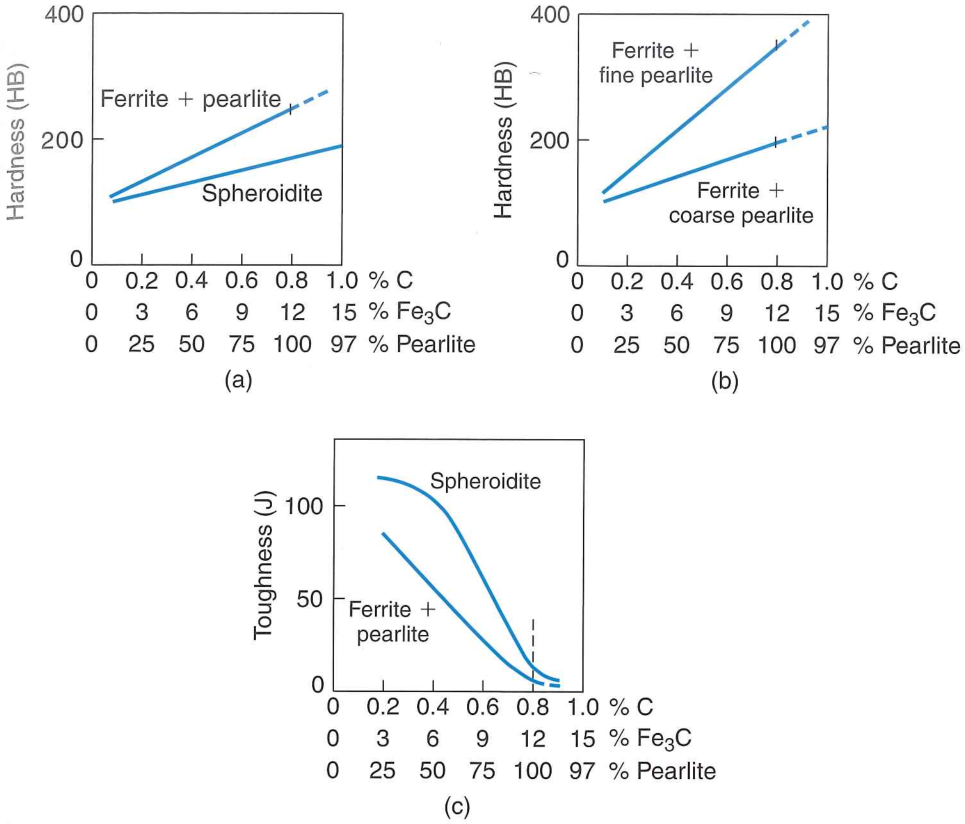


FIGURE 4.16 (a) and (b) Hardness and (c) toughness for annealed plain-carbon steels as a function of carbide shape. Carbides in the pearlite are lamellar. Fine pearlite is obtained by increasing the cooling rate. The spheroidite structure has sphere-like carbide particles.

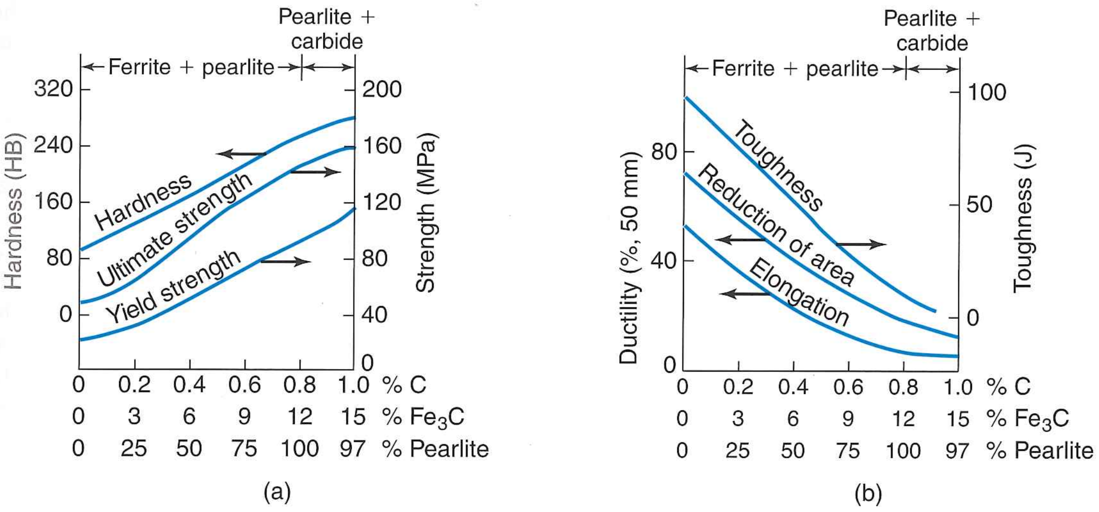


FIGURE 4.17 Mechanical properties of annealed steels as a function of composition and microstructure. Note in (a) the increase in hardness and strength, and in (b), the decrease in ductility and toughness, with increasing amounts of pearlite and iron carbide.

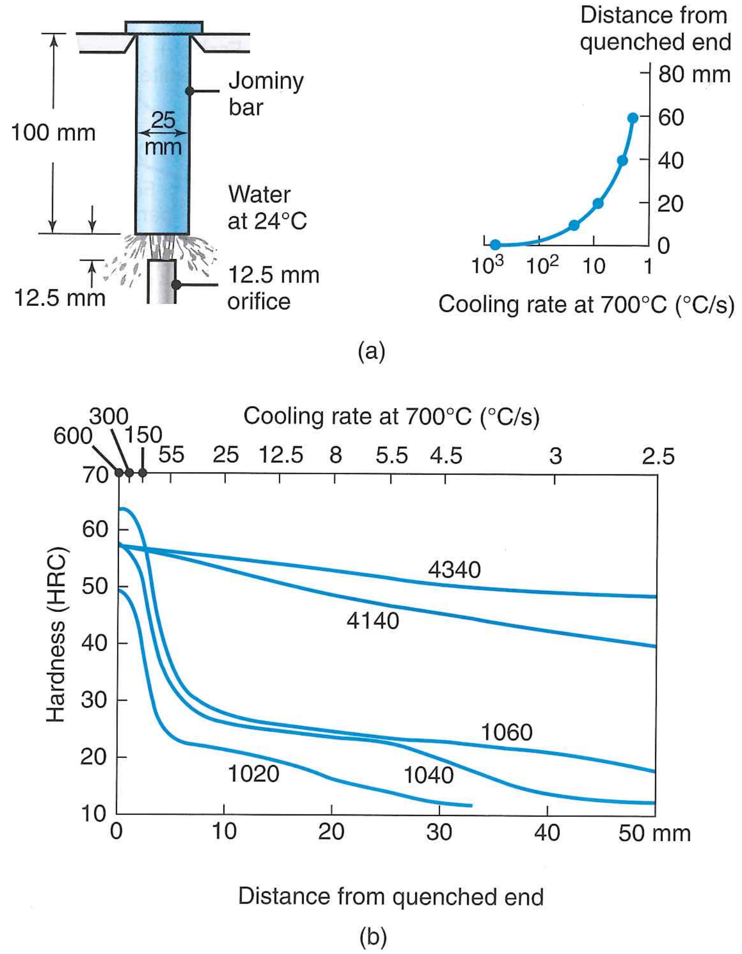


FIGURE 4.18 (a) End-quench test and cooling rate. (b) Hardenability curves for five different steels, as obtained from the end-quench test. Small variations in composition can change the shape of these curves. Each curve is actually a band, and its exact determination is important in the heat treatment of metals, for better control of properties.

highest at the lower end, being in direct contact with the water. The hardness along the length of the bar is then measured at various distances from the quenched end.

As expected from the discussion of the effects of cooling rates in Section 4.7, hardness decreases away from the quenched end of the bar (Fig. 4.18b). The greater the depth to which hardness increases, the greater the hardenability of the alloy. Each composition of an alloy has its particular **hardenability band.** Note that the hardness at the quenched end increases with increasing carbon content, and that 1040, 4140, and 4340 steels have the same carbon content (0.40%) and thus they have the same hardness (57 HRC) at the quenched end.

QR Code 4.2 Hardening and quenching balls with induction heating. (*Source:* Courtesy of GH Induction Atmospheres)

4.8.2 Quenching Media

The fluid used for quenching the heated specimen also has an effect on hardenability. Quenching may be carried out in water, brine (salt water), oil, molten salt, or air; caustic solutions, and polymer solutions; gases may also be used. Because of the differences in thermal conductivity, specific heat, and heat of vaporization of these media, the rate of cooling of the specimen (**severity of quench**) is also different. In relative terms and in decreasing order, the cooling capacities of several quenching media are: agitated brine, 5; still water, 1; still oil, 0.3; cold gas, 0.1; and still air, 0.02.

Agitation also is a significant factor in the rate of cooling; the more vigorous the agitation, the higher is the rate of cooling. In tool steels, the quenching medium is specified by a letter (see Table 5.7), such as W for water hardening, O for oil hardening, and A for air hardening. The cooling rate also depends on the surface-area-to-thickness or surface-area-to-volume ratio of the part to be quenched; the higher this ratio, the higher is the cooling rate. For example, a thick plate cools more slowly than a thin plate with the same surface area. These considerations are also significant in the cooling of metals and of plastics in casting and in molding processes (Sections 10.5.1 and 19.3).

Water is a common medium for rapid cooling. However, the heated specimen may form a **vapor blanket** along its surfaces due to the water-vapor bubbles that form when water boils at the metal–water interface. This blanket creates a barrier to heat conduction, because of the lower thermal conductivity of the vapor. Agitating the fluid or the part helps to reduce or eliminate the blanket; also, water may be sprayed onto the part under high pressure. Brine is an effective quenching medium, because salt helps to nucleate bubbles at the interfaces, which improves agitation; note, however, that brine can corrode the part.

Polymer quenchants can be used for ferrous as well as for nonferrous alloys; they have cooling characteristics that generally are between those of water and petroleum oils. Typical polymer quenchants are polyvinyl alcohol, polyalkaline oxide, polyvinyl pyrrolidone, and polyethyl oxazoline. These quenchants have such advantages as better control of hardness, elimination of fumes and fire (as may occur when oils are used as a quenchant), and reduction of corrosion (as may occur when water is used).

4.9 Heat Treatment of Nonferrous Alloys and Stainless Steels

Nonferrous alloys and some stainless steels cannot be heat treated by the techniques described for ferrous alloys. The reason is that nonferrous alloys do not undergo phase transformations like those in steels; the hardening and strengthening mechanisms for these alloys are fundamentally different. Heat-treatable aluminum alloys, copper alloys, and martensitic and some other stainless steels are hardened and strengthened by a process called **precipitation hardening.** In this process, small particles of a different phase, called **precipitates,** are uniformly dispersed in the matrix of the original phase (Fig. 4.3a). Precipitates form because the solid solubility of one element (one component of the alloy) in the other is exceeded.

Three stages are involved in precipitation hardening, which can best be described by reference to the phase diagram for the aluminum–copper system (Fig. 4.19a). For a composition of 95.5% Al–4.5% Cu, a single-phase (kappa phase) substitutional solid solution of copper (solute) in aluminum (solvent) exists between 500°C and 570°C. This *kappa phase* is aluminum rich, has an fcc structure, and is ductile. Below the lower temperature (that is, below the lower solubility curve) there are two phases: *kappa* (κ) and *theta* (θ) which is a hard intermetallic compound of $CuAl_2$. This alloy can be heat treated and its properties modified by two different methods: *solution treatment* and *precipitation hardening*.