

Part VII Property Enhancing and Surface Processing Operations

26 Heat Treatment of Metals

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The manufacturing processes covered in the preceding chapters involve the creation of part geometry. This part of the book considers processes that either enhance the properties of a work part (Chapter 26) or apply some surface treatment to it, such as cleaning or coating (Chapter 27). Property-enhancing operations are performed to improve mechanical or physical properties of the work material. They do not alter part geometry, at least not intentionally. The most important property-enhancing operations are heat treatments. **Heat treatment** involves various heating and cooling procedures performed to effect microstructural changes in a material, which in turn affect its mechanical properties. Its most common applications are on metals, discussed in this chapter. Similar treatments are performed on glass-ceramics (Section 7.4.3), tempered glass (Section 12.3.1), and powder metals and ceramics (Sections 15.3.3 and 16.2.3).

Heat treatment operations can be performed on a metallic work part at various times during its manufacturing sequence. In some cases, the treatment is applied before shaping (e.g., to soften the metal so that it can be more easily formed while hot). In other cases, heat treatment is used to relieve the effects of strain hardening that occur during forming, so that the material can

be subjected to further deformation. Heat treatment can also be accomplished at or near the end of the sequence to achieve the final strength and hardness required in the finished product. The principal heat treatments are annealing, martensite formation in steel, precipitation hardening, and surface hardening.

26.1 Annealing

Annealing consists of heating the metal to a suitable temperature, holding at that temperature for a certain time (called **soaking**), and slowly cooling. It is performed on a metal for any of the following reasons: (1) to reduce hardness and brittleness, (2) to alter microstructure so that desirable mechanical properties can be obtained, (3) to soften metals for improved machinability or formability, (4) to recrystallize cold-worked (strain-hardened) metals, and (5) to relieve residual stresses induced by prior processes. Different terms are used in annealing, depending on the details of the process and the temperature used relative to the recrystallization temperature of the metal being treated.

Full annealing is associated with ferrous metals (usually low and medium carbon steels); it involves heating the alloy into the austenite region, followed by slow cooling in the furnace to produce coarse pearlite. **Normalizing** involves similar heating and soaking cycles, but the cooling rates are faster. The steel is allowed to cool in air to room temperature. This results in fine pearlite, higher strength and hardness, but lower ductility than the full anneal treatment.

Cold-worked parts are often annealed to reduce effects of strain hardening and increase ductility. The treatment allows the strain-hardened metal to recrystallize partially or completely, depending on temperatures, soaking periods, and cooling rates. When annealing is performed to allow for further cold working of the part, it is called a **process anneal**. When performed on the completed (cold-worked) part to remove the effects of strain hardening and where no subsequent deformation will be accomplished, it is simply called an **anneal**. The process itself is pretty much the same, but different terms are used to indicate the purpose of the treatment.

If annealing conditions permit full recovery of the cold-worked metal to its original grain structure, then **recrystallization** has occurred. After this type of anneal, the metal has the new geometry created by the forming operation, but its grain structure and associated properties are essentially the same as before cold working. The conditions that tend to favor recrystallization are higher temperature, longer holding time, and slower cooling rate. If the annealing process only permits partial return of the grain structure toward its original state, it is termed a **recovery anneal**. Recovery allows the metal to retain most of the strain hardening obtained in cold working, but the toughness of the part is improved.

The preceding annealing operations are performed primarily to accomplish functions other than stress relief. However, annealing is sometimes performed solely to relieve residual stresses in the workpiece. Called **stress-relief annealing**, it helps to reduce distortion and dimensional variations that might otherwise occur in the stressed parts.

26.2 Martensite Formation in Steel

The iron–carbon phase diagram in Figure 6.4 indicates the phases of iron and iron carbide (cementite) present under equilibrium conditions. It assumes that cooling from high temperature is slow enough to permit austenite to decompose into a mixture of ferrite and cementite (Fe_3C) at room temperature. This decomposition

reaction requires diffusion and other processes that depend on time and temperature to transform the metal into its preferred final form. However, under conditions of rapid cooling, so that the equilibrium reaction is inhibited, austenite transforms into a nonequilibrium phase called martensite. **Martensite** is a hard, brittle phase that gives steel its unique ability to be strengthened to very high levels.

26.2.1 THE TIME-TEMPERATURE-TRANSFORMATION CURVE

The nature of the martensite transformation can best be understood using the time-temperature-transformation curve (TTT curve) for eutectoid steel, illustrated in Figure 26.1. The TTT curve shows how cooling rate affects the transformation of austenite into various possible phases. The phases can be divided between (1) alternative forms of ferrite and cementite and (2) martensite. Time is displayed (logarithmically for convenience) along the horizontal axis, and temperature is scaled on the vertical axis. The curve is interpreted by starting at time zero in the austenite region (somewhere above the A_1 temperature line for the given composition) and proceeding downward and to the right along a trajectory representing how the metal is cooled as a function of time. The TTT curve shown in the figure is for a specific composition of steel (0.80% carbon). The shape of the curve is different for other compositions.

At slow cooling rates, the trajectory proceeds through the region indicating transformation into pearlite or bainite, which are alternative forms of ferrite–carbide mixtures. Because these transformations take time, the TTT diagram shows two lines—the start and finish of the transformation as time passes, indicated for the different phase regions by the subscripts s and f , respectively. **Pearlite** is a mixture of ferrite and carbide phases in the form of thin parallel plates. It is obtained by slow cooling from austenite, so that the cooling trajectory passes through P_s above the “nose” of the TTT curve. **Bainite** is an alternative mixture of the same phases that

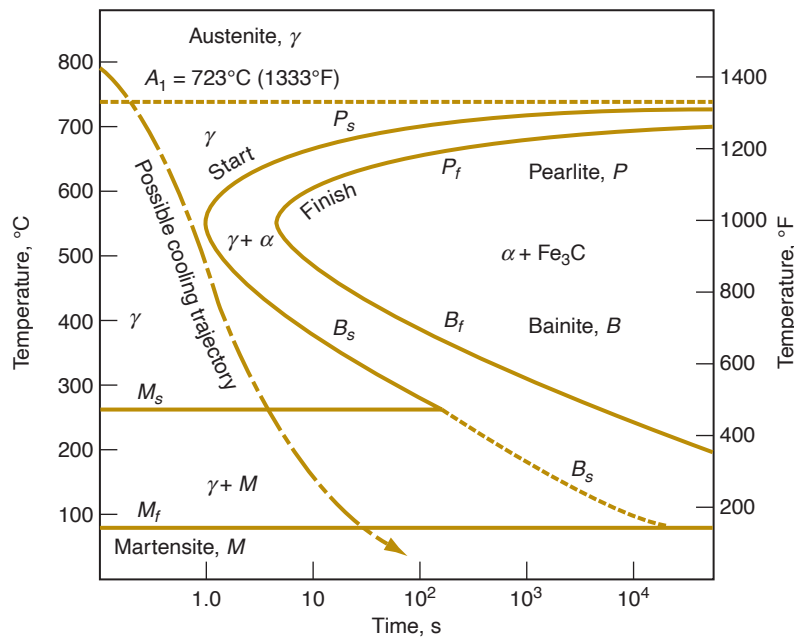


FIGURE 26.1 The TTT curve, showing the transformation of austenite into other phases as a function of time and temperature for a composition of about 0.80% C steel. The cooling trajectory shown here yields martensite.

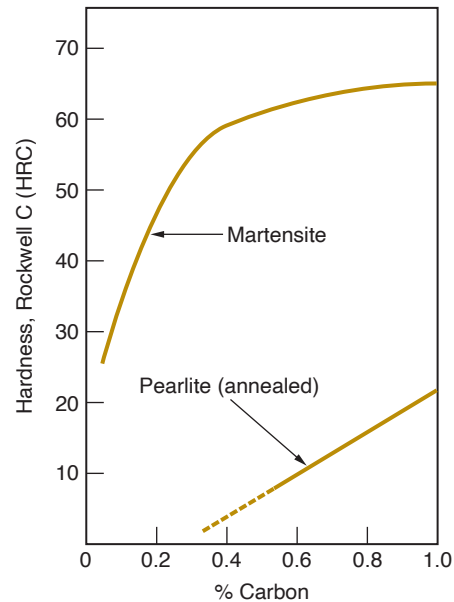


FIGURE 26.2 Hardness of plain carbon steel as a function of carbon content in (hardened) martensite and pearlite (annealed).

can be produced by initial rapid cooling to a temperature somewhat above M_s , so that the nose of the TTT curve is avoided; this is followed by much slower cooling to pass through B_s and into the ferrite–carbide region. Bainite has a needle-like or feather-like structure consisting of fine carbide regions.

If cooling occurs at a sufficiently rapid rate (indicated by the dashed line in Figure 26.1), austenite is transformed into martensite. **Martensite** is a unique phase consisting of an iron–carbon solution whose composition is the same as the austenite from which it was derived. The face-centered cubic structure of austenite is transformed into the body-centered tetragonal (BCT) structure of martensite almost instantly—without the time-dependent diffusion process needed to separate ferrite and iron carbide in the preceding transformations.

During cooling, the martensite transformation begins at a certain temperature M_s , and finishes at a lower temperature M_f , as shown in the TTT diagram. At points between these two levels, the steel is a mixture of austenite and martensite. If cooling is stopped at a temperature between the M_s and M_f lines, the austenite will transform to bainite as the time-temperature trajectory crosses the B_s threshold. The level of the M_s line is influenced by alloying elements, including carbon. In some cases, the M_s line is depressed below room temperature, making it impossible for these steels to form martensite by traditional heat-treating methods.

The extreme hardness of martensite results from the lattice strain created by carbon atoms trapped in the BCT structure, thus providing a barrier to slip. Figure 26.2 shows the significant effect that the martensite transformation has on the hardness of steel for increasing carbon contents.

26.2.2 THE HEAT TREATMENT PROCESS

The heat treatment to form martensite consists of two steps: austenitizing and quenching. These steps are often followed by tempering to produce tempered martensite. **Austenitizing** involves heating the steel to a sufficiently high temperature

that it is converted entirely or partially to austenite. This temperature can be determined from the phase diagram for the particular alloy composition. The transformation to austenite involves a phase change, which requires time as well as heat. Accordingly, the steel must be held at the elevated temperature for a sufficient period of time to allow the new phase to form and the required homogeneity of composition to be achieved.

The **quenching** step involves cooling the austenite rapidly enough to avoid passing through the nose of the TTT curve, as indicated in the cooling trajectory shown in Figure 26.1. The cooling rate depends on the quenching medium and the rate of heat transfer within the steel workpiece. Various quenching media are used in commercial heat treatment practice: (1) brine—salt water, usually agitated; (2) fresh water—still, not agitated; (3) still oil; and (4) air. Quenching in agitated brine provides the fastest cooling of the heated part surface, whereas air quench is the slowest. Trouble is, the more effective the quenching media is at cooling, the more likely it is to cause internal stresses, distortion, and cracks in the product.

The rate of heat transfer within the part depends largely on its mass and geometry. A large cubic shape will cool much more slowly than a small, thin sheet. The coefficient of thermal conductivity k of the particular composition is also a factor in the flow of heat in the metal. There is considerable variation in k for different grades of steel; for example, plain low carbon steel has a typical k value equal to 0.046 J/sec-mm-C (2.2 Btu/hr-in-F), whereas a highly alloyed steel might have one-third that value.

Martensite is hard and brittle. **Tempering** is a heat treatment applied to hardened steels to reduce brittleness, increase ductility and toughness, and relieve stresses in the martensite structure. It involves heating and soaking at a temperature below the austenitizing level for about one hour, followed by slow cooling. This results in precipitation of very fine carbide particles from the martensitic iron-carbon solution, and gradually transforms the crystal structure from BCT to BCC. This new structure is called **tempered martensite**. A slight reduction in strength and hardness accompanies the improvement in ductility and toughness. The temperature and time of the tempering treatment control the degree of softening in the hardened steel, because the change from untempered to tempered martensite involves diffusion.

Taken together, the three steps in the heat treatment of steel to form tempered martensite can be pictured as in Figure 26.3. There are two heating and cooling cycles, the first to produce martensite and the second to temper the martensite.

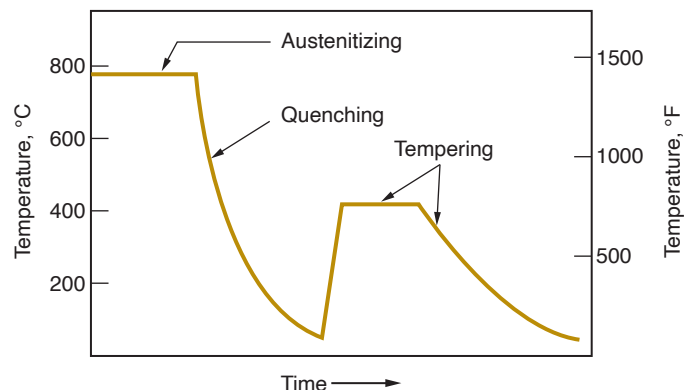
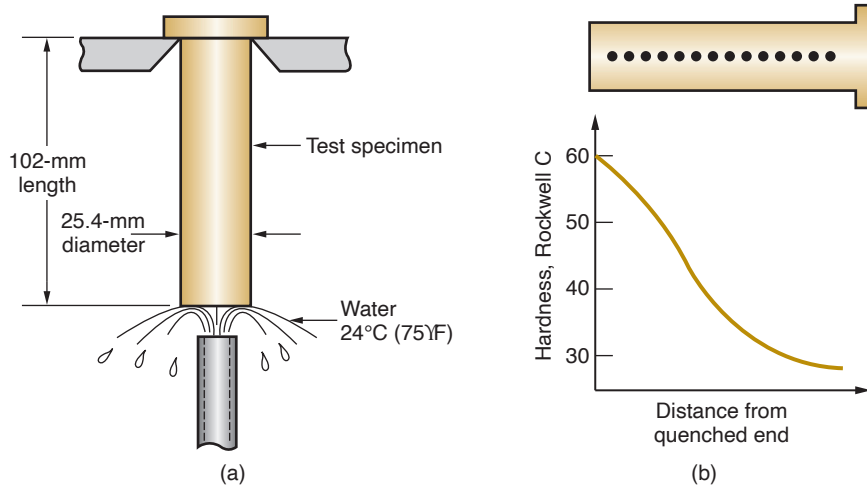


FIGURE 26.3 Typical heat treatment of steel: austenitizing, quenching, and tempering.

FIGURE 26.4 The Jominy end-quench test: (a) setup of the test, showing end quench of the test specimen; and (b) typical pattern of hardness readings as a function of distance from quenched end.



26.2.3 HARDENABILITY

Hardenability refers to the relative capacity of a steel to be hardened by transformation to martensite. It is a property that determines the depth below the quenched surface to which the steel is hardened, or the severity of the quench required to achieve a certain hardness penetration. Steels with good hardenability can be hardened more deeply below the surface and do not require high cooling rates. Hardenability does not refer to the maximum hardness that can be attained in the steel; that depends on the carbon content.

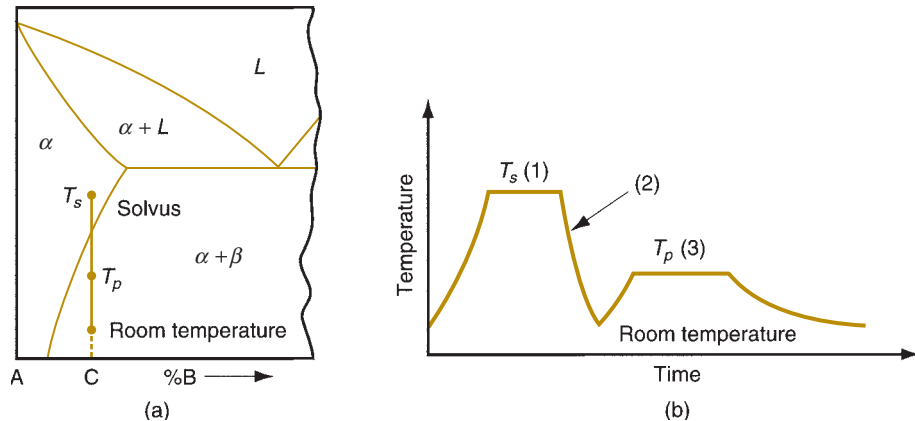
The hardenability of a steel is increased through alloying. Alloying elements having the greatest effect are chromium, manganese, molybdenum (and nickel, to a lesser extent). The mechanism by which these alloying ingredients operate is to extend the time before the start of the austenite-to-pearlite transformation in the TTT diagram. In effect, the TTT curve is moved to the right, thus permitting slower quenching rates during quenching. Therefore, the cooling trajectory is able to follow a less hastened path to the M_s line, more easily avoiding the nose of the TTT curve.

The most common method for measuring hardenability is the **Jominy end-quench test**. The test involves heating a standard specimen of diameter = 25.4 mm (1.0 in) and length = 102 mm (4.0 in) into the austenite range, and then quenching one end with a stream of cold water while the specimen is supported vertically as shown in Figure 26.4(a). The cooling rate in the test specimen decreases with increased distance from the quenched end. Hardenability is indicated by the hardness of the specimen as a function of distance from quenched end, as in Figure 26.4(b).

26.3 Precipitation Hardening

Precipitation hardening involves the formation of fine particles (precipitates) that act to block the movement of dislocations and thus ~~strengthen and harden the metal~~. It is the principal heat treatment for strengthening alloys of aluminum, copper, magnesium, nickel, and other nonferrous metals. Precipitation hardening can also be used to strengthen certain steel alloys. When applied to steels, the process is called **maraging** (an abbreviation of martensite and aging), and the steels are called maraging steels (Section 6.2.3).

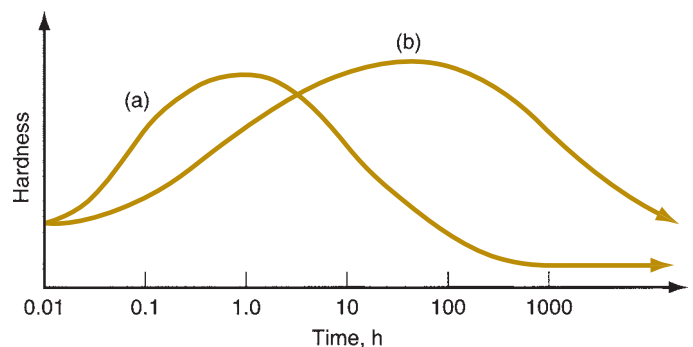
FIGURE 26.5
Precipitation hardening:
(a) phase diagram of an
alloy system consisting
of metals A and B that
can be precipitation
hardened; and (b) heat
treatment: (1) solution
treatment, (2) quenching,
and (3) precipita-
tion treatment.



The necessary condition that determines whether an alloy system can be strengthened by precipitation hardening is the presence of a sloping solvus line, as shown in the phase diagram of Figure 26.5(a). A composition that can be precipitation hardened is one that contains two phases at room temperature, but which can be heated to a temperature that dissolves the second phase. Composition C satisfies this requirement. The heat treatment process consists of three steps, illustrated in Figure 26.5(b): (1) **solution treatment**, in which the alloy is heated to a temperature T_s above the solvus line into the alpha phase region and held for a period sufficient to dissolve the beta phase; (2) **quenching** to room temperature to create a supersaturated solid solution; and (3) **precipitation treatment**, in which the alloy is heated to a temperature T_p , below T_s , to cause precipitation of fine particles of the beta phase. This third step is called **aging**, and for this reason the whole heat treatment is sometimes called **age hardening**. However, aging can occur in some alloys at room temperature, and so the term **precipitation hardening** seems more precise for the three-step heat treatment process under discussion here. When the aging step is performed at room temperature, it is called **natural aging**. When it is accomplished at an elevated temperature, as in the figure, the term **artificial aging** is often used.

It is during the aging step that high strength and hardness are achieved in the alloy. The combination of temperature and time during the precipitation treatment (aging) is critical in bringing out the desired properties in the alloy. At higher precipitation treatment temperatures, as in Figure 26.6(a), the hardness peaks in a relatively short time; whereas at lower temperatures, as in (b), more time is required to harden the alloy but its maximum hardness is likely to be greater than

FIGURE 26.6 Effect of
temperature and time
during precipitation
treatment (aging):
(a) high precipitation
temperature; and
(b) lower precipitation
temperature.



in the first case. As seen in the plot, continuation of the aging process results in a reduction in hardness and strength properties, called **overaging**. Its overall effect is similar to annealing.

26.4 Surface Hardening

Surface hardening refers to any of several thermochemical treatments applied to steels in which the composition of the part surface is altered by addition of carbon, nitrogen, or other elements. The most common treatments are carburizing, nitriding, and carbonitriding. These processes are commonly applied to low carbon steel parts to achieve a hard, wear-resistant outer shell while retaining a tough inner core. The term **case hardening** is often used for these treatments.

✓ **Carburizing** is the most common surface-hardening treatment. It involves heating a part of low carbon steel in the presence of a carbon-rich environment so that C is diffused into the surface. In effect the surface is converted to a high carbon steel, capable of higher hardness than the low-C core. The carbon-rich environment can be created in several ways. One method involves the use of carbonaceous materials such as charcoal or coke packed in a closed container with the parts. This process, called **pack carburizing**, produces a relatively thick layer on the part surface, ranging from around 0.6 to 4 mm (0.025–0.150 in). Another method, called **gas carburizing**, uses hydrocarbon fuels such as propane (C_3H_8) inside a sealed furnace to diffuse carbon into the parts. The case thickness in this treatment is thin, 0.13 to 0.75 mm (0.005 to 0.030 in). Another process is **liquid carburizing**, which employs a molten salt bath containing sodium cyanide (NaCN), barium chloride ($BaCl_2$), and other compounds to diffuse carbon into the steel. This process produces surface layer thicknesses generally between those of the other two treatments. Typical carburizing temperatures are 875° to 925°C (1600°–1700°F), well into the austenite range.

Carburizing followed by quenching produces a case hardness of around HRC = 60. However, because the internal regions of the part consist of low carbon steel, and its hardenability is low, it is unaffected by the quench and remains relatively tough and ductile to withstand impact and fatigue stresses.

✓ **Nitriding** is a treatment in which nitrogen is diffused into the surfaces of special alloy steels to produce a thin hard casing without quenching. To be most effective, the steel must contain certain alloying ingredients such as aluminum (0.85–1.5%) or chromium (5% or more). These elements form nitride compounds that precipitate as very fine particles in the casing to harden the steel. Nitriding methods include: **gas nitriding**, in which the steel parts are heated in an atmosphere of ammonia (NH_3) or other nitrogen-rich gas mixture; and **liquid nitriding**, in which the parts are dipped in molten cyanide salt baths. Both processes are carried out at around 500°C (950°F). Case thicknesses range as low as 0.025 mm (0.001 in) and up to around 0.5 mm (0.020 in), with hardnesses up to HRC 70.

As its name suggests, carbonitriding is a treatment in which both carbon and nitrogen are absorbed into the steel surface, usually by heating in a furnace containing carbon and ammonia. Case thickness is usually 0.07 to 0.5 mm (0.003–0.020 in), with hardness comparable with those of the other two treatments.

Two additional surface-hardening treatments diffuse chromium and boron, respectively, into the steel to produce casings that are typically only 0.025 to 0.05 mm (0.001–0.002 in) thick. **Chromizing** requires higher temperatures and longer treatment times than the preceding surface-hardening treatments, but the resulting casing is not

only hard and wear resistant, it is also heat and corrosion resistant. The process is usually applied to low carbon steels. Techniques for diffusing chromium into the surface include: packing the steel parts in chromium-rich powders or granules, dipping in a molten salt bath containing Cr and Cr salts, and chemical vapor deposition (Section 27.5.2).

Boronizing is performed on tool steels, nickel- and cobalt-based alloys, and cast irons, in addition to plain carbon steels, using powders, salts, or gas atmospheres containing boron. The process results in a thin casing with high abrasion resistance and low coefficient of friction. Casing hardnesses reach 70 HRC. When boronizing is used on low carbon and low alloy steels, corrosion resistance is also improved.

26.5 Heat Treatment Methods and Facilities

Most heat treatment operations are performed in furnaces. In addition, other techniques can be used to selectively heat only the work surface or a portion of the work surface. It should be mentioned that some of the equipment described in this section is utilized for other processes in addition to heat treatment; these include melting metals for casting (Section 11.4.1); heating before warm and hot working (Section 17.3); brazing, soldering, and adhesive curing (Chapter 30); and semiconductor processing (Chapter 33).

26.5.1 FURNACES FOR HEAT TREATMENT

Furnaces vary greatly in heating technology, size and capacity, construction, and atmosphere control. They usually heat the work parts by a combination of radiation, convection, and conduction. Heating technologies divide between fuel-fired and electric heating. **Fuel-fired furnaces** are normally **direct-fired**, which means that the work is exposed directly to the combustion products. Fuels include gases (such as natural gas or propane) and oils that can be atomized (such as diesel fuel and fuel oil). The chemistry of the combustion products can be controlled by adjusting the fuel-air or fuel-oxygen mixture to minimize scaling (oxide formation) on the work surface. **Electric furnaces** use electric resistance for heating; they are cleaner, quieter, and provide more uniform heating, but they are more expensive to purchase and operate.

A conventional furnace is an enclosure designed to resist heat loss and accommodate the size of the work to be processed. Furnaces are classified as batch or continuous. **Batch furnaces** are simpler, basically consisting of a heating system in an insulated chamber, with a door for loading and unloading the work. **Continuous furnaces** are generally used for higher production rates and provide a means of moving the work through the interior of the heating chamber.

Special atmospheres are required in certain heat treatment operations, such as some of the surface hardening treatments. These atmospheres include carbon- and nitrogen-rich environments for diffusion of these elements into the surface of the work. Atmosphere control is also desirable in conventional heat treatment operations to avoid excessive oxidation or decarburization.

Other furnace types include salt bath and fluidized bed. **Salt bath furnaces** consist of vessels containing molten salts of chlorides and/or nitrates. Parts to be treated are immersed in the molten media. **Fluidized bed furnaces** have a container in which small inert particles are suspended by a high-velocity stream of hot gas. Under proper conditions, the aggregate behavior of the particles is fluid-like; thus, rapid heating of parts immersed in the particle bed occurs.

26.5.2 SELECTIVE SURFACE-HARDENING METHODS

These methods heat only the surface of the work, or local areas of the work surface. They differ from surface-hardening methods (Section 26.4) in that no chemical changes occur. Here the treatments are only thermal. The selective surface hardening methods include flame hardening, induction hardening, high-frequency resistance heating, electron beam heating, and laser beam heating.

Flame hardening involves heating the work surface by means of one or more torches followed by rapid quenching. As a hardening process, it is applied to carbon and alloy steels, tool steels, and cast irons. Fuels include acetylene (C_2H_2), propane (C_3H_8), and other gases. The name flame hardening invokes images of a highly manual operation with general lack of control over the results; however, the process can be set up to include temperature control, fixtures for positioning the work relative to the flame, and indexing devices that operate on a precise cycle time, all of which provide close control over the resulting heat treatment. It is fast and versatile, lending itself to high production as well as big components such as large gears that exceed the capacity of furnaces.

Induction heating involves application of electromagnetically induced energy supplied by an induction coil to an electrically conductive work part. Induction heating is widely used in industry for processes such as brazing, soldering, adhesive curing, and various heat treatments. When used for hardening steel, quenching follows heating. A typical setup is illustrated in Figure 26.7. The induction heating coil carries a high-frequency alternating current that induces a current in the encircled work part to effect heating. The surface, a portion of the surface, or the entire mass of the part can be heated by the process. Induction heating provides a fast and efficient method of heating any electrically conductive material. Heating cycle times are short, so the process lends itself to high production as well as midrange production.

High-frequency (HF) resistance heating is used to harden specific areas of steel work surfaces by application of localized resistance heating at high frequency (400 kHz typical). A typical setup is shown in Figure 26.8. The apparatus consists of a water-cooled proximity conductor located over the area to be heated. Contacts are attached to the work part at the outer edges of the area. When the HF current is applied, the region beneath the proximity conductor is heated rapidly to high temperature—heating to the austenite range typically requires less than

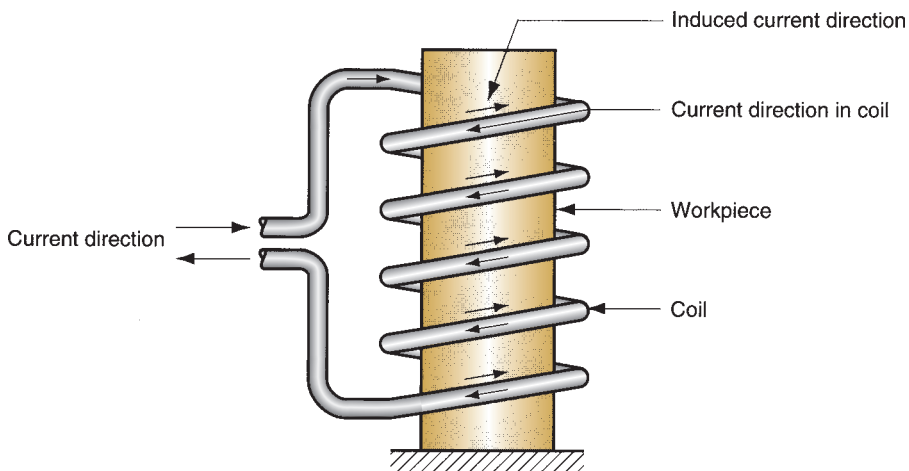


FIGURE 26.7 Typical induction heating setup. High-frequency alternating current in a coil induces current in the work part to effect heating.

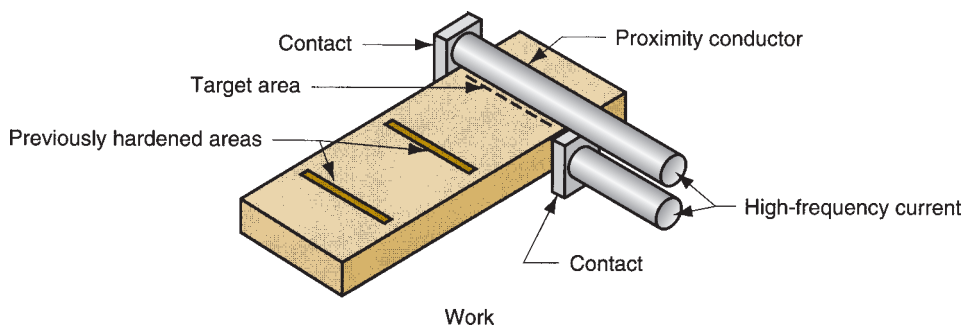


FIGURE 26.8 Typical setup for high-frequency resistance heating.

a second. When the power is turned off, the area, usually a narrow line as in the figure, is quenched by heat transfer to the surrounding metal. Depth of the treated area is around 0.63 mm (0.025 in.); hardness depends on carbon content of the steel and can range up to 60 HRC [11].

Electron beam (EB) heating involves localized surface hardening of steel in which the electron beam is focused onto a small area, resulting in rapid heat buildup. Austenitizing temperatures can often be achieved in less than a second. When the directed beam is removed, the heated area is immediately quenched and hardened by heat transfer to the surrounding cold metal. A disadvantage of EB heating is that best results are achieved when the process is performed in a vacuum. A special vacuum chamber is needed, and time is required to draw the vacuum, thus slowing production rates.

Laser beam (LB) heating uses a high-intensity beam of coherent light focused on a small area. The beam is usually moved along a defined path on the work surface, causing heating of the steel into the austenite region. When the beam is moved, the area is immediately quenched by heat conduction to the surrounding metal. **Laser** is an acronym for **light amplification by stimulated emission of radiation**. The advantage of LB over EB heating is that laser beams do not require a vacuum to achieve best results. Energy density levels in EB and LB heating are lower than in cutting or welding.

References

- [1] *ASM Handbook*. Vol. 4, **Heat Treating**. ASM International, Materials Park, Ohio, 1991.
- [2] Babu, S. S., and Totten, G. E. **Steel Heat Treatment Handbook**, 2nd ed. CRC Taylor & Francis, Boca Raton, Florida, 2006.
- [3] Brick, R. M., Pense, A. W., and Gordon, R. B. **Structure and Properties of Engineering Materials**, 4th ed. McGraw-Hill, New York, 1977.
- [4] Chandler, H. (ed.). **Heat Treater's Guide: Practices and Procedures for Irons and Steels**. ASM International, Materials Park, Ohio, 1995.
- [5] Chandler, H. (ed.). **Heat Treater's Guide: Practices and Procedures for Nonferrous Alloys**. ASM International, Materials Park, Ohio, 1996.
- [6] Dossett, J. L., and Boyer, H. E. **Practical Heat Treating**, 2nd ed. ASM International, Materials Park, Ohio, 2006.
- [7] Flinn, R. A., and Trojan, P. K. **Engineering Materials and Their Applications**, 5th ed. John Wiley & Sons, New York, 1995.
- [8] Guy, A. G., and Hren, J. J. **Elements of Physical Metallurgy**, 3rd ed. Addison-Wesley, Reading, Massachusetts, 1974.
- [9] Ostwald, P. F., and Munoz, J. **Manufacturing Processes and Systems**, 9th ed. John Wiley & Sons, New York, 1997.