Nitriding and Nitrocarburizing

Nitriding is a surface-hardening heat treat- ment that introduces nitrogen into the surface of steel at a temperature range (500 to 550 °C, or 930 to 1020 °F), while it is in the ferritic condition. Because nitriding does not involve heating into the austenite phase with quenching to form martensite, nitride components exhibit minimum distortion and excellent dimensional control. Nitriding has the additional advantage of improving corrosion resistance in salt spray tests.

The mechanism of nitriding is generally known, but the specific reactions that occur in different steels and with different nitriding media are not always known. Nitrogen has par- tial solubility in iron. It can form a solid solu- tion with ferrite at nitrogen contents up to approximately 6%. At approximately 6% N, a compound called gamma prime (g$^{\prime}$), with a composition of Fe_4N, is formed. At nitrogen contents greater than 8%, the equilibrium reaction product is Ε compound, Fe_3N. Nitrided cases are stratified. The outermost surface can be all g^{0}, and, if this is the case, it is referred to as the white layer (it etches white in metallographic preparation). Such a surface layer is undesirable; it is very hard but is so brittle that it may spall in use. Usually it is removed; special nitriding processes are used to reduce this layer or make it less brittle. The Ε zone of the case is hardened by the formation of the Fe_3N compound, and below this layer there is some solid-solution strengthening from the nitrogen in solid solution (Fig. 6). The Fe_3N (Ε) formed on the outer layer is harder than Fe_4N, which is more ductile. Controlling the formation of each of these compound layers is vital to application and degree of distortion.

The depth of case and its properties are greatly dependent on the concentration and type of nitride-forming elements in the steel. In general, the higher the alloy content, the higher the case hardness. However, higher-alloying elements retard the N_2 diffusion rate, which slows the case depth development. Thus, nitriding requires longer cycle times to achieve a given case depth than that required for carburizing. Figure 7 shows some typical cycle times for nitriding versus case depth relationship for commonly used materials, such as Nitralloy 135M, Nitralloy N, AISI 4140, AISI 4330M, and AISI 4340.

Nitrided steels (Ref 9) are generally medium-carbon (quenched and tempered) steels that contain strong nitride-forming elements such as aluminum, chromium, vanadium, and molybdenum. The most significant hardening is achieved with a class of alloy steels (nitralloy type) that contain approximately 1% Al (Fig. 6). When these steels are nitrided, the aluminum forms AlN particles, which strain the ferrite lattice and create strengthening dislocations. Titanium and chromium are also used to enhance case hardness (Fig. 8a), although case depth decreases as alloy content increases (Fig. 8b). The microstructure plays an important role in nitriding, because nitrogen can readily diffuse through ferrite, and a low carbide content favors both diffusion and case hardness. Usually, alloy steels in the heat treated (quenched and tempered) conditions are used for nitriding (Ref 6).

Nitriding steels used in the United States fall in one of two groups: aluminum-containing Nitralloys and AISI low- or high-alloy steels. There is, however, a wide gap between the characteristics of these two groups of steels, which, in Europe, is filled by CrMo and CrMoV steels with 2.5 to 3.5% Cr. Chromium provides good hardenability and higher hardness in nitrided case than AISI low-alloy steels. Molybdenum resists softening on tempering so that high strengths can be retained even after tempering at well over the nitriding temperature. It also minimizes susceptibility to embrittlement during nitriding and increases hardenability and hot hardness. Vanadium permits easier control of heat treatment and gives higher hot hardness.

For surface hardness and toughness, the nitrided CrMo and CrMoV steels occupy a position in between Nitralloy 135M and AISI low-alloy steels. Because of lower case hardness, these materials are less brittle. Furthermore, they are less sensitive to grinding cracks and have higher hardenability. Also, they can be heat treated to higher core hardness prior to nitriding. For example, 3.5Cr-AlMo, a British

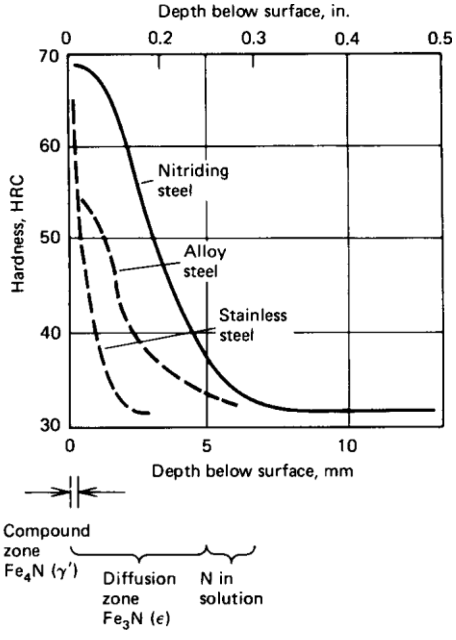

Fig. 6 Nitride case profiles for various steels. Source: Ref 1

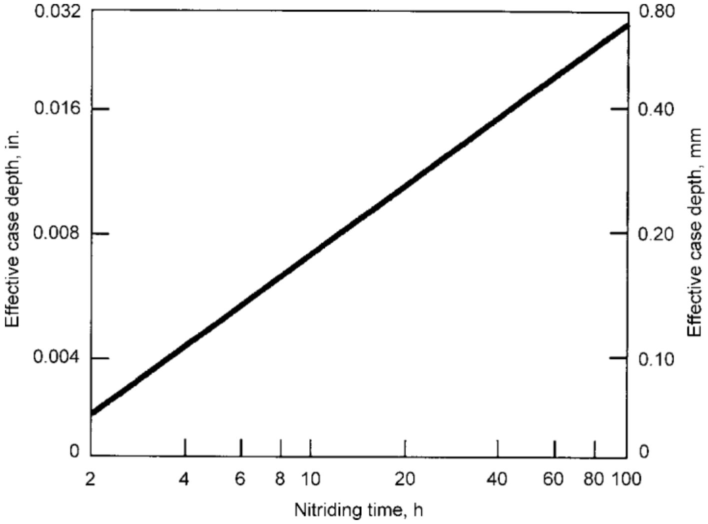

Fig. 7 Nominal time for different nitrided case depths. Source: Ref 9

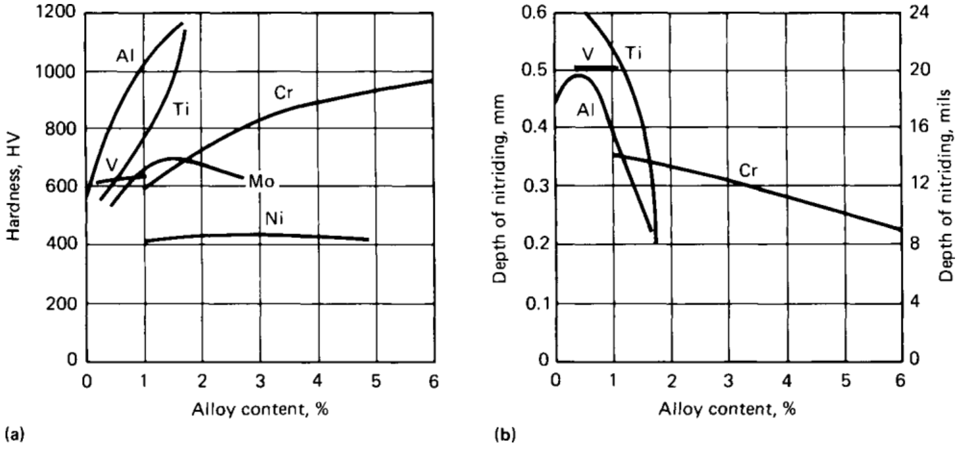

Fig. 8 Influence of alloying elements on (a) hardness after nitriding (base alloy, 0.35% C, 0.30% Si, 0.70% Mn) and (a) depth of nitriding measured at 400 HV (nitriding for 8 h at 520 °C, or 970 °F). Source: Ref 6

Steel (EN 40C), can be heat treated to 375 to 444 Brinell hardness in sections up to 63.5 mm (2.5 in.), whereas Nitralloy 135M can be heat treated to only 248 to 302 Brinell hardness in that size. In addition, the steels with 2.5 to 3.5% Cr come with low nonmetallic inclusions (higher cleanliness), even in the air-melted condition, whereas the aluminum-containing steels, such as Nitralloy 135M, require vacuum melting or degassing to achieve similar cleanliness. In general, the cleaner the material, the lower the distortion during any hardening process. Nitrided gears made from air-melted CrMo steels produce negligible distortion.

Process methods for nitriding include gas (box furnace or fluidized bed), liquid (salt bath), and plasma (ion) nitriding. In a survey of 800 commercial shops in the United States and Canada, 30% offered nitriding services, of which (Ref 10):

- 21% offered gas nitriding
- 7% offered salt bath nitriding
- 6% offered fluidized-bed nitriding
- 5% offered plasma nitriding

The advantages and disadvantages of these techniques are similar to those of carburizing. However, process times for gas nitriding can be quite long, that is, from 10 to 130 h depending on the application, and the case depths are relatively shallow, usually less than 0.5 mm (0.020 in.). Plasma nitriding allows faster nitriding times, and the quickly attained surface saturation of the plasma process results in faster diffusion. Plasma nitriding may clean the surface by sputtering.

Nitrocarburizing is a surface-hardening process that uses both carbon and nitrogen, but with more nitrogen than carbon, when compared to carbonitriding (see the article "Carbonitriding of Steels" in this Volume). Carbonitriding produces a martensitic case with nitrogen levels less than carbon levels. In contrast, nitrocarburizing involves higher levels of nitrogen with a compound layer. There are two types of nitrocarburizing: ferritic and austenitic (Ref 11). Ferritic nitrocarburizing occurs at lower temperatures in the ferritic temperature range and involves diffusion of nitrogen into the case. Austenitic nitrocarburizing is a more recently developed process with process temperatures in the range of 675 to 775 °C (1245 to 1425 °F). It also uses much higher ammonia additions and thus higher nitrogen levels in the case. This allows the formation of a surface compound zone, which is not typical of the carbonitriding process. Austenitic nitrocarburizing differs from ferritic nitrocarburizing in the ability for deeper case depths with a better load-carrying capability but may result in greater part distortion because of the higher processing temperatures and the required quenching process. Although ferritic and aus- tenitic nitrocarburizing have higher processing temperatures than does nitriding (Table 2), they have the advantage of being suitable for plain carbon steels.

Applied Energy Methods

Surface hardening of steel can be achieved by localized heating and quenching, without any chemical modification of the surface. The more common methods currently used to harden the surface of steels include flame and induction hardening. However, each of these methods has shortcomings that can prevent its use in some applications. For example, the disadvantages of flame hardening include the possibility of part distortion, while induction hardening requires close coupling between the part and the coil (especially when using high frequencies), which must be precisely maintained.

Flame hardening consists of austenitizing the surface of a steel by heating with an oxy-acetylene or oxyhydrogen torch and immediately quenching with water or water-based polymer. The result is a hard surface layer of martensite over a softer interior core with a ferrite-pearlite structure. There is no change in composition, and therefore, the flame-hardened steel must have adequate carbon content for the desired surface hardness. The rate of heating and the conduction of heat into the interior appear to be more important in establishing case depth than the use of a steel of high hardenability.

Flame-heating equipment may be a single torch with a specially designed head or an elaborate apparatus that automatically indexes, heats, and quenches parts. Large parts such as gears and machine toolways, with sizes or shapes that would make furnace heat treatment impractical, are easily flame hardened. With improvements in gas-mixing equipment, infrared temperature measurement and control, and burner design, flame hardening has been accepted as a reliable heat treating process that is adaptable to general or localized surface hardening for small and medium-to-high production requirements.

Induction heating is an extremely versatile heating method that can perform uniform surface hardening, localized surface hardening, through hardening, and tempering of hardened pieces. Heating is accomplished by placing a steel ferrous part in the magnetic field generated by high-frequency alternating current passing through an inductor, usually a water-cooled copper coil. The depth of heating produced by induction is related to the frequency of the alternating current, power input, time, part coupling and quench delay.

The higher the frequency, the thinner or more shallow the heating. Therefore, deeper case depths and even through hardening are produced by using lower frequencies. The electrical considerations involve the phenomena of hysteresis and eddy currents. Because secondary and radiant heat are eliminated, the process is suited for in-line production. Some of the benefits of induction hardening are faster process, energy efficiency, less distortion, and small footprints. Care must be exercised when holes, slots, or other special geometric features must be induction hardened, which can concentrate eddy currents and result in overheating and cracking without special coil and part designs. For details, see the articles "Induction Surface Hardening of Steels" and "Induction Heat Treating Systems" in this Volume.

Laser surface heat treatment is widely used to harden localized areas of steel and cast iron machine components. This process is sometimes referred to as laser transformation hardening to differentiate it from laser surface melting phenomena (Fig. 9). There is no chemistry change produced by laser transformation hardening, and the process, like induction and flame hardening, provides an effective technique to harden ferrous materials selectively. Other methods of laser surface treatments include surface melting and surface alloying. Laser surface melting results in a refinement of the structure due to the rapid quenching from the melt. In surface alloying, elements are added to the melt pool to change the composition of the surface. The novel structures produced by laser surface melting and alloying can exhibit improved electrochemical behavior.

Laser transformation hardening produces thin surface zones that are heated and cooled very rapidly, resulting in very fine martensitic microstructures, even in steels with relatively low hardenability. High hardness and good wear resistance with less distortion result from this process. The laser method differs from induction and flame heating in that the laser can be located at some distance from the workpieces. Also, the laser light is reflected by mirrors to the focusing lens, which controls the width of the heated spot or track.

Molian (Ref 12) has tabulated the characteristics of 50 applications of laser transformation hardening. The materials hardened include plain carbon steels (1040, 1050, 1070), alloy steels (4340, 52100), tool steels, and cast irons (gray, malleable, ductile). Because the absorption of laser radiation in cold metals is low, laser surface hardening often requires energy-absorbing coatings on surfaces. Reference 12 lists some energy-absorbing coatings.

Typical case depths for steels are 250 to 750 mm (0.01 to 0.03 in.) and for cast irons are approximately 1000 mm (0.04 in.). The flexibility of laser delivery systems and the low distortion and high surface hardness obtained have made lasers very effective in the selective hardening of wear- and fatigue-prone areas on irregularly shaped machine components, such as camshafts and crankshafts.

Electron beam (EB) hardening, like laser treatment, is used to harden the surfaces of steels. The EB heat treating process uses a concentrated beam of high-velocity electrons as an

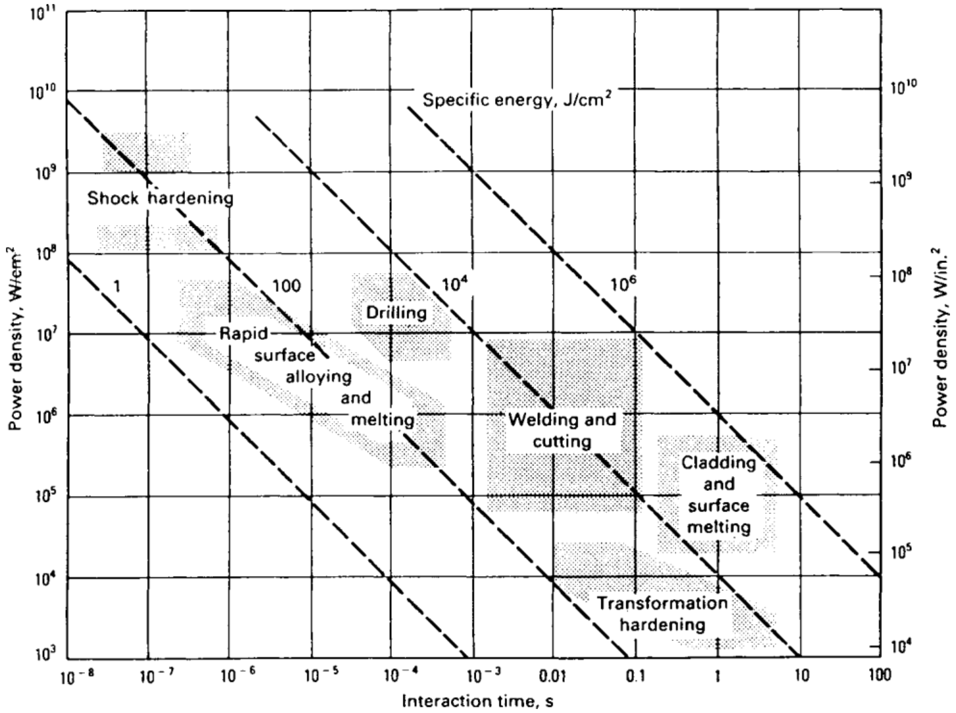

Fig. 9 Interaction times and power densities necessary for various laser surface modification processes

energy source to heat selected surface areas of ferrous parts. Electrons are accelerated and are formed into a directed beam by an EB gun. After exiting the gun, the beam passes through a focus coil, which precisely controls beam density levels (spot size) at the workpiece surface and then passes through a deflection coil. To produce an electron beam, a high vacuum of 10^{-5} torr (1.3×10^{-3} Pa) is needed in the region where the electrons are emitted and accelerated. This vacuum environment protects the emitter from oxidizing and avoids scattering of the electrons while they are still traveling at a relatively low velocity.

Like laser beam hardening, the EB process eliminates the need for quenchants but requires a sufficient workpiece mass to permit self-quenching. A mass of up to eight times that of the volume to be EB hardened is required around and beneath the heated surfaces. Electron beam hardening does not require energy-absorbing coatings, as does laser beam hardening. Processing considerations and property changes associated with EB hardening are covered in Ref 13 and 14 and in the article "Electron Beam Surface Hardening of Steels" in this Volume.

Other Methods

Diffusion coatings are deposited either by heating the components to be treated in contact with the powder coating material in an inert atmosphere (solid-state diffusion) or by heating them in an atmosphere of a volatile compound of the coating material (out-of-contact gas-phase deposition, or chemical vapor deposition). As the coating bond is developed by diffusion, the bond strength is enhanced.

Solid-state diffusion methods include pack cementation, which is the most widely employed diffusion coating method and includes coatings based on aluminum (aluminizing), chromium (chromizing), and silicon (siliconizing). Substrate materials include nickel- and cobalt-base superalloys, steels (including carbon, alloy, and stainless steels), and refractory metals and alloys. Diffusion coatings for wear resistance are also based on boriding (boronizing) and the thermoreactive deposition/diffusion process. Of these, boron and titanium treatments offer high levels of hardness (Fig. 2), while aluminum, chromium, and silicon treatments are primarily used for corrosion resistance.

Boriding involves the diffusion of boron into metal surfaces for the enhancement of hardness and wear resistance. Boriding is most often applied to tool steels that may be hardened by heat treatment. Boriding techniques include metallizing, chemical vapor deposition, and pack cementation. For additional information, see the article "Boriding (Boronizing) of Metals" in this Volume.

Titanium Carbide. With process temperatures in the range of 900 to 1010 °C (1650 to 1850 °F), titanium and carbon will diffuse to form a diffused case of titanium carbide during chemical vapor deposition. This treatment is most commonly applied to tool steels and hardenable stainless steels. Because the treatment is performed above the austenitizing temperatures of these steels, the core must be hardened by quenching.

Ion implantation is a surface-modification process in which ions with very high energy are driven into a substrate. Ions of almost any atom species can be implanted, but nitrogen is widely used to improve corrosion resistance and the tribological properties of steels and other alloys. Although the nitrogen content of alloy surfaces is increased by both nitrogen ion implantation and plasma nitriding, major differences exist between the two processes and the surface modifications they create. The major difference is that ion implantation can be performed at room temperature.

Ion implantation machines accelerate ions, generated by specially designed sources, at very high energies (from 10 to 500 keV). In contrast, the energy of ions and atoms in plasma nitriding is much lower (<1 keV). Ion implantation is carried out with the substrate at approximately room temperature, thereby minimizing the diffusion-controlled formation of precipitates and coarsening of the subsurface microstructure. Because the temperature of application is low and the process is carried out in accelerators with very good vacuums (10^{-5} torr, or $1.3\leq 10^{-3}$ Pa), clean surfaces are ensured and undesirable surface chemical reactions such as oxidation are lessened. Ion implantation is a line-of-sight process (similar to laser); that is, only relatively small areas directly exposed to the ion beam are implanted. For the coverage of areas larger than the beam, either the specimen must be translated or the ion beam must be rastered over the specimen surface.

Because of the virtual absence of diffusion-controlled case formation during ion implantation, case depths are shallow (generally <0.25 mm, or 0. 010 mil). Very high strengths or hardnesses of the nitrogen-implanted surface layers compensate for the shallow case depths of ion implantation. Ion implantation is a complex, nonequilibrium process that creates significant lattice damage in the form of vacancies and interstitial point defects. Concentrations of implanted species much higher than equilibrium solubility limits may be introduced. In fact, the incorporation of high densities of atoms of significantly different size than those of the substrate lattice may produce amorphous structures or metastable phases (Ref 15).

The properties of ion-implanted surfaces and shallow case depths make ion implantation suitable for very special applications. Because the surface of the part itself is modified, the adhesion problems sometimes encountered with coated layers of high hardness do not arise. Also, because ion implantation is usually accomplished with very little heating, dimensional stability is excellent. Examples of applications of ion implantation include the surface hardening of razor blades (Ref 4) and knives (Ref 15), a variety of tool steel applications (Ref 16), and the implantation of 52100 and 440C bearings with titanium and/or nitrogen to improve rolling-contact fatigue resistance (Ref 17–19). In the latter applications, titanium was found to reduce the coefficient of friction, and nitrogen was found to raise hardness by intermetallic compound formation. Additional information on ion implantation is given in Ref 20 and in *Corrosion*, Volume 13 of *ASM Handbook*, formerly *Metals Handbook*, 9th edition.

Surface hardening with arc lamps is used in applications that involve surface remelting or surface hardening by solid-phase recrystallization. Examples include the surface remelting of cast iron and the large-area remelting of titanium in the presence of nitrogen or methane to produce titanium carbides in the surface layer. In the surface remelting of cast irons, lasers are also used. Another area in which arc lamps are finding application is in the selective hardening of the edges on agricultural sweeps and tilling equipment blades.

Surface treating using white light from a high-power arc lamp offers several advantages over traditional methods and the beam techniques. For example, arc lamp treatment can achieve higher surface radiation intensities than can flame heating, making the procedure faster and less likely to cause distortion. Compared with induction hardening, arc lamp treatment allows much larger distances between the part and heat source, providing more flexibility in treating irregularly shaped surfaces. Unlike the EB treatment, this method does not require the use of a vacuum chamber, and an arc lamp can deliver greater power to the part surface than can a laser beam.

However, with the arc lamp method, significant power loss is encountered if arc radiation is concentrated onto surface areas smaller than the arc itself. Therefore, the illuminated spot on the sample surface should always be larger than the arc. This necessitates extremely high arc power to achieve the surface intensities needed for thermal treatment. Such high power is achieved in a very small space with specially designed arc lamps.

Process Selection

The benefits of the most common methods of surface hardening are compared in Table 3. Flame and induction hardening are generally limited to certain families of steels, such as medium-carbon steels, medium-carbon alloy steels, some cast irons, and the lower-alloy tool steels. There is no size limit to parts that can be flame hardened, because only the portion of the part to be hardened need be heated. Flame hardening is generally used for very heavy cases (in the range of approximately 1.2 to 6 mm, or 0.6 to 0.25 in.); thin case depths are difficult to control because of the nature of the heating process. Diffusion methods are compared in Table 2.

Table 3 Relative benefits of five common surface-hardening processes

Process	Benefits
Carburizing	Hard, highly wear-resistant surface (medium case depths); excellent capacity for contact load; good bending fatigue strength; good resistance to seizure; excellent freedom from quench cracking; low-to-medium-cost steels required; high capital investment required
Carbonitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; good resistance to seizure; good dimensional control possible; excellent freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required; improved salt corrosion resistance
Nitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; excellent resistance to seizure; excellent dimensional control possible; good freedom from quench cracking (during pretreatment); medium-to-high-cost steels required; medium capital investment required; improved salt corrosion resistance
Induction hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required
Flame hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; low capital investment required

Transformation hardening introduces surface compressive residual stresses, which are beneficial for fatigue strength. In selective hardening, however, some residual tensile stress will exist in the region where the hardened zone meets the unhardened zone. Consequently, selective hardening by methods such as flame or induction heating should be applied away from geometric stress concentrations. Both nitriding and carburizing provide good resistance to surface fatigue and are widely used for gears and cams. In terms of bending fatigue resistance, the ideal case depth appears to be reached where the failure initiation point is transferred from the core to the surface (Ref 21). However, specification of required case depth is a complex subject, which is briefly discussed in Ref 21 for carburized steels.