

Introduction to Surface Hardening of Steels*

Revised by Michael J. Schneider, The Timken Company, and Madhu S. Chatterjee, Bodycote

SURFACE HARDENING, a process that includes a wide variety of techniques (Table 1), is used to improve the wear resistance of parts without affecting the more soft, tough interior of the part. This combination of hard surface and resistance to breakage upon impact is useful in parts such as a cam or ring gear, bearings or shafts, turbine applications, and automotive components that must have a very hard surface to resist wear, along with a tough interior to resist the impact that occurs during operation. Most surface treatments result in compressive residual stresses at the surface that reduce the probability of crack initiation and help arrest crack propagation at the case-core interface. Further, the surface hardening of steel

can have an advantage over through hardening because less expensive low-carbon and medium-carbon steels can be surface hardened with minimal problems of distortion and cracking associated with the through hardening of thick sections.

There are two distinctly different approaches to the various methods for surface hardening (Table 1):

- Methods that involve an intentional buildup or addition of a new layer
- Methods that involve surface and subsurface modification without any intentional buildup or increase in part dimensions

The first group of surface-hardening methods includes the use of thin films, coatings, or weld overlays (hardfacings). Films, coatings, and overlays generally become less cost-effective as production quantities increase, especially when the entire surface of workpieces must be hardened. The fatigue performance of films, coatings, and overlays may also be a limiting factor, depending on the bond strength between the substrate and the added layer. Fusion-welded overlays have strong bonds, but the primary surface-hardened steels used in wear applications with fatigue loads include heavy case-hardened steels and flame- or induction-hardened steels. Nonetheless, coatings and overlays can be effective in some applications. With tool steels, for example, TiN and Al₂O₃ coatings are effective not only because of their hardness but also because their chemical inertness reduces crater wear and the welding of chips to the tool. Some overlays can impart corrosion-resistant properties. Overlays can be effective when the selective hardening of large areas is required.

This introductory article on surface hardening focuses exclusively on the second group of methods, which is further divided into diffusion methods and selective-hardening methods (Table 1). Diffusion methods modify the

chemical composition of the surface with hardening species such as carbon, nitrogen, or boron. Diffusion methods may allow effective hardening of the entire surface of a part and are generally used when a large number of parts are to be surface hardened. In contrast, selective surface-hardening methods allow localized hardening. Selective hardening generally involves transformation hardening (from heating and quenching), but some selective-hardening methods (selective nitriding, ion implantation, and ion beam mixing) are based solely on compositional modification. Factors affecting the choice of these surface-hardening methods are discussed in the section "Process Selection" in this article.

Diffusion Methods of Surface Hardening

As previously mentioned, surface hardening by diffusion involves the chemical modification of a surface. The basic process used is thermochemical because some heat is needed to enhance the diffusion of hardening elements into the surface and subsurface regions of a part. The depth of diffusion exhibits a time-temperature dependence such that:

$$\text{Case depth} = K\sqrt{\text{Time}} \quad (\text{Eq 1})$$

where the diffusivity constant, K , depends on temperature, the chemical composition of the steel, and the concentration gradient of a given hardening element. In terms of temperature, the diffusivity constant increases exponentially as a function of absolute temperature. Concentration gradients depend on the surface kinetics and reactions of a particular process.

Methods of hardening by diffusion include several variations of hardening elements (such as carbon, nitrogen, or boron) and of the

Table 1 Engineering methods for surface hardening of steels

Layer additions

- **Hardfacing:**
 - Fusion hardfacing (welded overlay)
 - Thermal spray (nonfusion-bonded overlay)
- **Coatings:**
 - Electrochemical plating
 - Chemical vapor deposition (electroless plating)
 - Thin films (physical vapor deposition, sputtering, ion plating)
 - Ion mixing

Substrate treatment

- **Diffusion methods:**
 - Carburizing
 - Nitriding
 - Carbonitriding
 - Nitrocarburizing
 - Boriding
 - Titanium-carbon diffusion
 - Toyota diffusion process
- **Selective-hardening methods:**
 - Flame hardening
 - Induction hardening
 - Laser hardening
 - Electron beam hardening
 - Ion implantation
 - Selective carburizing and nitriding
 - Use of arc lamps

* Revised from S. Lamman, Introduction to Surface Hardening of Steels, *Heat Treating*, Vol 4, *ASM Handbook*, ASM International, 1991, p 259–267

process method used to handle and transport the hardening elements to the surface of the part. Process methods for exposure involve the handling of hardening species in forms such as gas, liquid, or ions. These process variations naturally produce differences in typical case depth and hardness (Table 2). Factors influencing the suitability of a particular diffusion method include the type of steel (Fig. 1), the desired case hardness (Fig. 2), case depth (Fig. 3), the desired case profile, and cost.

It is also important to distinguish between total case depth and effective case depth. The effective case depth is typically about two-thirds to three-fourths the total case depth. (In some cases, the depth to the hardness value of 50 HRC or five points lower than the surface hardness is also specified.) The required

effective depth and the measurement technique must be specified so that the heat treater can process the parts for the correct time at the proper temperature.

Carburizing and Carbonitriding

Carburizing is the addition of carbon to the surface of low-carbon steels at temperatures (generally between 850 and 980 °C, or 1560 and 1800 °F) at which austenite, with its high solubility for carbon, is the stable crystal structure. With grades of steel engineered to resist grain coarsening at high temperatures and properly designed furnaces such as vacuum furnaces, carburizing above 980 °C (1800 °F) is practical to dramatically reduce carburizing time.

Hardening is accomplished when the high-carbon surface layer is quenched to form martensitic case with good wear and fatigue resistance superimposed on a tough, low-carbon steel core. Of the various diffusion methods (Table 2), gas carburization is the most widely used, followed by gas nitriding and carbonitriding.

Case hardness of carburized steels is primarily a function of carbon content. When the carbon content of the steel exceeds approximately 0.65%, additional carbon has no effect on hardness but does enhance hardenability. Carbon in excess of 0.65% may not be dissolved, which would require high temperatures to ensure carbon-austenite solid solution. Higher levels of carbon in the case will impact microstructural properties that can enhance performance characteristics such as wear, sliding contact fatigue,

Table 2 Typical characteristics of diffusion treatments

Process	Nature of case	Process temperature		Typical case depth	Case hardness, HRC	Typical base metals	Process characteristics
		°C	°F				
Carburizing							
Pack	Diffused carbon	815–1090	1500–2000	125 µm–1.5 mm (5–60 mils)	50–63(a)	Low-carbon steels, low-carbon alloy steel	Low equipment costs; difficult to control case depth accurately
Gas	Diffused carbon	815–980	1500–1800	75 µm–1.5 mm (3–60 mils)	50–63(a)	Low-carbon steels, low-carbon alloy steels	Good control of case depth; suitable for continuous operation; good gas controls required; can be dangerous
Liquid	Diffused carbon and possibly nitrogen	815–980	1500–1800	50 µm–1.5 mm (2–60 mils)	50–65(a)	Low-carbon steels, low-carbon alloy steels	Faster than pack and gas processes; can pose salt disposal problem; salt baths require frequent maintenance
Vacuum/LPC	Diffused carbon	815–1090	1500–2000	75 µm–1.5 mm (3–60 mils)	50–63(a)	Low-carbon steels, low-carbon alloy steels	Excellent process control; bright parts; faster than gas carburizing; high equipment costs
Nitriding							
Gas/LPN	Diffused nitrogen, nitrogen compounds	480–590	900–1100	125 µm–0.75 mm (5–30 mils)	50–70	Alloy steels, nitriding steels, stainless steels	Hardest cases from nitriding steels; quenching not required; low distortion; process is slow; is usually a batch process
Salt	Diffused nitrogen, nitrogen compounds	510–565	950–1050	2.5 µm–0.75 mm (0.1–30 mils)	50–70	Most ferrous metals including cast irons	Usually used for thin hard cases < 25 µm (1 mil); no continuous white layer; most are proprietary processes
Ion	Diffused nitrogen, nitrogen compounds	340–565	650–1050	75 µm–0.75 mm (3–30 mils)	50–70	Alloy steels, nitriding steels, stainless steels	Faster than gas nitriding; no white layer; high equipment costs; close case control
Carbonitriding							
Gas	Diffused carbon and nitrogen	760–870	1400–1600	75 µm–0.75 mm (3–30 mils)	50–65(a)	Low-carbon steels, low-carbon alloy steels, stainless steels	Lower temperature than carburizing (less distortion); slightly harder case than carburizing; gas control critical
Liquid (cyaniding)	Diffused carbon and nitrogen	760–870	1400–1600	2.5–125 µm (0.1–5 mils)	50–65(a)	Low-carbon steels	Good for thin cases on noncritical parts; batch process; salt disposal problems
Ferritic nitrocarburizing	Diffused carbon and nitrogen	565–675	1050–1250	2.5–25 µm (0.1–1 mil)	40–60(a)	Low-carbon steels	Low-distortion process for thin case on low-carbon steel; most processes are proprietary
Other							
Aluminizing (pack)	Diffused aluminum	870–980	1600–1800	25 µm–1 mm (1–40 mils)	< 20	Low-carbon steels	Diffused coating used for oxidation resistance at elevated temperatures
Siliconizing by chemical vapor deposition	Diffused silicon	925–1040	1700–1900	25 µm–1 mm (1–40 mils)	30–50	Low-carbon steels	For corrosion and wear resistance, atmosphere control is critical
Chromizing by chemical vapor deposition	Diffused chromium	980–1090	1800–2000	25–50 µm (1–2 mils)	Low-carbon steel, < 30; high-carbon steel, 50–60 > 70(a)	High- and low-carbon steels	Chromized low-carbon steels yield a low-cost stainless steel; high-carbon steels develop a hard corrosion-resistant case
Titanium carbide	Diffused carbon and titanium, TiC compound	900–1010	1650–1850	2.5–12.5 µm (0.1–0.5 mil)		Alloy steels, tool steels	Produces a thin carbide (TiC) case for resistance to wear; high temperature may cause distortion
Boriding	Diffused boron, boron compound	400–1150	750–2100	12.5–50 µm (0.5–2 mils)	40–> 70	Alloy steels, tool steels, cobalt and nickel alloys	Produces a hard compound layer; mostly applied over hardened tool steels; high process temperature can cause distortion

(a) Requires quench from austenitizing temperature. Source: Ref 1

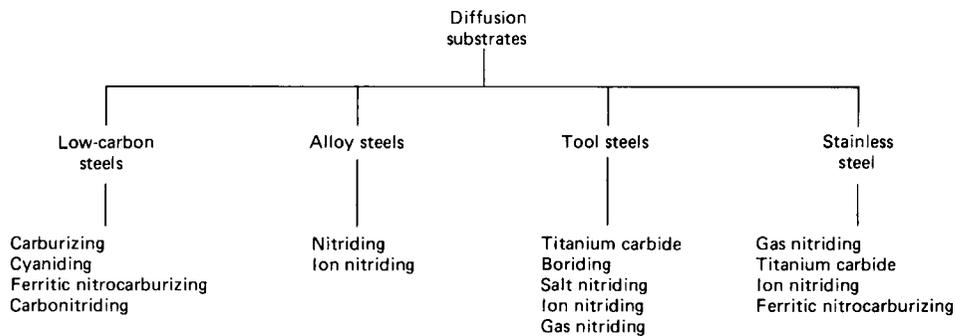


Fig. 1 Types of steels used for various diffusion processes

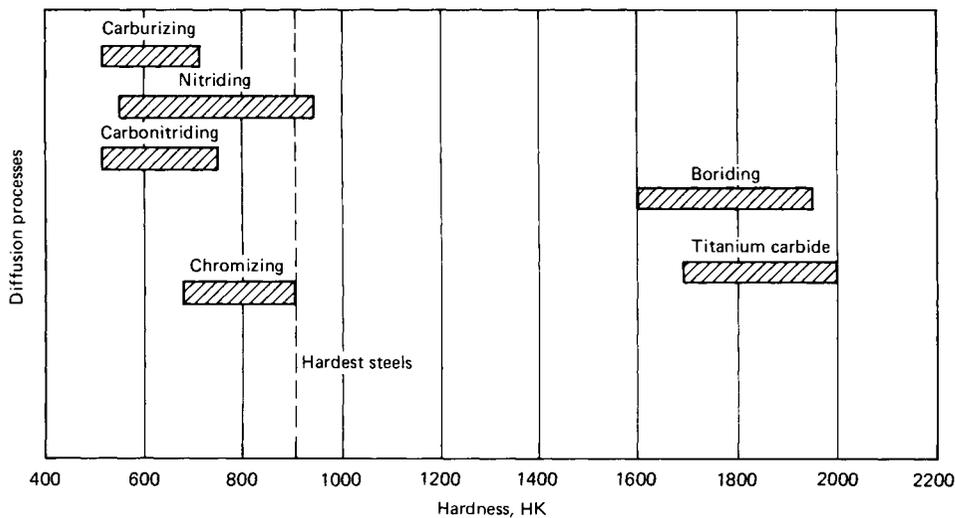


Fig. 2 Spectrum of hardness obtainable with selected diffusion processes of steel

and rolling contact fatigue. Too high a carbon level can result in excessive carbide formation and carbide networking or massive carbides that may be detrimental to performance. Therefore, it is important to understand the carbon profile needed and define it when necessary.

Case depth of carburized steel is a function of carburizing time, the steel chemistry, and available carbon (carbon potential) at the surface. When prolonged carburizing times are used for deep case depths, a high carbon potential produces a high surface-carbon content, which may thus result in excessive retained austenite or free carbides. These two microstructural elements can have adverse effects on the distribution of residual stress in the case-hardened part. Consequently, a high carbon potential may be suitable for short carburizing times but not for prolonged carburizing. Selection of carbon potential also depends on the carburizing response of a particular steel.

Carburizing Steels

Carburizing steels for case hardening usually have base-carbon contents of approximately 0.2%, with the carbon content of the carburized

layer generally being controlled at between 0.7 and 1% C (Ref 2). However, surface carbon is often limited to 0.9% (Ref 3) because too high a carbon content can result in retained austenite and brittle martensite (due to the formation of proeutectoid carbides on the grain boundaries).

Most steels that are carburized are killed steels (deoxidized by the addition of aluminum), which maintain fine grain sizes to temperatures of approximately 1040 °C (1900 °F). Steels made to coarse grain practices can be carburized if a double quench is introduced to provide grain refinement. Double quenching usually consists of a direct quench followed by a requery from a lower temperature.

Many alloy steels for case hardening are now specified on the basis of core hardenability. Although the same considerations generally apply to the selection of uncarburized grades, there are some distinct characteristics in carburizing applications.

First, in a case-hardened steel, the hardenability of both case and core must be considered. Because of the difference in carbon content, case and core have quite different hardenabilities, and this difference is much greater for some grades of steels than for

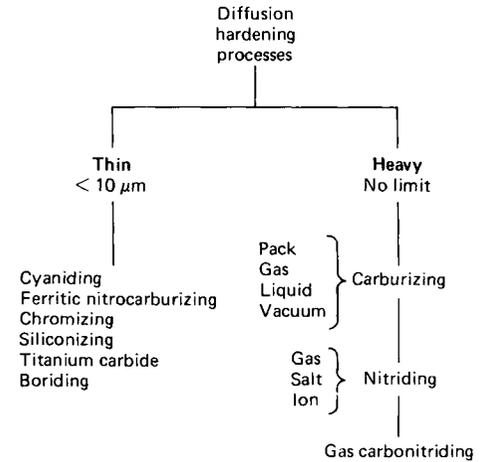


Fig. 3 Categorization of diffusion processes by typical case depth

others. Moreover, the two regions have different in-service functions to perform. Until the introduction of lean alloy steels such as the 51xx, or 86xx series, with and without boron, there was little need to be concerned about case hardenability because the alloy content combined with the high carbon content always provided adequate hardenability. This is still somewhat true when the steels are direct quenched from carburizing, so that the carbon and alloying elements are in solution in the case austenite. In parts that are reheated for hardening and in heavy-sectioned parts, however, both case and core hardenability requirements should be carefully evaluated.

The hardenability of the steels as purchased is the core hardenability. Because these low-carbon steels, as a class, are shallow hardening and because of the wide variation in the section sizes of case-hardened parts, the hardenability of the steel must be related to some critical section of the part, for example, the pitch line or the root of a gear tooth or the largest inscribed circle of a cross section such as a bearing. This is best accomplished by making a part of a steel of known hardenability, heat treating it, and then, by means of equivalence of hardness, relating the hardenability in the critical section or sections to the proper positions on the end-quench hardenability specimens, for both carburized and noncarburized part. Finally, the relationship between the thermal gradient and the carbon (hardenability) gradient during quenching of a carburized part can make a difference in the case depth measured by hardness. That is, an increase in base hardenability can produce a higher proportion of martensite for a given carbon level, yielding an increased measured case depth. Therefore, a shallower carbon profile and shorter carburizing time could be used to attain the desired result in a chosen steel.

Core Hardness. A common mistake is to specify too narrow a range of core hardness.

When the final quench is from a temperature high enough to allow the development of full core hardness, the hardness variation at any location will be that of the hardenability band of the steel at the corresponding position on the end-quenched hardenability specimen. One way to alter this state of affairs is to use higher-alloy steels. In the commonly used alloy steels having a maximum of 2% total alloy content, the range for the core hardness of sections such as gear teeth is 12 to 15 HRC points. Higher-alloy steels exhibit a narrower range; for example, in 4815 the range is 10 HRC points, while in 3310 it is 8 HRC points. Narrow-range steels are justified only for severe service or special applications.

In standard steels purchased to chemical composition requirements rather than to hardenability, the range can be 20 or more HRC points; for example, 8620 may vary from 20 to 45 HRC at the $\frac{1}{16}$ in. position. The 25-point range emphasizes the advantage of purchasing (cost) to hardenability specifications to avoid the intolerable variation possible within the ranges for standard-chemistry steels. Another way to control core hardness within narrow limits without resorting to the use of high-alloy steels is to use a final quench from a lower temperature, so that full hardness in the case will be developed without the disadvantage of excessive core hardness.

Gears, Bearings, and Low-Distortion Applications. Gears and bearings are almost always oil quenched or high-pressure gas quenched, because distortion must be held to the lowest possible level. Therefore, alloy steels are usually preferred. The lower-alloy steels such as 4023, 5120, 4118, 8620, and 4620, with a carbon range between 0.15 and 0.25%, are widely used to achieve satisfactory results. In most applications, 8620 or 5120 are preferred. The final choice, based on service experience or dynamometer testing, should be the least expensive steel that will do the job. Another steel, 1524, could be considered; although not classified commercially as an alloy steel, it has sufficient manganese to make it oil harden up to an end-quench correlation point of $\frac{3}{16}$.

For heavy-duty applications or heavy cross sections requiring core strength, higher-alloy grades such as 4320, 4817, and 9310 are justifiable if based on actual performance tests. Rather than the bench tests, actual life testing of gears in the same mountings used in service to prove both the design and the steel selection is particularly important.

The carbonitriding process extends the use of carbon steels such as 1016, 1018, 1019, and 1022 into the field of light-duty gearing by permitting the use of oil quenching in teeth of eight diametral pitch and finer. Steels selected for such applications should be specified silicon-killed or aluminum-killed fine grained to ensure uniform case hardness and dimensional control. The core properties of gears made from these types of steel resemble that of low-carbon steel, oil quenched. In the thin sections of fine-pitch

teeth, this may be up to 25 HRC. The carbonitriding process is usually limited, for economic reasons, to maximum case depths of approximately 0.6 mm (0.025 in.). In some bearing applications, 52100 materials are also carbonitrided to enhance galling properties.

Non-Gear/Bearing Applications. In other applications, when distortion is not a major factor, the carbon steels described previously, water quenched, can be used up to a 50 mm (2 in.) diameter. In larger sizes, low-alloy steels, water quenched, such as 5120, 4023, and 6120, can be used, but possible distortion and quench cracking must be avoided.

Carburizing Methods

While the basic principle of carburizing has remained unchanged since it was first introduced, the methodology has gone through continuous evolution. In its earliest application, parts were simply placed in a suitable container and covered with a thick layer of carbon powder (pack carburizing). Although effective in introducing carbon, this method was exceedingly slow, and as the production demand grew, a new method using a gaseous atmosphere was developed. In gas carburizing, the parts are surrounded by a carbon-bearing atmosphere that can be continuously replenished so that a high carbon potential can be maintained. While the rate of carburizing is substantially increased in the gaseous atmosphere, the method requires the use of a multicomponent atmosphere whose composition must be very closely controlled to avoid deleterious side effects, for example, surface and grain-boundary oxides. In addition, a separate piece of equipment is required to generate the atmosphere and control its composition or liquids, such as methanol, which must be vaporized. Despite this increased complexity, gas carburizing has become the most effective and widely used method for carburizing steel parts in high volume.

In efforts required to simplify the atmosphere, carburizing in an oxygen-free environment at very low pressure (vacuum carburizing) has been explored and developed into a viable and important alternative. Although the furnace enclosure in some respects becomes more complex, the atmosphere is greatly simplified. A single-component atmosphere consisting solely of a simple gaseous hydrocarbon, for example, methane or acetylene, may be used. Furthermore, because the parts are heated in an oxygen-free environment, the carburizing temperature may be increased substantially without the risk of surface or grain-boundary oxidation. The higher temperature permitted increases not only the solid solubility of carbon in the austenite but also its rate of diffusion, so that the time required to achieve the case depth desired is reduced. When carburizing at temperatures over 980 °C (1800 °F), properly engineered steel chemistries are recommended to mitigate the potential for grain coarsening.

Although vacuum carburizing overcomes some of the complexities of gas carburizing, it introduces a serious new problem that must be addressed. Because vacuum carburizing is conducted at very low pressures, and the rate of flow of the carburizing gas into the furnace is very low, the carbon potential of the gas in deep recesses and blind holes is quickly depleted. Unless this gas is replenished, a distinct nonuniformity in case depth over the surface of the part is likely to occur. If, in an effort to overcome this problem, the gas pressure is increased significantly, another problem arises, that of free-carbon formation, or sooting. Thus, to obtain cases of reasonably uniform depth over a part of complex shape, the gas pressure must be increased periodically to replenish the depleted atmosphere in recesses and then reduced again to the operating pressure. Clearly, a delicate balance exists in vacuum carburizing: The process conditions must be adjusted to obtain the best compromise between case uniformity, risk of sooting, and carburizing rate. Surface area and alloy content of the component are two important considerations of vacuum carburizing.

A method that overcomes the major limitations of gas carburizing yet retains the desirable features of a simple atmosphere and a higher permissible operating temperature is plasma or ion carburizing.

To summarize, carburizing methods include:

- Gas carburizing
- Vacuum carburizing or low-pressure carburizing
- Plasma carburizing
- Salt bath carburizing
- Pack carburizing

These methods introduce carbon by the use of gas (atmospheric gas, plasma, and vacuum carburizing), liquids (salt bath carburizing), or solid compounds (pack carburizing). All of these methods have limitations and advantages, but gas carburizing is used most often for high-volume production because it can be accurately controlled and requires minimal special handling.

Vacuum carburizing and plasma carburizing have found applications because the absence of oxygen in the furnace atmosphere thus eliminates grain-boundary oxidation. Salt bath and pack carburizing are still done occasionally but have relatively little commercial importance today (2013).

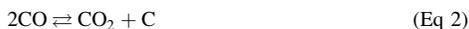
Process characteristics of the aforementioned carburizing methods fall into two general groups:

- Conventional methods, which introduce carbon by gas atmospheres, salt baths, or charcoal packs
- Plasma methods, which impinge positive carbon ions on the surface of a steel part (the cathode)

The main difference between the conventional and glow-discharge (or plasma) methods is the

reduced carburizing times in plasma-assisted methods. The quickly attained surface saturation also results in faster diffusion kinetics. Furthermore, plasma carburizing can produce very uniform case depths, even in parts with irregular surfaces (Ref 4, 5). This uniformity is caused by the glow-discharge plasma, which closely envelops the specimen surface, provided that recesses or holes are not too small (Ref 5).

With the conventional methods, carburization always takes place by means of a gaseous phase of carbon monoxide; however, each method also involves different reaction and surface kinetics, producing different case-hardening results. In general, with conventional methods, carbon monoxide dissociates at the steel surface:



The liberated carbon is readily dissolved by the austenite phase and diffuses into the body of the steel. For some process methods (gas and pack carburizing), the carbon dioxide produced may react with the carbon atmosphere or pack charcoal to produce new carbon monoxide by the reverse reaction of Eq 2. Because the reaction can proceed in both directions, an equilibrium relationship exists between the constituents (Fig. 4). If the temperature is increased at constant pressure, more carbon monoxide is produced (Fig. 4). In turn, the equilibrium percentages of carbon monoxide and carbon dioxide influence the carbon concentrations in steel (Fig. 5).

Quantitative algorithms for estimating case depth from carburization often focus on making the proportional relation of Eq 1 explicit (Case depth = $K\sqrt{\text{Time}}$) for gas carburization only (Ref 2, 3). However, even in gas carburization, the kinetics of carbon diffusion gives an incomplete picture of carburizing. A

comprehensive model of gas carburization must include algorithms that describe:

- Carbon diffusion
- Kinetics of the surface reaction
- Effects of steel chemistry
- Kinetics of the reaction between endogas and enriching gas
- Purging (for batch processes)
- Atmosphere control system

Reference 8 discusses possible modeling of each of these factors for gas carburization. The effects of process variables are also covered in the article "Gas Carburizing" in this Volume.

Selective Carburizing. Sometimes it is necessary to prevent carburization on certain areas of a part. For example, carburization prevention may be necessary on areas to be machined further after heat treating, or to prevent a thin area from being carburized all the way through its section, thereby becoming brittle (Ref 3). Preventing carburization in selective areas can be done with mechanical masking, stop-off compounds, or copper plating (see the article "Stop-off Technologies for Heat Treatment" for more details). Close attention to cleanliness and handling is needed to achieve the desired stop-off, and application instructions should be closely followed to achieve effective and good results. In copper plate thicknesses of approximately 0.03 mm (0.001 in.) are required.

After case hardening, selective areas of the workpieces also can be "softened" by induction tempering. External threads of gears or shafts are typical applications. This method is not suitable for steels of high hardenability. Another method of selective hardening is to remove case prior to quenching. The areas of the part that were machined after the carburize cycle will only show the core hardness because

the case layer had been removed prior to quench.

Carbonitriding

Carbonitriding is a surface-hardening heat treatment that introduces carbon and nitrogen into the austenite of steel. This treatment is similar to carburizing in that the austenite composition is changed and high surface hardness is produced by quenching to form martensite. However, because nitrogen enhances hardenability, carbonitriding makes possible the use of low-carbon steel to achieve surface hardness equivalent to that of high-alloy carburized steel without the need for drastic quenching, resulting in less distortion and minimizing potential for cracks. In some cases, hardening may be dependent on nitride formation.

Although the process of carbonitriding can be performed with gas atmospheres or salt baths, the term *carbonitriding* often refers solely to treatment in a gas atmosphere (see the article "Carbonitriding of Steels" in this Volume). Basically, carbonitriding in a salt bath is the same as cyanide bath hardening. In both processes, nitrogen enhances hardenability and case hardness but inhibits the diffusion of carbon. In many instances, carbonitriding of coarse-grained steels is more appropriate than carburizing, because of the lower temperatures and shorter cycle times.

Like carbon, nitrogen is an austenite stabilizer. Therefore, considerable austenite may be retained after quenching a carburized part. If the retained austenite content is so high that it reduces hardness and wear resistance, it may be controlled by reducing the ammonia content of the carbonitriding gas either throughout the cycle or during the latter portion of the cycle. Another result of excessive nitrogen content in the carbonitrided case is porosity (see the article "Carbonitriding of Steels" in this Volume).

Nitriding and Nitrocarburizing

Nitriding is a surface-hardening heat treatment 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 partial solubility in iron. It can form a solid solution with ferrite at nitrogen contents up to approximately 6%. At approximately 6% N, a compound called gamma prime (γ'), with a

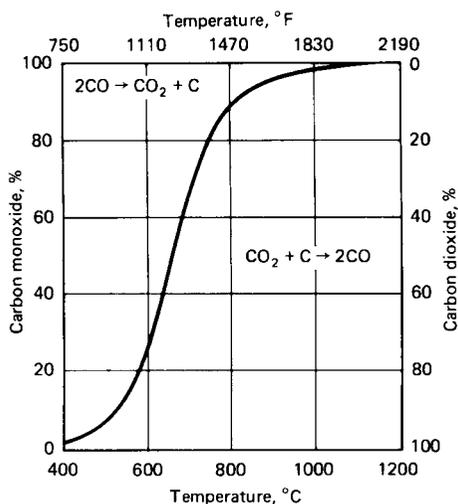


Fig. 4 Equilibrium diagram for reaction $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$ at pressure of one atmosphere. Source: Ref 6

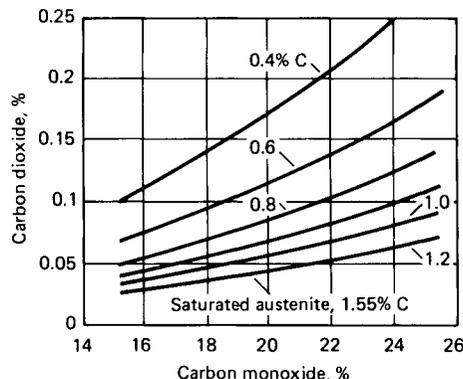


Fig. 5 Equilibrium percentages of carbon monoxide and carbon dioxide required to maintain various carbon concentrations at 975 °C (1790 °F) in plain carbon and certain low-alloy steels. $K = 89.67$. Source: Ref 7

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 γ' , 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

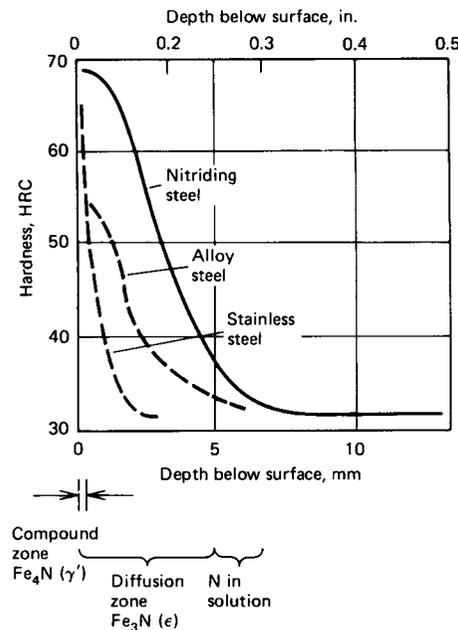


Fig. 6 Nitride case profiles for various steels. Source: Ref 1

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

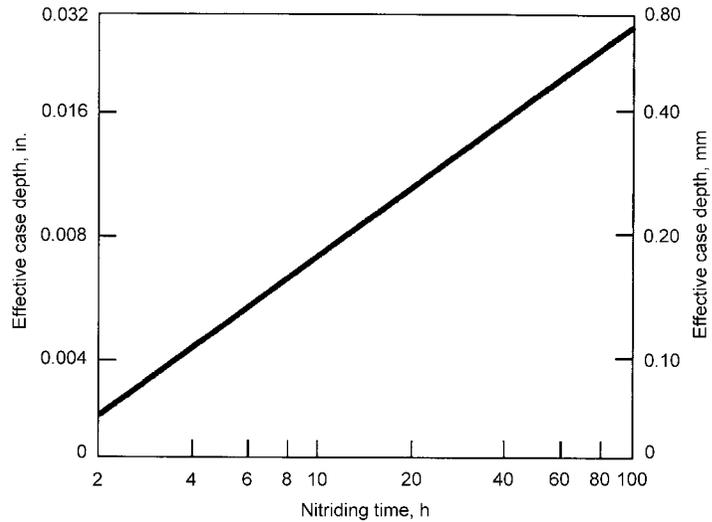
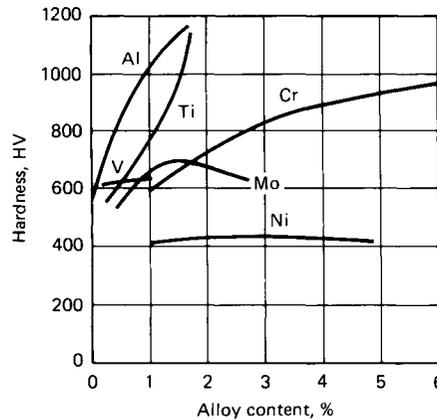
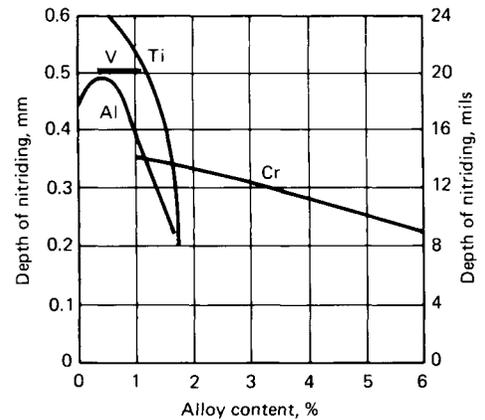


Fig. 7 Nominal time for different nitrided case depths. Source: Ref 9



(a)



(b)

Fig. 8 Influence of alloying elements on (a) hardness after nitriding (base alloy, 0.35% C, 0.30% Si, 0.70% Mn) and (b) 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 Nitalloy 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 Nitalloy 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 austenitic 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 μm (0.01 to 0.03 in.) and for cast irons are approximately 1000 μm (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

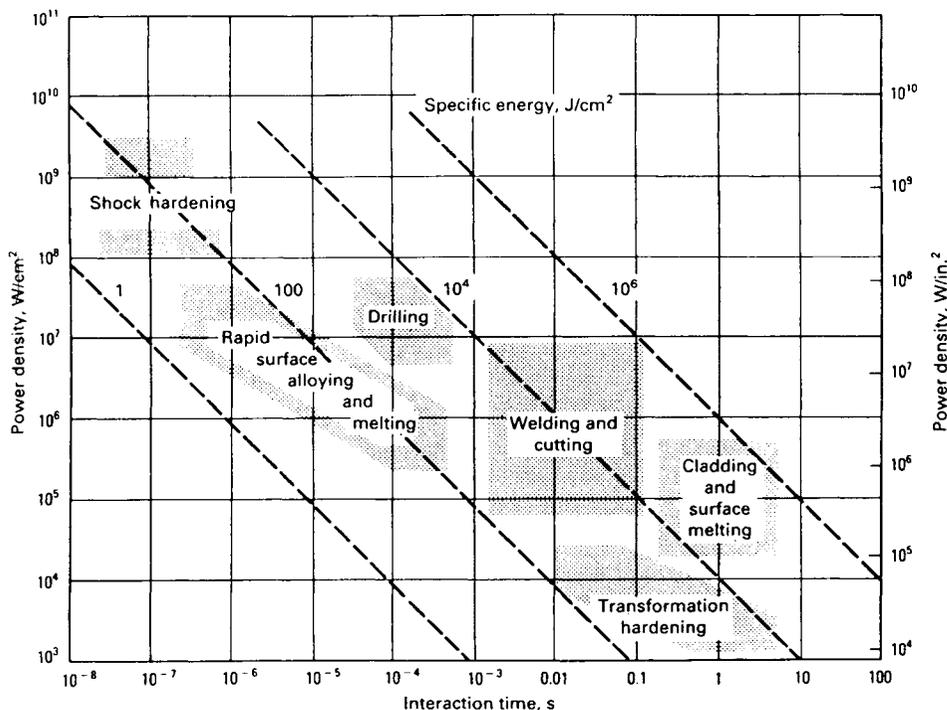


Fig. 9 Interaction times and power densities necessary for various laser surface modification processes

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 ($\geq 10^{-5}$ torr, or 1.3×10^{-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 μm , 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.

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