

Introduction to Surface Hardening of Steels*

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

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

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:

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

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

* Revised from S. Lampman, 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,

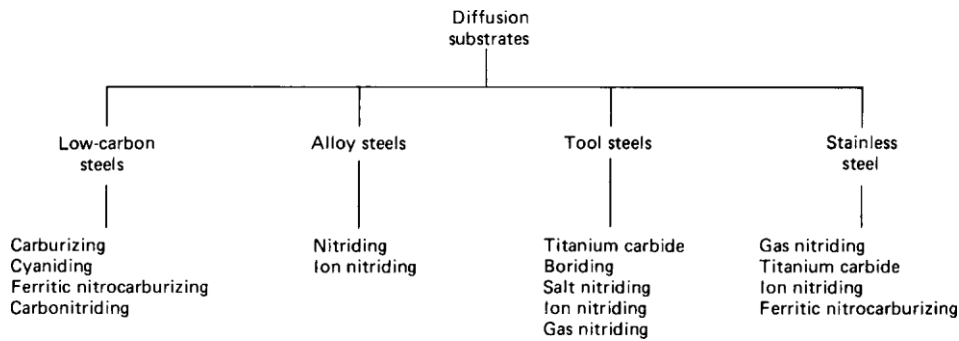


Fig. 1 Types of steels used for various diffusion processes

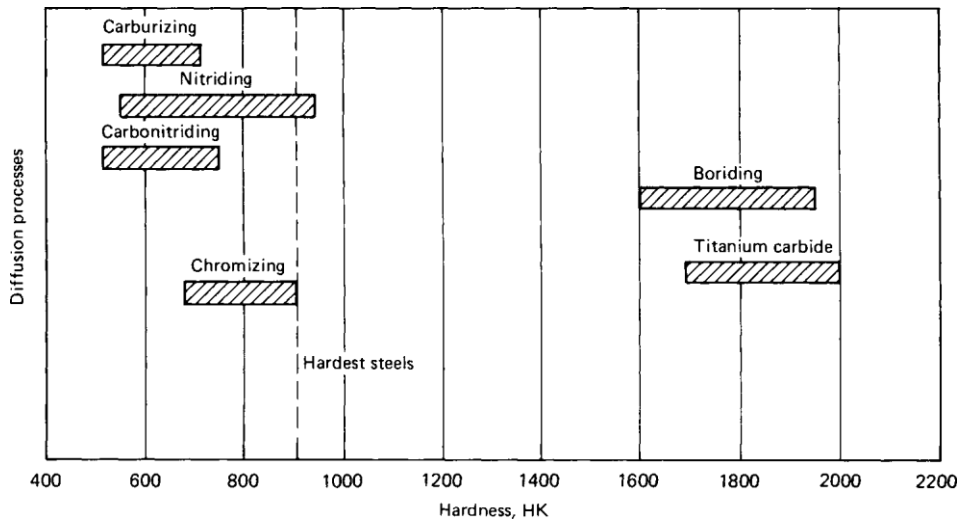


Fig. 2 Spectrum of hardness obtainable with selected diffusion processes of steel

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 re-quench 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

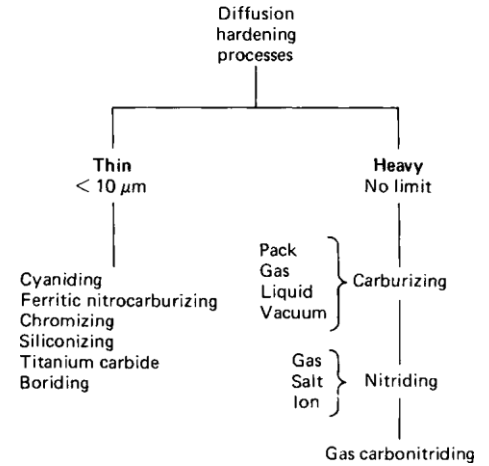


Fig. 3 Categorization of diffusion processes by typical case depth

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.

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 $\propto \sqrt{K \text{ Time}}$) 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).

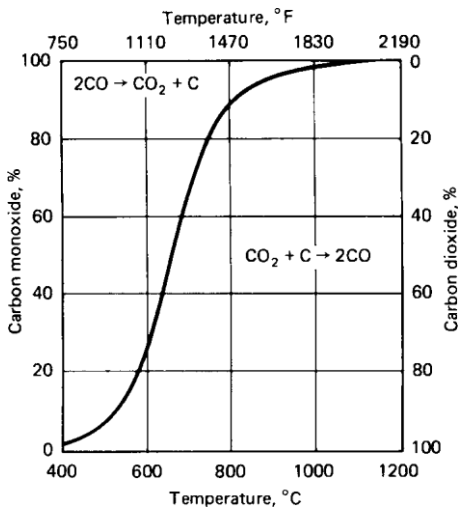


Fig. 4 Equilibrium diagram for reaction $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$ at pressure of one atmosphere. Source: Ref 6

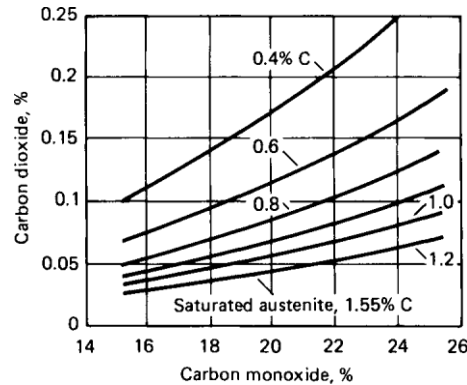


Fig. 5 Equilibrium percentages of carbon monoxide and carbon dioxide required to maintain various carbon concentrations at 975 °C (1790 °F) in plain carbon and certain low-alloy steels. $K = 89.67$. Source: Ref 7