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 on impact is useful in parts such as a cam or ring gear that must have a very hard surface to resist wear, along with a tough interior to resist the impact that occurs during operation. Further, the surface hardening of steel has an advantage over through hardening, because less expensive low- and medium-carbon steels can be surface hardened without the problems of distortion and cracking associated with the through hardening of thick sections.

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

- Thermochemical diffusion methods, which modify the chemical composition of the surface with hardening species such as carbon, nitrogen, and boron. Diffusion methods 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.
- Applied energy or thermal methods, which do not modify the chemical composition of the surface but rather improve properties by altering the surface metallurgy; that is, they produce a hard quenched surface without additional alloying species.
- Surface coating or surface-modification methods, which involve the intentional buildup of a new layer on the steel substrate or, in the case of ion implantation, alter the subsurface chemical composition.

Each of these approaches for surface hardening is briefly reviewed in this chapter, with emphasis placed on process comparisons to facilitate process selection. More detailed information on the various methods described can be found in subsequent chapters.

### Table 1 Engineering methods for surface hardening of steels

<table>
<thead>
<tr>
<th>Diffusion methods</th>
<th>Applied energy methods</th>
<th>Coating and surface modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carburizing</td>
<td>Flame hardening</td>
<td>Hard chromium plating</td>
</tr>
<tr>
<td>Nitriding</td>
<td>Induction hardening</td>
<td>Electroless nickel plating</td>
</tr>
<tr>
<td>Carbonitriding</td>
<td>Laser beam hardening</td>
<td>Thermal spraying</td>
</tr>
<tr>
<td>Nitrocarburizing</td>
<td>Electron beam hardening</td>
<td>Weld hardfacing</td>
</tr>
<tr>
<td>Boriding</td>
<td></td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>Thermal diffusion process</td>
<td></td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ion implantation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Laser surface processing</td>
</tr>
</tbody>
</table>

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 species into the surface and subsurface regions of a part. The depth of diffusion exhibits a time-temperature dependence such that:

\[
\text{Case depth} \propto K \sqrt{\text{Time}} \quad (\text{Eq 1})
\]

where the diffusivity constant, \( K \), depends on temperature, the chemical composition of the
steel, and the concentration gradient of a given hardening species. 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 species (such as carbon, nitrogen, or boron) and of the process method used to handle and transport the hardening species 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, the desired case hardness, and the case depth.

It is also important to distinguish between total case depth and effective case depth. The effective case depth is typically approximately two-thirds to three-fourths the total case depth. The required effective depth must be specified so that the heat treater can process the parts for the correct time at the proper temperature.

**Carburizing**

Carburizing is the addition of carbon to the surface of low-carbon steels at temperatures (generally between 850 and 950 °C, or 1560 and 1740 °F) at which austenite, with its high solubility for carbon, is the stable crystal structure. Hardening of the component is accomplished by removing the part and quenching or allowing the part to slowly cool and then reheating to the austenitizing temperature to maintain the very hard surface property. On quenching, a good wear- and fatigue-resistant high-carbon martensitic case is superimposed on a tough, low-carbon steel core. Carburized steels used in case-hardening usually have base carbon contents of approximately 0.2 wt%, with the carbon content of the carburized layer being fixed between 0.8 and 1.0 wt%. Carburizing methods include gas carburizing, vacuum carburizing, plasma (ion) carburizing, salt bath carburizing, and pack carburizing. These methods introduce carbon by use of an atmosphere (atmospheric gas, plasma, and vacuum), liquids (salt bath), or solid compounds (pack). The vast majority of carburized parts are processed by gas carburizing, using natural gas, propane, or butane. Vacuum and plasma carburizing are useful because of the absence of oxygen in the furnace atmosphere. Salt bath and pack carburizing have little commercial importance but are still done occasionally.

**Gas carburizing** can be run as a batch or a continuous process. Furnace atmospheres consist of a carrier gas and an enriching gas. The carrier gas is supplied at a high flow rate to ensure a positive furnace pressure, minimizing air entry into the furnace. The type of carrier gas affects the rate of carburization. Carburization by methane is slower than by the decomposition of carbon monoxide (CO). The enriching gas provides the source of carbon and is supplied at a rate necessary to satisfy the carbon demand of the work load.

Most gas carburizing is done under conditions of controlled carbon potential by measurement of the CO and carbon dioxide (CO₂) content. The objective of the control is to maintain a constant carbon potential by matching the loss in carbon to the workpiece with the supply of enriching gas. The carburization process is complex, and a comprehensive model of carburization requires algorithms that describe the various steps in the process, including carbon diffusion, kinetics of the surface reaction, kinetics of the reaction between the endogas and enriching gas, purging (for batch processes), and the atmospheric control system.

**Vacuum carburizing** is a nonequilibrium, boost-diffusion-type carburizing process in which austenitizing takes place in a rough vacuum, followed by carburization in a partial pressure of hydrocarbon gas, diffusion in a rough vacuum, and then quenching in either oil or gas. Vacuum carburizing offers the advantages of excellent uniformity and reproducibility because of the improved process control with vacuum furnaces, improved mechanical properties due to the lack of intergranular oxidation, and reduced cycle time. The disadvantages of vacuum carburizing are predominantly related to equipment costs and throughput.

**Plasma (ion) carburizing** is basically a vacuum process using glow-discharge technology to introduce carbon-bearing ions to the steel surface for subsequent diffusion. This process is effective in increasing carburization rates, because the process bypasses several dissociation steps that produce active soluble carbon. For example, because of the ionizing effect of the plasmas, active carbon for adsorption can be formed directly from methane (CH₄) gas. High temperatures can be used in plasma carburizing,
### Table 2  Typical characteristics of diffusion treatments

<table>
<thead>
<tr>
<th>Process</th>
<th>Nature of case</th>
<th>Process temperature, °C (°F)</th>
<th>Typical case depth, µm</th>
<th>Case hardness, HRC</th>
<th>Typical base metals</th>
<th>Process characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carburizing</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pack</td>
<td>Diffused carbon</td>
<td>815–1090 (1500–2000)</td>
<td>125 µm–1.5 mm</td>
<td>50–63(a)</td>
<td>Low-carbon steels, low-carbon alloy steels</td>
<td>Low equipment costs, difficult to control case depth accurately</td>
</tr>
<tr>
<td>Gas</td>
<td>Diffused carbon</td>
<td>815–980 (1500–1800)</td>
<td>75 µm–1.5 mm</td>
<td>50–63(a)</td>
<td>Low-carbon steels, low-carbon alloy steels</td>
<td>Good control of case depth, suitable for continuous operation, high gas controls required, can be dangerous</td>
</tr>
<tr>
<td>Liquid</td>
<td>Diffused carbon</td>
<td>815–980 (1500–1800)</td>
<td>50 µm–1.5 mm</td>
<td>50–65(a)</td>
<td>Low-carbon steels, low-carbon alloy steels</td>
<td>Faster than pack and gas processes, can pose salt disposal problem, salt baths require frequent maintenance</td>
</tr>
<tr>
<td>Vacuum</td>
<td>Diffused carbon</td>
<td>815–1090 (1500–2000)</td>
<td>75 µm–1.5 mm</td>
<td>50–63(a)</td>
<td>Low-carbon steels, low-carbon alloy steels</td>
<td>Excellent process control, bright parts, faster than gas carburizing, high equipment costs</td>
</tr>
<tr>
<td><strong>Nitriding</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>Diffused nitrogen,</td>
<td>480–590 (900–1100)</td>
<td>125 µm–0.75 mm</td>
<td>50–70</td>
<td>Alloy steels, nitriding steels, stainless steels</td>
<td>Hardest cases from nitriding steels, quenching not required, low distortion, process is slow, it usually a batch process</td>
</tr>
<tr>
<td>Sack</td>
<td>Nitrogen compounds</td>
<td>510–565 (950–1050)</td>
<td>2.5 µm–0.75 mm</td>
<td>50–70</td>
<td>Most ferrous metals including cast irons</td>
<td>Usually used for thin hard cases &lt;25 µm (1 mil), no white layer, most are proprietary processes</td>
</tr>
<tr>
<td>Ion</td>
<td>Nitrogen compounds</td>
<td>340–565 (650–1050)</td>
<td>75 µm–0.75 mm</td>
<td>50–70</td>
<td>Alloy steels, nitriding steels, stainless steels</td>
<td>Faster than gas nitriding, no white layer, high equipment costs, close case control</td>
</tr>
<tr>
<td><strong>Carbonitriding</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>Diffused carbon</td>
<td>760–870 (1400–1600)</td>
<td>75 µm–0.75 mm</td>
<td>50–65(a)</td>
<td>Low-carbon steels, low-carbon alloy steels</td>
<td>Lower temperature than carburizing (less distortion), slightly harder case than carburizing, gas control critical</td>
</tr>
<tr>
<td>Liquid (cyaniding)</td>
<td>Diffused carbon</td>
<td>760–870 (1400–1600)</td>
<td>2.5–125 µm</td>
<td>50–65(a)</td>
<td>Low-carbon steels</td>
<td>Good for thin cases on noncritical parts, batch process, salt disposal problems</td>
</tr>
<tr>
<td>Ferritic</td>
<td>Nitrocarburizing</td>
<td>565–675 (1050–1250)</td>
<td>2.5–25 µm</td>
<td>40–60(a)</td>
<td>Low-carbon steels</td>
<td>Low-distortion process for thin case on low-carbon steel, most processes are proprietary</td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boriding</td>
<td>Diffused boron</td>
<td>400–1150 (750–2100)</td>
<td>12.5–50 µm</td>
<td>40–70</td>
<td>Alloy steels, tool steels, cobalt and nickel alloys</td>
<td>Produces a hard compound layer, mostly applied over hardened tool steels, high process temperature can cause distortion</td>
</tr>
<tr>
<td>Thermal diffusion</td>
<td>Carburized layers</td>
<td>800–1250°C (1475–2285 °F)</td>
<td>2–20 µm</td>
<td>&gt;70</td>
<td>Tool steels, alloy steels, medium-carbon steels</td>
<td>Produces a hard compound layer, mostly applied over hardened tool steels, high process temperature can cause distortion</td>
</tr>
</tbody>
</table>

(a) Requires quench from austenitizing temperature
because the process takes place in an oxygen-free vacuum, thus producing a greater carburized case depth than both atmospheric gas and vacuum carburizing.

**Salt bath or liquid carburizing** is a method of case hardening steel in a molten salt bath that contains the chemicals required to produce a case comparable with one resulting from gas or pack carburizing. Carburizing in liquid salt baths provides a convenient method of case hardening, with low distortion and considerable flexibility and uniformity of control of the case. However, the expense and environmental problems associated with disposing of salt baths, particularly those containing cyanide, have limited the use of this process, although non-cyanide-containing salts have been developed.

**Pack carburizing** is the oldest carburizing process. In this case-hardening method, parts are packed in a blend of coke and charcoal with “activators” and then heated in a closed container. Although a labor-intensive process, pack carburizing is still practiced in some tool rooms, because facility requirements are minimal.

### Nitriding

Nitriding is a process similar to carburizing, in which nitrogen is diffused into the surface of a ferrous product to produce a hard case. Unlike carburizing, nitrogen is introduced between 500 and 550 °C (930 and 1020 °F), which is below the austenite formation temperature (Ac1) for ferritic steels, and quenching is not required. As a result of not austenitizing and quenching to form martensite, nitriding results in minimum distortion and excellent control. The various nitriding processes (Table 2) include gas nitriding, liquid nitriding, and plasma (ion) nitriding.

**Gas nitriding** is a case-hardening process that takes place in the presence of ammonia gas. Either a single-stage or a double-stage process can be used when nitriding with anhydrous ammonia. The single-stage process, in which a temperature of 495 to 525 °C (925 to 975 °F) is used, produces the brittle nitrogen-rich compound zone known as the white nitride layer at the surface of the nitrided case. The double-stage process, or Floe process, has the advantage of reducing the white nitrided layer thickness. After the first stage, a second stage is added either by continuing at the first-stage temperature or increasing the temperature to 550 to 565 °C (1025 to 1050 °F). The use of the higher-temperature second stage lowers the case hardness and increases the case depth.

**Liquid nitriding** (nitriding in a molten salt bath) uses temperatures similar to those used in gas nitriding and a case-hardening medium of molten, nitrogen-bearing, fused salt bath containing either cyanides or cyanates. Similar to salt bath carburizing, liquid nitriding has the advantage of processing finished parts because dimensional stability can be maintained due to the subcritical temperatures used in the process. Furthermore, at the lower nitriding temperatures, liquid nitriding adds more nitrogen and less carbon to ferrous materials than that obtained with high-temperature treatments because ferrite has a much greater solubility for nitrogen (0.4% max) than carbon (0.02% max).

**Plasma (ion) nitriding** is a method of surface hardening using glow-discharge technology to introduce nascent (elemental) nitrogen to the surface of a metal part for subsequent diffusion into the material. The process is similar to plasma carburizing in that a plasma is formed in a vacuum using high-voltage electrical energy, and the nitrogen ions are accelerated toward the workpiece. The ion bombardment heats the part, cleans the surface, and provides active nitrogen. The process provides better control of case chemistry, case uniformity, and lower part distortion than gas nitriding.

### Carbonitriding and Ferritic Nitrocarburizing

**Carbonitriding** introduces both carbon and nitrogen into the austenite of the steel. The process is similar to carburizing in that the austenite composition is enhanced and the high surface hardness is produced by quenching to form martensite. This process is a modified form of gas carburizing in which ammonia is introduced into the gas-carburizing atmosphere. As in gas nitriding, elemental nitrogen forms at the work-piece surface and diffuses along with carbon into the steel. Typically, carbonitriding takes place at a lower temperature and a shorter time than gas carburizing, producing a shallower case. Steels with carbon contents up to 0.2% are commonly carbonitrided.

**Ferritic nitrocarburizing** is a subcritical heat treatment process, carried out by liquid, gaseous, or plasma techniques, and involves the diffusion of carbon and nitrogen into the ferritic phase. The process results in the formation of a thin white layer or compound layer with an underlying diffusion zone of dissolved nitrogen in iron, or alloy nitrides. The white layer improves surface resistance to wear, and the dif-
fusion zone increases the fatigue endurance limit, especially in carbon and low-alloy steels. Alloy steels, cast irons, and some stainless steels can be treated. The process is used to produce a thin, hard skin, usually less than 25 μm (1 mil) thick, on low-carbon steels in the form of sheet metal parts, powder metallurgy parts, small shaft sprockets, and so forth.

**Boriding**

Boriding, or boronizing, is a thermochemical surface-hardening process that can be applied to a wide variety of ferrous, nonferrous, and cermet materials. The boronizing pack process is similar to pack carburizing, with the parts to be coated being packed with a boron-containing compound such as boron powder or ferroboron. Activators such as chlorine and fluorine compounds are added to enhance the production of the boron-rich gas at the part surface. Processing of high-speed tool steels that were previously quenched hardened is accomplished at 540 °C (1000 °F). Boronizing at higher temperatures up to 1090 °C (2000 °F) causes diffusion rates to increase, thus reducing the process time. The boron case does not have to be quenched to obtain its high hardness, but tool steels processed in the austenitizing temperature range need to be quenched from the coating temperature to harden the substrate.

Boriding is most often applied to tool steels or other substrates that are already hardened by heat treatment. The thin (12 to 15 μm, or 0.48 to 0.6 mil) boride compound surfaces provide even greater hardness, improving wear service life. Distortion from the high processing temperatures is a major problem for boronized coatings. Finished parts that are able to tolerate a few thousandths of an inch (75 μm) distortion are better suited for this process sequence, because the thin coating cannot be finish ground.

**Thermal Diffusion Process**

The thermal diffusion (TD) process is a method of coating steels with a hard, wear-resistant layer of carbides, nitrides, or carbonitrides. In the TD process, the carbon and nitrogen in the steel substrate diffuse into a deposited layer with a carbide-forming or nitride-forming element, such as vanadium, niobium, tantalum, chromium, molybdenum, or tungsten. The diffused carbon or nitrogen reacts with the carbide- and nitride-forming elements in the deposited coating to form a dense and metallurgically bonded carbide or nitride coating at the substrate surface.

The hard alloy carbide, nitride, and carbonitride coatings in the TD method can be applied to steels by means of salt bath processing or fluidized beds. The salt bath method uses molten borax with additions of carbide-forming elements, such as vanadium, niobium, titanium, or chromium, which combine with carbon from the substrate steel to produce alloy carbide layers. Because the growth of the layers is dependent on carbon diffusion, the process requires a relatively high temperature, from 800 to 1250 °C (1470 to 2280 °F), to maintain adequate coating rates. Carbide coating thicknesses of 4 to 7 μm are produced in 10 min to 8 h, depending on bath temperature and type of steel. The coated steels may be cooled and reheated for hardening, or the bath temperature may be selected to correspond to the steel austenitizing temperature, permitting the steel to be quenched directly after coating.

**Surface Hardening by Applied Energy**

The surface methods described in this section include conventional thermal treatments, such as flame and induction hardening, and technologies that incorporate high-energy laser or electron beams. All of these methods may be classified as simply a thermal treatment without chemistry changes. They can be used to harden the entire surface or localized areas. When localized heating is carried out, the term selective surface hardening is used to describe these methods.

**Flame hardening** consists of austenitizing the surface of steel by heating with an oxyacetylene or oxyhydrogen torch and immediately quenching with water. After quenching, the microstructure of the surface layer consists of hard martensite over a lower-strength interior core of other steel morphologies, such as ferrite and pearlite. A prerequisite for proper flame hardening is that the steel must have adequate carbon and other alloy additions to produce the desired hardness, because there is no change in composition. Flame-hardening equipment uses direct impingement of a high-temperature flame or high-velocity combustion product gases to austenitize the component surface and quickly cool the surface faster than the critical cooling rate to produce martensite in the steel. This is necessary because the hardenability of the component is fixed by the original composition of
the steel. Thus, equipment design is critical to the success of the operation. Flame-heating equipment may be a single torch with a specially designed head or an elaborate apparatus that automatically indexes, heats, and quenches parts. With improvements in gas-mixing equipment, infrared temperature measurement and control, and burner rig design, flame hardening has been accepted as a reliable heat treating process that is adaptable to general or localized surface hardening for small or 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 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: the higher the frequency is, 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 production line areas. Table 3 compares the flame- and induction-hardening processes.

**Laser surface heat treatment** is widely used to harden localized areas of steel and cast iron machine components. The heat generated by the absorption of the laser light is controlled to prevent melting and is therefore used in the selective austenitization of local surface regions, which transform to martensite as a result of rapid cooling (self-quenching) by the conduction of heat into the bulk of the workpiece. This process is sometimes referred to as laser transformation hardening to differentiate it from laser surface melting phenomena. There is no chemistry change produced by laser transformation hardening, and the process, similar to induction and flame hardening, provides an effective technique to harden ferrous materials selectively.

The process produces typical case depths for steel ranging from 0.75 to 1.3 mm (0.030 to 0.050 in.), depending on the laser power range, and hardness values as high as 60 HRC. Laser processing has advantages over electron beam hardening in that laser hardening does not require a vacuum, wider hardening profiles are possible, and there can be greater accessibility to hard-to-get areas with the flexibility of optical manipulation of light energy.

**Electron Beam Hardening.** In electron beam hardening, the surface of the hardenable steel is heated rapidly to the austenitizing temperature, usually with a defocused electron beam to prevent melting. The mass of the workpiece conducts the heat away from the treated surface at a rate that is rapid enough to produce hardening. Materials for application of electron beam hardening must contain sufficient carbon and alloy content to produce martensite. With the rapid heating associated with this process, the carbon and alloy content should be in a form that quickly allows complete solid solution in the austenite at the temperatures produced by the electron beam. In addition, the mass of the workpiece should be sufficient to allow proper quenching; for example, the part thickness must be at least ten times the depth of hardening, and hardened areas must be properly spaced to prevent tempering of previously hardened areas.

To produce an electron beam, a high vacuum of 10^-3 Pa (10^-5 torr) is required in the region where the electrons are emitted and accelerated. This vacuum environment protects the emitter

---

Table 3 Comparison of flame- and induction-hardening processes

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Flame</th>
<th>Induction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>Oxyfuel torch,</td>
<td>Power supply,</td>
</tr>
<tr>
<td></td>
<td>special head</td>
<td>inductor,</td>
</tr>
<tr>
<td></td>
<td>quench system</td>
<td>quench system</td>
</tr>
<tr>
<td>Applicable material</td>
<td>Ferrous alloys,</td>
<td>Same</td>
</tr>
<tr>
<td></td>
<td>carbon steels,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>alloy steels,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cast irons</td>
<td></td>
</tr>
<tr>
<td>Speed of heating</td>
<td>Few seconds to</td>
<td>1–10 s</td>
</tr>
<tr>
<td></td>
<td>few minutes</td>
<td></td>
</tr>
<tr>
<td>Depth of hardening</td>
<td>1.2–6.2 mm</td>
<td>0.4–1.5 mm</td>
</tr>
</tbody>
</table>
|                         | (0.050–0.250 in.)| (0.015–0.060 in.);
|                         |                  | 0.1 mm (0.004 in.)|
| Processing              | One part at a    | Same              |
| Part size               | time             |                   |
| Tempering               | Required         | Must fit in coil |
| Can be automated        | Yes              | Same              |
| Operator skills         | Significant skill| Little skill      |
|                         | required         | required after   |
| Control of process      | Attention required| setup            |
| Operator comfort        | Hot, eye protection| Very precise     |
|                         | required         | Can be done in   |
|                         |                   | suit             |
| Cost                    | Equipment Low    | High              |
| Per piece               | Best for large   | Best for small    |
|                         | work             | work              |
from oxidizing and avoids scattering of the electrons while they are still traveling at a relatively low velocity. Electron beam hardening in hard vacuum units requires that the part be placed in a chamber that is sufficiently large to manipulate the electron beam gun or the workpiece. Out-of-vacuum units usually involve shrouding the workpiece; a partial vacuum (13 Pa, or $10^{-2}$ torr), is obtained in the work area by mechanical pumps.

**Surface Hardening by Coating or Surface Modification**

Plating or coating treatments deposit hard surface layers of completely different chemistry, structure, and properties on steel substrates and are applied by well-established technologies such as electrodeposition, electroless deposition, thermal spraying, and weld hardfacing. In more recent years, coating or surface-modification methods long used in the electronics industry to fabricate thin films and devices have been used to treat steels. These include vapor deposition techniques and ion implantation. Laser surface processing (melting, alloying, and cladding) has also been carried out on steels. These various surface-engineering treatments can deposit very thin films (e.g., 1 to 10 µm for physical vapor deposition) or thick coatings (e.g., 3 to 10 mm for weld hardfacing).

**Hard Chromium Plating**

**Process Description.** Hard chromium plating is produced by electrodeposition from a solution containing chromic acid ($\text{CrO}_3$) and a catalytic anion in proper proportion. The metal so produced is extremely hard (850 to 1000 HV) and corrosion resistant. Plating thickness ranges from 2.5 to 500 µm (0.1 to 20 mils).

**Applications.** Hard chromium plating is used for products such as piston rings, shock absorbers, struts, brake pistons, engine valve stems, cylinder liners, and hydraulic rods. Other applications are for aircraft landing gears, textile and gravure rolls, plastic rolls, and dies and molds. The rebuilding of mismatched or worn parts comprises large segments of the industry.

**Advantages:**
- Low-temperature treatment (60 °C, or 140 °F)
- High hardness and wear resistance

**Disadvantages:**
- Poor thickness uniformity on complex components
- Hydrogen embrittlement
- Environmental problems associated with plating bath disposal. Chromium replacement coatings, such as electroless nickel and thermal spray coatings, are being used increasingly.

**Electroless Nickel Coating**

**Process Description.** The coating is deposited by an autocatalytic chemical reduction of nickel ions by hydrophosphite, amino-borane, or borohydride compounds. Currently, hot acid hypophosphite-reduced baths are most frequently chosen to coat steel. Heat-treated deposit hardness exceeds 1000 HV.

**Applications.** Electroless nickel coatings have good resistance to corrosion and wear and are used to protect machinery found in the petroleum, chemicals, plastics, optics, printing, mining, aerospace, nuclear, automotive, electronics, computers, textiles, paper, and food industries.

**Advantages:**
- Low-temperature treatment (<100 °C, or 212 °F)
- More corrosion resistance than electroplated chromium
- Ability to coat complex shapes uniformly
- Incorporation of hard particles to increase hardness
- Good solderability and brazeability

**Disadvantages:**
- Higher costs than electroplating
- Poor welding characteristics
- Slower plating rate, as compared to rates for electrolytic methods
- Heat treatment needed to develop optimal properties

**Thermal Spraying**

**Process Description.** Thermal spraying is a generic term for a group of processes in which a metallic, ceramic, cermets, and some polymeric materials in the form of powder, wire, or rod are fed to a torch or gun with which they are heated to
or slightly above their melting point. The resulting molten or nearly molten droplets of material are accelerated in a gas stream and projected against the substrate to form a coating. Commonly employed methods of deposited thermal spray coatings can be classified as wire flame spray, powder flame spray, electric arc, plasma spray, and high-velocity oxyfuel (HVOF) spray. Process characteristics are compared in Table 4.

**Applications.** Thermal spray coatings are used for prevention against wear, corrosion, or oxidation. Table 19 in Chapter 11 lists a wide variety of wear-resistant applications for thermal spraying. Thermal spray coatings, particularly HVOF coatings, are being used increasingly to replace chromium electrodeposits.

**Advantages:**
- Most metals, ceramics, and some polymers can be sprayed.
- Significant substrate heating does not occur with most thermal spray processes.
- Worn or damaged coatings can be stripped without changing the properties or dimensions of the part.
- Localized treatments are possible.

**Disadvantages:**
- Line-of-sight process employed.
- Most sprayed coatings contain some porosity.
- The adhesion of sprayed coatings is generally poor, compared to other processes.

### Table 4 Comparison of major thermal spray coating processes

<table>
<thead>
<tr>
<th>Property or characteristic</th>
<th>Coating type</th>
<th>Wire flame spray</th>
<th>Powder flame spray</th>
<th>Electric arc</th>
<th>Plasma spray</th>
<th>High-velocity oxyfuel (HVOF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond strength, MPa (10^3 psi)</td>
<td>Ferrous metals</td>
<td>14 (2)</td>
<td>28 (4)</td>
<td>41 (6)</td>
<td>34+ (5+)</td>
<td>62 (9)</td>
</tr>
<tr>
<td>Nonferrous metals</td>
<td>21 (3)</td>
<td>21 (3)</td>
<td>41+ (6+)</td>
<td>34+ (5+)</td>
<td>70 (10.2)</td>
<td></td>
</tr>
<tr>
<td>Self-fluxing alloys</td>
<td>...</td>
<td>69+ (10+)</td>
<td>...</td>
<td>...</td>
<td>62 (9)</td>
<td></td>
</tr>
<tr>
<td>Ceramics</td>
<td>...</td>
<td>14–34 (2–5)</td>
<td>...</td>
<td>21+ (3+)</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Caricides</td>
<td>...</td>
<td>34–48 (5–7)</td>
<td>...</td>
<td>55–69 (8–10)</td>
<td>83+ (12+)</td>
<td></td>
</tr>
<tr>
<td>Density, % that of equivalent wrought material</td>
<td>Ferrous metals</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>95</td>
<td>98+</td>
</tr>
<tr>
<td>Nonferrous metals</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>95</td>
<td>98+</td>
<td></td>
</tr>
<tr>
<td>Self-fluxing alloys</td>
<td>...</td>
<td>100(a)</td>
<td>...</td>
<td>...</td>
<td>100(a)</td>
<td></td>
</tr>
<tr>
<td>Ceramics</td>
<td>...</td>
<td>95</td>
<td>...</td>
<td>95+</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Caricides</td>
<td>...</td>
<td>90</td>
<td>...</td>
<td>95+</td>
<td>98+</td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>Ferrous metals</td>
<td>84 HRB–35 HRC</td>
<td>80 HRB–35 HRC</td>
<td>95 HRB–40 HRC</td>
<td>80 HRB–40 HRC</td>
<td>90 HRB–50 HRC</td>
</tr>
<tr>
<td>Nonferrous metals</td>
<td>95 HRB–40 HRC</td>
<td>30 HRB–40 HRC</td>
<td>40 HRB–50 HRC</td>
<td>80 HRB–50 HRC</td>
<td>90 HRB–55 HRC</td>
<td></td>
</tr>
<tr>
<td>Self-fluxing alloys</td>
<td>...</td>
<td>30–60 HRC</td>
<td>...</td>
<td>...</td>
<td>50–60 HRC</td>
<td></td>
</tr>
<tr>
<td>Ceramics</td>
<td>...</td>
<td>50–65 HRC</td>
<td>...</td>
<td>50–70 HRC</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Caricides</td>
<td>...</td>
<td>50–60 HRC</td>
<td>...</td>
<td>50–60 HRC</td>
<td>55–65 HRC</td>
<td></td>
</tr>
<tr>
<td>Permeability</td>
<td>Ferrous metals</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
<td>Negligible</td>
</tr>
<tr>
<td>Nonferrous metals</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td>Self-fluxing alloys</td>
<td>...</td>
<td>None(a)</td>
<td>...</td>
<td>...</td>
<td>None(a)</td>
<td></td>
</tr>
<tr>
<td>Ceramics</td>
<td>...</td>
<td>Medium</td>
<td>...</td>
<td>Low</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Caricides</td>
<td>...</td>
<td>Low</td>
<td>...</td>
<td>Negligible</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Coating-thickness limitation, mm (in.)</td>
<td>Ferrous metals</td>
<td>1.25–2.5</td>
<td>1.25–2.5</td>
<td>1.25–2.5</td>
<td>1.25–2.5</td>
<td>1.25–2.5</td>
</tr>
<tr>
<td>Nonferrous metals</td>
<td>1.25–5</td>
<td>1.25–5</td>
<td>1.25–5</td>
<td>1.25–5</td>
<td>1.25–5</td>
<td></td>
</tr>
<tr>
<td>Self-fluxing alloys</td>
<td>...</td>
<td>0.4–2.5</td>
<td>...</td>
<td>1.25</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Ceramics</td>
<td>...</td>
<td>0.4</td>
<td>...</td>
<td>0.4</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Caricides</td>
<td>...</td>
<td>0.4</td>
<td>...</td>
<td>0.4 max</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

(a) Fused coating. (b) Unfused coating
• High-quality coatings on reentrant surfaces produced with difficulty.

**Weld Hardfacing**

**Process Description.** Welding is a solidification method for applying coatings with corrosion, wear, and erosion resistance. Weld-overlay coatings, sometimes referred to as hardfacing, offer unique advantages over other coating systems in that the overlay/substrate weld provides a metallurgical bond that is not susceptible to spallation and can easily be applied free of porosity or other defects. Welded deposits of surface alloys can be applied in thicknesses greater than most other techniques, typically in the range of 3 to 10 mm. Most welding processes are used for application of surface coatings, and on-site deposition can be more easily carried out, particularly for repair purposes.

**Applications.** Hardfacing applications for wear control vary widely, ranging from very severe abrasive wear service, such as rock crushing and pulverizing, to applications to minimize metal-to-metal wear, such as control valves where a few thousandths of an inch of wear is intolerable. Hardfacing is used for controlling abrasive wear, such as encountered by mill hammers, digging tools, extrusion screws, cutting shears, parts of earthmoving equipment, ball mills, and crusher parts. It is also used to control the wear of unlubricated or poorly lubricated metal-to-metal sliding contacts, such as control valves, undercarriage parts of tractors and shovels, and high-performance bearings. Hardfacing also is used to control combinations of wear and corrosion.

**Advantages:**
- Inexpensive
- Applicable to large components
- Localized coating possible
- Excellent coating/substrate adhesion
- High deposition rates possible

**Disadvantages:**
- Residual stresses and distortion can cause serious problems.
- Weld defects can lead to joint failure.
- Minimum thickness limits (it is impractical to produce layers less than 2 to 3 mm thick)
- Limited number of coating materials available, compared to thermal spraying

**Chemical Vapor Deposition (CVD)**

**Process Description.** Chemical vapor deposition involves the formation of a coating on a heated surface by a chemical reaction from the vapor or gas phase. Deposition temperatures are generally in the range of 800 to 1000 °C (1470 to 1830 °F). The most widely deposited wear-resistant coatings are titanium carbide (TiC), titanium nitride (TiN), chromium carbide, and alumina. Thicknesses are restricted to approximately 10 µm due to thermal expansion mismatch stresses that develop on cooling.

**Applications.** The use of the CVD process for steels has been largely limited to the coating of tool steels for wear resistance.

**Advantages:**
- High coating hardness; for example, TiN coatings have a hardness of 2500 HV.
- Good adhesion (provided the coating is not too thick)
- Good throwing power (i.e., uniformity of coating)

**Disadvantages:**
- High-temperature process (distortion a problem)
- Shard edge coating is difficult due to thermal expansion mismatch stresses.
- Limited range of materials can be coated.
- Environmental concerns about process gases

**Physical Vapor Deposition (PVD)**

**Process Description.** Physical vapor deposition processes involve the formation of a coating on a substrate by physical deposition of atoms, ions, or molecules of the coating species. There are three main techniques for applying PVD coatings: thermal evaporation, sputtering, and ion plating. Thermal evaporation involves heating of the material until it forms a vapor that condenses on a substrate to form a coating. Sputtering involves the electrical generation of a plasma between the coating species and the substrate. Ion plating is essentially a combination of these two processes. A comparison of the process characteristics of PVD, CVD, and ion implantation is provided in Table 5.

**Applications.** Similar to CVD, the PVD process is used to increase the wear resistance of tool steels by the deposition of thin TiN or TiC coatings at temperatures ranging from 200 to
550 °C (400 to 1025 °F). This temperature range is much more suitable for the coating of tool steels than the temperatures required for CVD.

**Advantages:**
- Excellent process control
- Low deposition temperature
- Dense, adherent coatings
- Elemental, alloy, and compound coatings possible

**Disadvantages:**
- Vacuum process with high capital cost
- Limited component size treatable
- Relatively low coating rates
- Poor throwing power without manipulation of components

**Ion Implantation**

**Process Description.** Ion implantation involves the bombardment of a solid material with medium- to high-energy ionized atoms and offers the ability to alloy virtually any elemental species into the near-surface region of any substrate. The advantage of such a process is that it produces improved surface properties without the limitations of dimensional changes or delamination found in conventional coatings.

**Applications.** For steels, the most common application of ion implantation is nitrogen-implanted tool steels used for forming and cutting tools. Titanium plus carbon implantation has also proved beneficial for tool steels.

**Advantages:**
- Produces surface alloys independent of thermodynamic criteria
- No delamination concerns
- No significant dimensional changes
- Ambient-temperature processing possible
- Enhance surface properties while retaining bulk properties
- High degree of control and reproducibility

**Disadvantages:**
- Very thin treated layer (1 µm or less)
- High-vacuum process
- Line-of-sight process
- Alloy concentrations dependent on sputtering
- Relatively costly process; intensive training required, compared to other surface-treatment processes
- Limited commercial treatment facilities available

**Laser Surface Processing**

**Process Description.** Laser surface processing involves the melting of a surface with a...
laser, with or without surface additions. With laser surface melting, melting and controlled cooling are combined to refine the microstructure or to produce an amorphous (or nearly amorphous) structure. No external material is added during this process. The composition and properties of the surface can also be modified by adding external material via powder injection or wire feed. External material can also be placed on the surface by powder deposition, electroplating, vapor deposition, or thermal spray, then incorporated by laser scanning. The nature of incorporating material in the modified surface varies depending on laser processing parameters, such as energy density and traverse speed. Alloy, clad, and composite surface layers may be formed in this way.

**Applications.** Although laser surface processing has not reached commercial significance for steels, various carbon and low-alloy steels, tool steels, and stainless steels have been laser processed to varying degrees of success. See Chapter 11 for application examples.

**Advantages:**

- Rapid rates of processing produce novel structures in the surface region not possible with conventional processing.
- For laser cladding, low weld-metal dilution rates and distortion, compared with competing arc welding methods

**Disadvantages:**

- High capital equipment costs
- Some substrate materials are not compatible with the laser thermal conduction requirements.

**Important Considerations for Process Selection**

**Performance Requirements.** The key to proper selection of surface-hardening techniques is in the identification of the performance requirements for a given surface-modified material system in a given application. Not only must the properties of the surface be considered but also the properties of the substrate and the interface between the surface and substrate. In some systems there is a gradual change in properties between the surface and interior, as, for example, in nitrided and carburized components, while in others there is an abrupt change, as, for example, for parts where a coating of vapor-deposited titanium nitride has been deposited on steel. Such interface characteristics may significantly influence the performance of a surface-modified system.

The performance requirements of surface-engineered systems may vary widely. For example, heavily loaded systems, such as bearings and gears, require deep cases to resist rolling contact and bending stresses that result in fatigue damage. Other applications may require only very thin surface films to resist near-surface abrasion or scuffing or to reduce friction between moving surfaces. Many of these requirements are based on complex interactions between applied static and cyclic stress states and gradients in structures and properties of the surface-modified systems (see, for example, the discussion of bending fatigue strength of carburized steels in Chapter 2).

**Design Constraints.** The component design constraints include consideration of the size and shape of the component, because they may affect surface-treatment process capabilities. Will the component fit in the coating equipment? Can a line-of-sight process be used? Do small holes or channels require a process with high throwing power? What kind of masking will be required to prevent coating unwanted areas? Is the temperature required by the surface treatment compatible with the temperature limitations of the component material? What kind of postcoating treatment, including heat treatment and finishing, will be required?

**Economic Analysis.** The economic issue of fundamental importance is a cost/benefit analysis. This analysis should be based on the full life-cycle costs of the surface treatment, including the process costs (preparation, application, finishing, quality control, waste disposal), utilization costs and benefits (productivity of coated components), and added value of any products produced or treated. Other economic factors that must be considered include the availability of the process, number of components to be treated, quality-control requirements, delivery schedules, and so on. Note that the analysis should not be based on just the initial cost of the surface treatment. Life-cycle costs are as important when comparing the cost of various surface treatments as in comparing a surface treatment to an untreated surface.
Process Comparisons

Hardness versus Wear Resistance. The wear processes that are usually mitigated by the use of hard surfaces are low-stress abrasion, wear in systems involving relative sliding of conforming solids, fretting wear, galling, and, to some extent, solid-particle erosion. Unfortunately, there are many caveats to this statement, and substrate/coating selection should be carefully studied, with proper tests carried out if necessary. Coating suppliers should also be consulted. Chapter 3 provides additional information on wear processes and the means to prevent specific types of wear.

Figure 1 shows typical ranges in hardness for many of the surface-engineering processes used to control wear. All of the treatments shown in this figure have hardness values greater than ordinary constructional steel or low-carbon steel. The surface-hardening processes that rely on martensitic transformations all have comparable hardness, and the diffusion treatments that produce harder surfaces are nitriding, boronizing (boriding), and chromizing. The hardest metal coating is chromium plate, although hardened electroless nickel plate can attain values just under that of chromium. The surfaces that exceed the hardness of chromium are the cermets or ceramics or surfaces that are modified so that they are cermets or ceramics. These include nitrides, carbides, borides, and similar compounds. The popular solid ceramics used for wear applications—aluminum oxide, silicon carbide, and silicon nitride—generally have hardnesses in the range of 2000 to 3000 kg/mm². As shown in Fig. 1, when materials such as aluminum oxide are applied by plasma spraying or other thermal spray process, they have hardnesses that are less than the same material in solid pressed-and-sintered form. This is because the sprayed materials contain porosity and oxides that are not contained in the sintered solid form.

Cost must be weighed against the performance required for the surface-treatment system. A low-cost surface treatment that fails to perform its function is a wasted expense. Unfortu-
nately, it is nearly impossible to give absolute comparative costs for different surface-engineering options. Often, a range of prices is offered for a particular job from different, equally competent candidate suppliers. Probably the most important factor that relates to costs of producing a wear-resistant surface on a part is part quantity. Treating many parts usually allows economies in treatment and finishing.

Another consideration when assessing surface-treatment costs is part size. There are some critical sizes for each surface-treatment process above which the cost of obtaining the treatment may be high. A number of surface treatments require that the part fit into the work zone of a vacuum chamber. The cost of vacuum equipment goes up exponentially with chamber volume.

Other factors to be considered are:
- The time required for a given surface treatment
- Fixturing, masking, and inspection costs
- Final finishing costs
- Material costs
- Energy costs
- Labor costs
- Environmentally related costs, for example, disposal of spent plating solutions
- Expected service life of the coating

Because of these various factors, it is difficult to compare costs with a high degree of accuracy. Figure 2 provides some general guidelines for cost comparisons.

**Distortion or Size Change Tendencies.** Figure 3 shows the surface temperatures that are encountered in various surface-engineering processes. As indicated in the figure, the processes are categorized into two groups: one group produces negligible part distortion, and the other group contains processes that have varying potential for causing distortion. Obviously, if a part could benefit from a surface treatment but distortion cannot be tolerated, processes that require minimal heating should be considered.

**Coating Thickness Attainable.** Figure 4 shows the typical thickness/penetration capabilities of various coating and surface treatments. As indicated in the figure, some surface-engineering treatments penetrate into the surface,
Fig. 3 Maximum surface temperatures that can be anticipated for various surface-engineering processes. The dashed vertical line at 540 °C (1000 °F) represents the temperature limit for distortion for ferrous metals. Obviously, a temperature of 540 °C (1000 °F) would melt a number of nonferrous metals, and it would cause distortion on metals such as aluminum or magnesium. However, this process temperature information can be used to compare the heating that will be required for a particular process. EB, electron beam

Fig. 4 Typical coating thickness/depth of penetration for various coating and surface-hardening processes. SAW, submerged arc welding; FCAW, flux cored arc welding; GMAW, gas metal arc welding; PAW, plasma arc welding; GTAW, gas tungsten arc welding; EB, electron beam; OAW, oxyacetylene welding; FLSP, flame spraying; PSP, plasma spraying
and there is no intentional buildup on the surface. Other surface treatments coat or intentionally build up the surface. This is a selection factor. Can a part tolerate a buildup on the surface? If not, the selection process is narrowed to the treatments that penetrate into the surface. Other factors affecting the thickness of a given surface treatment include dimensional requirements, the service conditions, the anticipated/allowable corrosion or wear depth, and anticipated loads on the surface. Questions or concerns related to coating thickness should be discussed with the contractor. Available specifications should also be reviewed.

SELECTED REFERENCES
