METAL SURFACE TREATMENTS

1. Case Hardening

1.1. Introduction. The performance of many metallic components can be markedly improved by developing a surface region which is harder than that of the underlying region. Processes to achieve this are called case hardening. The case is the surface region which is hardened, and the region under the case is called the core (Fig. 1**a**). The original surface region is an intrinsic part of the case, unlike treatments such as electroplating (qv) where material is deposited on the original surface. Although case hardening is at times restricted to processes which change the chemistry of the surface region, eg, carburizing, herein this term is used in a broader sense to represent changing the surface region either physically, such as by cold working or surface heating and quenching, or by altering the chemistry of the surface region by addition of elements, such as by carburizing ion implantation (qv).

There are many characteristics of hard cases that make their development desirable. One is wear resistance. Usually, the process is designed to develop high compressive residual stresses in the surface which counteract tensile stresses induced by the loading condition during use of the component (1) (Fig. 1**b**).

Machine components are commonly subjected to loads, and hence stresses, which vary over time. The response of materials to such loading is usually examined by a fatigue test. The cylinder, loaded elastically to a level below that for plastic deformation, is rotated. Thus the axial stress at all locations on the surface alternates between a maximum tensile value and a maximum compressive value. The cylinder is rotated until fracture occurs, or until a large number of cycles is attained, eg, 10^6. The test is then repeated at a different maximum stress level. The results are presented as a plot of maximum stress, $\sigma_{\max}$, versus number of cycles to fracture. For many steels, there is a maximum stress level below which fracture does not occur called the fatigue strength or fatigue limit. The fatigue fracture begins by formation of a crack at the surface during the tensile stress part of the loading cycle. Failure can be reduced by the presence of compressive residual stresses, and the development of these stresses is an important purpose of case hardening (Fig. 1**b**). The relationship between the residual stress and fatigue strength is given in Table 1 for three types of steel (qv), the most common metallic material that is case hardened, and the material emphasized herein. The three main characteristics to control in case hardening are case depth, case microstructure, and case hardness and strength. The methods and steels chosen for case hardening are closely related to these factors.

1.2. Conventional Hardening of Steels. *The Iron–Carbon Phase Diagram.* The hardening of steels begins with the formation of the high temperature phase austenite, denoted γ, which is iron with a fcc crystal structure. Austenite can dissolve up to about 2 wt % carbon in the interstices between the iron (qv) atoms, where small atoms like carbon locate. Also larger atoms such as manganese and chromium can replace iron atoms on lattice sites. The presence of these alloying elements incorporated into the crystal structure of austenite produces a solid solution. Austenite is stable only above about 723°C

(Fig. 2). At lower temperatures, iron has bcc crystal structure, designated α. In this arrangement of iron atoms, the size of the interstices is much smaller than in the austenite, so that carbon solubility is much less, being a maximum of about 0.02 wt% C at 723°C. Iron combines with carbon to form a high melting temperature compound iron carbide, sometimes called cementite, which has 6.67 wt% C. In heat-treating steels, the precursor structure is austenite. Austenite, ferrite, and Fe_3C phases are the ones of interest herein.

Decomposition of Austenite. In heat-treating steels, the initial step is usually to heat the steel into the austenite region (>723°C) and then control the cooling process to produce the desired structure. The phase diagram (Fig. 2) shows that austenite decomposes into the two phases α and Fe_3C upon cooling to below 723°C (3). The size and distribution of these phases, ie, the microstructure, depend on how the austenite is cooled. This has a critical bearing on the hardness because Fe_3C is very hard, and the smaller the carbide particles and the finer their distribution, the harder the steel.

When a steel is cooled sufficiently rapidly from the austenite region to a low (eg, 25°C) temperature, the austenite decomposes into a nonequilibrium phase not shown on the phase diagram. This phase, called martensite, is body-centered tetragonal. It is the hardest form of steel, and its formation is critical in hardening. To form martensite, the austenite must be cooled sufficiently rapidly to prevent the austenite from first decomposing to the softer structure of a mixture of ferrite and carbide. Martensite begins to form upon reaching a temperature called the martensite start, M_s, and is completed at a lower temperature, the martensite finish, M_f. These temperatures depend on the carbon and alloy content of the particular steel.

When a component at an austenitizing temperature is placed in a quenchant, eg, water or oil, the surface cools faster than the center. The formation of martensite is more favored for the surface. A main function of alloying elements, eg, Ni, Cr, and Mo, in steels is to retard the rate of decomposition of austenite to the relatively soft products. Whereas use of less expensive plain carbon steels is preferred, alloy steels may be required for deep hardening.

Tempering. Although martensite is hard and strong, it is also brittle, and therefore must be heat treated to improve toughness and ductility. This is achieved by reheating the quenched steel to a temperature in the ferrite $+Fe_3C$ region of the phase diagram, eg, <723°C (Fig. 2). During this treatment, the single-phase, metastable martensite decomposes into a structure of fine particles of Fe_3C in ferrite. This heat treatment is called tempering, and the structure is called tempered martensite. The longer the tempering time and the higher the tempering temperature, the coarser the structure. This reduces the hardness and strength but increases ductility and toughness. Thus the desired mechanical properties are obtained by proper choice of the tempering temperature and time.

1.3. Case Hardening by Heat Treatment.

No Chemical Change. By proper choice of the quenching process and the steel, a heat-treated component can be produced that is hard in the surface region, ie, all martensite, and softer in the center portion. However, for many applications the desired properties are obtained if the hardened region (case) is relatively shallow, eg, 0.2 cm. It is difficult to achieve this by conventional methods. Instead, the component is heat treated to achieve desired core properties, eg, low hardness but good ductility. Then only the surface region is heated to the austenite range, which is subsequently cooled rapidly to form martensite. This is case hardening without any chemical change in the surface region.

To prevent the core from attaining a high temperature, the surface is heated using a high energy flux for only a relatively short time. Before the core begins to heat, the energy source is removed and the surface is rapidly cooled, eg, by a water spray. The surface region also cools rapidly by conduction of heat into the cold core. This case hardening heat treatment takes only a short time to heat to the austenite region, and then to cool to room temperature. The short time is an essential characteristic of this type of case hardening.

Because the time at high temperature is much less, austenite is produced, which is chemically inhomogeneous especially with undissolved carbides, and has a fine grain crystal size. The formation of the hard martensite requires more rapid cooling than for conventional hardening. Thus case hardening by heat treatment intrinsically requires that the surface region to be hardened be relatively thin and cooled rapidly.

Case Hardening by Flame Heating. In case hardening by heating with a flame, gas burners of appropriate geometry and configuration are used to heat selected localized or general regions of the surface of the steel component. The case depth is controlled by the burner and flame characteristics, distance from the burner face to the surface of the component, and heating time. Figure 3**a** shows a typical heating curve (4). Note that several seconds are required for the surface region to heat to the temperature range of austenite stability (see Fig. 2). When the desired temperature is reached, the flame is removed and the surface is sprayed with water, cooling the case to room temperature in a few seconds. This is sufficiently rapid to produce some martensite in the case for even plain carbon and low alloy steels. Figure 3**b** shows a typical hardness distribution curve. The flame hardening process can be readily automated.

Case Hardening by Induction Heating. Electric current flow can be induced by placing an electrically conducting material in the vicinity of an alternating magnetic field. If the frequency is sufficiently high (eg, 10^4–10^6 Hz), this current is concentrated in the surface layers. The flow of current causes resistive or Joule heating, so high frequency (eg, 10^4–10^6 Hz) magnetic fields can be used to selectively heat the surface layer of steel components. The coupling of induction heating to heat the surface region to the austenitizing temperature with subsequent rapid cooling of this region produces a hard surface region. This method is called induction hardening. Following surface hardening, the component can be tempered by induction heating, in some cases using the same equipment.

A wide range of shapes can be induction hardened and a system for quenching can be incorporated into the coil assembly. The process can be automated to harden components in an essentially continuous manner. The case depth is controlled by the coil design, frequency, power, and time of application.

Typical hardness distribution curves obtained by induction hardening are available (5). Case depths of ca 0.05–0.5 cm are commonly obtained.

Case Hardening by Laser Heating. The process of heating surfaces using lasers (qv) is not fundamentally different from that of flame and induction heating. The energy density is much higher, however, producing a very high heating rate. To prevent heating to too high, ie, above melting temperature, the heating time is very short. Usually temperature–time curves are not measured, but calculated (6). The surface region that is heated is considerably thinner than in flame and induction heating. Thus the underlying core remains at room temperature and serves as a heat sink for cooling. Because the surface is intimately connected to the core, the surface is self-quenched, and the cooling rate controlled only by the thermal diffusivity of the steel. Cooling times are of the order of only a few seconds. In some cases, the surface must be coated to increase the amount of light absorbed.

Figure 4 shows a typical hardness distribution (7). The case depth is considerably less than that for flame and induction hardening. The case has a high compressive residual stress, which improves the fatigue properties (8).

Case Hardening by Electron Beam Heating. Surfaces can be heated effectively using electron beams which can be focused by magnetic and electric lenses to control the spot size, and hence the energy density at the surface. Also, the beam can be moved in a controlled fashion to cover areas of the surface to be hardened. The process must be conducted in vacuum because of excessive scattering of electrons by air, thus cooling of the heated surface region is restricted to conduction into the cold core. This limits the case hardened region to a relatively thin layer.

Chemical Change. *Gas Carburizing.* In case hardening by carburizing, carbon atoms are deposited by chemical reaction on the surface of the steel while at high temperature in the austenite region. The atoms then move by diffusion into the steel, but are continuously replaced at the surface by more carbon atoms. The rate of deposition exceeds that of diffusion, so that a carbon gradient builds up with time, as depicted in Figure 5. The steel is then quenched to convert this surface region to martensite, forming a hard surface with a favorable compressive residual stress.

If the gas has the correct composition, the carbon content at the surface increases to the saturation value, ie, the solubility limit of carbon in austenite (Fig. 2), which is a function of temperature. Continued addition of carbon to the surface increases the carbon content curve. The surface content is maintained at this saturation value (9) (Fig. 5). The gas carburizing process is controlled by three factors: (*1*) the thermodynamics of the gas reactions which determine the equilibrium carbon content at the surface; (*2*) the kinetics of the chemical reactions which deposit the carbon; and (*3*) the diffusion of carbon into the austenite.

Chemical Thermodynamics. Consider carburizing using a mixture of CO and CO_2. The chemical reaction can be represented by

$$CO_2 + C^{\gamma} \longrightarrow 2\,CO$$

where C^{γ} is the carbon in solution in austenite. The equilibrium concentration of the gaseous species, ie, vol% CO and vol% CO_2, or the partial pressure, p_i, of each species, and the carbon content of the austenite in wt % C are related through an equilibrium constant, K.

$$K = p_{\mathrm{CO}}^2/(p_{\mathrm{CO_2}} \cdot \mathrm{C}^{\gamma})$$

The temperature dependence of K is well known experimentally. At a given temperature, if the composition of the gas is fixed, then equilibrium carbon content is fixed. This composition is sometimes referred to as the carbon potential.

The relationship between the gas composition, austenite carbon content, and temperature is known. For example, a gas in equilibrium with austenite containing 0.8% C must have the partial pressure ratio $p_{\mathrm{CO}}^2/(p_{\mathrm{CO_2}}) = 20$. If the gas is comprised of only CO and CO_2, then the sum of the partial pressures must equal the total pressure of the system. These thermodynamic relations can be presented in several graphical forms (10,11).

In commercial carburizing, the gas mixture contains not only CO and CO_2, but also CH_4, H_2, and H_2O, as well as the inert N_2. Reactions characterized by their equilibrium constants such as

$$\mathrm{CO_2} + \mathrm{H_2} \longrightarrow \mathrm{CO} + \mathrm{H_2O}$$

occur. For example, at 926°C, where K for this latter equation equals 1.43,

$$1.43 = (X_{\mathrm{H_2O}})\,(X_{\mathrm{CO}})/(X_{\mathrm{H_2}})\,(X_{\mathrm{CO_2}})$$

where X_i represents mol % of the various species. This equation and the equilibrium equation for CO, CO_2, and the carbon content of the steel, must be simultaneously satisfied. Thus the carbon content of the austenite can be controlled by controlling the water vapor content of the gas, which is usually monitored and reported as the dew point.

Many commercial gases are generated by burning hydrocarbons (qv) eg, natural gas or propanes, in air (see GAS, NATURAL; LIQUEFIED PETROLEUM GAS). The combustion process, especially the amount of air used, determines the gas composition. For a given fuel-to-air ratio, the gas composition can be used to determine the water vapor content required to achieve a desired equilibrium carbon content of the austenite (see COMBUSTION SCIENCE AND TECHNOLOGY).

The equilibrium carbon content of austenite also depends on the alloy content, eg, Cr or Ni of the steel. A given gas composition equilibrates with a carbon content of the austenite which is different for a plain carbon steel than for an alloy steel.

Diffusion of Carbon.

When carbon atoms are deposited on the surface of the austenite, these atoms locate in the interstices between the iron atoms. As a result of natural vibrations the carbon atoms rapidly move from one site to another, statistically moving away from the surface. Carbon atoms continue to be deposited on the surface, so that a carbon gradient builds up, as shown schematically in Figure 5. When the carbon content of the surface attains the equilibrium value, this value is maintained at the surface if the kinetics of the gas reactions are sufficient to produce carbon atoms at least as fast as the atoms diffuse away from the surface into the interior of the sample.

The rate of diffusion of the carbon atoms is given by Fick's laws of diffusion. In one dimension,

$$\text{number of carbon atoms}/(\text{time} \cdot \text{area}) = -D[dC/dx]$$

where C is concentration of carbon, x is distance, and D is the diffusion coefficient, which has temperature dependence

$$D = D_0 \exp[-Q/RT]$$

where D_0 is a constant, Q is the activation energy dependent on the carbon and alloy content, R is the ideal gas constant, and T is temperature in Kelvin. Thus the rate of diffusion of carbon is exponentially related to temperature.

Relations exist between the temperature, T, and the average time, t, it takes a carbon atom to move a given distance, x. One approximation is

$$x \simeq (D \cdot t)^{1/2}$$

Similar expressions relate the diffusion distance to the case depth, d, for example, $d \approx (660\ t^{1/2})\exp(-8287/T)$, where d is in mm, t in hours, and T in degrees Kelvin. This equation is based on the surface being saturated, ie, at the solubility limit, at each temperature. At 927°C, carburizing for four hours gives a case depth of about 1.3 mm. A higher temperature allows the use of a shorter time, but the risk of an unacceptable increase in the austenite grain size must be considered. Using much lower temperatures may require inordinately long times.

The maximum surface carbon content is usually set by the gas composition via the equilibrium constant. If the gas reaction kinetics deposit carbon at a rate which cannot be equaled by the diffusion of carbon into the steel, then the surface value may be less than the possible equilibrium value.

In some cases, the carbon profile may not provide the necessary hardness or other properties. For example, if the carbon content is too high, quenching to room temperature may not produce all martensite at the surface because the high carbon content places the martensite finish temperature, M_f, below room temperature. This results in the presence of soft retained austenite, and a low surface hardness. Conversion to martensite by subzero cooling to below the M_f temperature can increase the hardness (Fig. 6) (12).

The high carbon content at the surface can be lowered by reheating the steel to the austenite region in a noncarburizing atmosphere. This allows the carbon to diffuse toward the center, lowering the carbon content and raising the M_f above room temperature. Then upon quenching all martensite is formed. This second heat treatment, often referred to as a diffusion treatment, can also be achieved at the end of the carburizing time by changing the gas atmosphere to minimize carburizing. This procedure is sometimes called boost diffusion carburizing.

An important advancement in carburizing has been the development of diffusion models to calculate the carbon gradient as a function of time as the gas composition and temperature change (13). Such models can be coupled with computer control of the gas composition and temperature to produce desired carbon profiles.

Selective Carburizing. In most components, it is desirable to carburize only parts of the surface. To prevent other regions from carburizing, they must be protected. For holes, simple plugs of copper may be used. In some cases, copper plating can be applied, but diffusion into the steel must be considered, and the copper may have to be machined off later. Coatings (qv), which can be applied as a paste and then removed after heat treatment, are also available and include copper plating, ceramic coatings, and copper and tin pastes.

Gas Nitriding. The nitrogen atom, similar in size to carbon, is quite soluble in the high temperature austenite phase of iron. Thus nitrogen can be used to form a hard iron–nitrogen martensite. Nitrogen can also be added simultaneously with carbon to austenite to form hard martensite. However, the nitriding temperature is usually well below that of the formation of austenite ($<723^\circ$C) (Fig. 2), and because martensite forms only from austenite, hardening by nitrogen addition occurs by another mechanism. The solubility of nitrogen is very low in ferrite, as is that of carbon (Fig. 2). Sufficient nitrogen cannot, therefore, be added to ferrite to impart significant solid solution hardening. Instead, the nitrogen added to the steel surface reacts with iron or specific alloying elements to form a fine dispersion of very hard nitrogen compounds, ie, nitrides (qv) and the nitrides produce a very hard case.

A problem in nitriding is that a layer of nitrides may form on the surface which does not have desirable properties. For example, if the layer is too thick, it is brittle and may spall off. This is called the white layer or compound layer, and may have to be machined or ground off after nitriding.

Molecular nitrogen, N_2, is stable and relatively inert. It does not decompose to atomic nitrogen to form a nitrogen case. Instead, a gaseous compound containing nitrogen must be used. The common carrier of nitrogen in gas nitriding is ammonia (qv) (4).

Plasma or Ion Nitriding. Nitrogen can be produced for deposition on the steel surface by ionization of gaseous nitrogen to form an ionic plasma. The components to be nitrided are electrically insulated and become the cathode (negative) of a d-c power supply. A metal plate serves as the anode. When a potential of $\sim$1000 V is applied to the components at sufficiently low pressure of nitrogen, the gas becomes positively ionized, forming a plasma. These ions are accelerated toward and strike the surface of the components to be nitrided. The plasma gives off visible radiation, the color of which depends on the type of gas being ionized. This process is sometimes called glow discharge nitriding (14) (see PLASMA TECHNOLOGY).

The nitrogen ions have sufficient energy to cause the parts to heat. Heaters can be used if necessary to achieve the correct temperature. The nitrogen ions are neutralized at the surface, forming atomic nitrogen, which then diffuses into the surface and reacts with iron and alloying elements to form the hard nitrides. A distinct advantage of this method is that the plasma generally deposits nitrogen uniformally on the surface, so that less uneven deposition occurs than is sometimes found with nitriding by flowing hydrogen–ammonia gas.

Nitriding Temperature and Time. Because nitriding is carried out inthe ferrite and carbide region of the phase diagram (see Fig. 2) at lower temperatures than in carburizing, the diffusion rate of nitrogen is relatively low and hence the time to attain a suitable case is longer than in carburizing. Figure 7**a** shows typical nitrogen content–depth profiles for nitriding. The hardness profiles in Figure 7**b** shows that the case hardness is very high (3,15). For example, in Figure 6**a** the hardness at the surface of the carburized steel, after cooling to −196°C, was about 900 DPH (Vickers); the maximum hardness for nitriding was about 1100 Vickers. To obtain the case of about 0.12 cm by carburizing (Fig. 6) takes about two hours; to get a case depth of about 0.05 cm by the nitriding process for the data in Figure 7**b** requires about 15 hours.

An advantage of nitriding is that the core properties can be set by prior heat treatment, such as by quenching and tempering, then the surface nitrided. During nitriding the steel is not heated back into the austenite region, thus no phase changes occur in the core during nitriding or following cooling to room temperature. However, the core properties can be affected by coarsening during nitriding. If the core properties are set by quenching and tempering, then the tempering temperature must be about 50°C above the nitriding temperature to prevent any significant changes in core properties from occurring during nitriding.

Properties of Case Nitrided Steels. Nitrided components possess outstanding fatigue properties. In one example, the fatigue strength of crankshafts made from quenched and tempered steel is about 280 MPa (40,000 psi), whereas the same steel after nitriding has a fatigue strength of ca 790 MPa (115,000 psi). These case nitrided crankshafts also have about the same fatigue strength as those that are induction hardened (16).

Nitriding can impart significant wear resistance to steel surfaces, as illustrated in Figure 8. The resistance to abrasion of an uncase hardened steel compared to that of the same steel nitrided, and the steel having a carburized case, is shown (3,17). Improvement in weight loss is related directly to the hardness of the case.

Case Hardening by Surface Deformation. When a metallic material is plastically deformed at sufficiently low temperature, eg, room temperature for most metals and alloys, it becomes harder. Thus one method to produce a hard case on a metallic component is to plastically deform the surface region. This can be accomplished by a number of methods, such as by forcing a hardened rounded point onto the surface as it is moved. A common method is to impinge upon the surface fine hard particles such as hardened steel spheres (shot) at high velocity. This process is called shot peening.

The surface may gain a very high (eg, ~1000 Vickers) hardness from this process. Surface deformation also produces a desired high compressive residual stress. Figure 9 illustrates the improvement in fatigue properties of a carburized surface that has been peened (18).

1.4. Case Hardening by Ion Implantation. One method of changing the chemistry of the surface of a component without heat treatment or chemical reaction is ion implantation (qv). Not only can elements such as carbon and nitrogen be added, but larger elements such as titanium can be also. A gas of the implant species is produced by vaporization, if necessary, and ionized in some manner, such as by heating or forming a plasma. The ions are removed from the region of formation by a negative electrostatic field, then they enter an accelerator. The ions exit the accelerator with a velocity sufficient to penetrate the surface of the target. The ion beam is focused and its direction controlled by a magnetic or electrostatic lens system. Hence the location of implantation on the surface can be controlled.

The ions not only are implanted in the surface, but cause considerable lattice damage displacing the host atoms. An amorphous layer may be formed and the structure is not an equilibrium one. Thus the solubility of the implanted ions may greatly exceed the solubility limit. All of these effects combine to produce a hard case.

The complexity of the apparatus needed for ion implantation makes this method of case hardening of limited application. Further, the case depth is considerably lower than that produced by carburizing or nitriding. The depth of implantation of nitrogen in a steel is about 0.00006 cm (19), ie, so thin that it is difficult to measure the hardness profile by conventional microhardness measurements.

The improvement in wear resistance from ion implantation is shown in Figure 10 (20). However, the thin case cannot sustain very heavy loads. Hence this application for improved wear resistance is limited to special situations, eg, low loads.

Ion implantation is being used to form a thin hard case on materials other than steels. Titanium alloys have been successfully implanted with nitrogen. The process has been applied to ceramics to modify the surface region.

1.5. Other Methods of Case Hardening. There are a multitude of methods available for case hardening, and the technical details of implementation may be complicated.

Pack Carburizing. In pack carburizing, the components to be case hardened are placed in the center of a box filled with carbon particles, usually charcoal, and air. Upon heating to the carburizing temperature, the carbon reacts with the air to form CO, which in turn decomposes on the steel surface to deposit carbon. This is the same chemical reaction as described for gaseous carburizing. The CO_2 released in turn is reduced by the carbon in the charcoal, producing more CO for carburizing. To enhance the rate of the chemical reaction, energizers such as barium carbonate, $BaCO_3$, are added to the charcoal. These compounds decompose at relatively low temperature to release CO_2 which then is reduced by the carbon in the charcoal to form CO for carburizing. There is no direct control of the gas composition in pack carburizing, so the surface carbon content is determined by the carburizing temperature and time.

An advantage of pack carburizing is that the charcoal pack supports the work load which minimizes distortion. However, the components must be removed from the pack for quenching, or the mass cooled to room temperature and then the components reaustenitized and quenched.

Drip Carburizing. The gases CO and CH_4, needed for decomposition to provide carbon at the surface of a component to be carburized, can, in principle, be produced by the decomposition of many carbon-containing organic chemicals. One method is to insert liquid methanol into the hot furnace containing the components, where CH_3OH decomposes to produce the carburizing gas. This process can be used with air where the reaction of the oxygen in the air and the vaporized methanol form the carburizing gas. The reaction rate is controlled by the rate of addition of the liquid methanol, usually by the release of drops, hence drop carburizing.

Vacuum Carburizing. In vacuum carburizing, part of the carburizing cycle involves heating the carburized component in a vacuum to allow diffusion of carbon to occur without significantly affecting the surface. The steel is heated to the austenitizing (carburizing) temperature under partial vacuum, then a carburizing gas is introduced to the steel and retained until the desired carbon gradient is obtained. The system is then evacuated and the carbon allowed to diffuse inward under the protective vacuum until the gradient is reduced to the desired profile. The steel components are quenched in oil or air under vacuum.

Plasma Carburizing. Plasma carburizing generates carbon atoms at the surface by ionization of a carbon-containing gas, eg, methane. The process is similar to that described for ion nitriding. Because the process is carried out in partial vacuum, there is less chance of oxidation.

Liquid Carburizing. Case hardening by carburizing can be achieved by the use of carbon-containing molten salts. Thermal gradients are minimized with the use of molten salts. The most common chemicals in liquid carburizing are cyanide salt baths, in which case the process is referred to as cyaniding. Because nitrogen is also formed from the decomposition of these salts, the case may contain nitrogen, which is favored by the use of high concentrations of the cyanide salts. A critical disadvantage in the use of cyanide salts is that they are extremely poisonous.

Carbonitriding. A modification of gaseous carburizing where ammonia is added to provide nitrogen is called carbonitriding. The effect of adding both carbon and nitrogen is similar to that of cyaniding. This terminology refers to the addition of carbon and nitrogen to austenite, which is then quenched to form a case of hard martensite.

Liquid Nitriding. As in gas nitriding, the process is carried out below the austenite region, and hardening is associated with the formation of hard nitrides in the ferrite. Liquid cyanide salts are used with others to provide the source of nitrogen.

Ferritic Nitrocarburizing. This process is similar to carbonitriding, except that it is carried out in the temperature range of the stability of ferrite and carbide ($<723^\circ$C). Therefore hardening is not by martensite formation, but because of the formation of very hard carbonitrides.

Plasma Nitrocarburizing. This process is similar to plasma nitriding and plasma carburizing, except that a gas is used which when ionized releases both carbon and nitrogen at the surface of the component. Mixtures of hydrogen, nitrogen, and a carbonaceous gas are used. The process is carried out in the temperature range of stability of ferrite and carbide, and case hardening occurs as a result of the formation of hard carbonitride particles and a hard nitride layer on the surface.

Austenitic Nitrocarburizing. This is similar to ferritic nitrocarburizing except that the temperature may extend into the austenite range. The case usually consists of hard carbonitride particles, and quenching to achieve hardening is not required.

Boriding or Boronizing. Boron, also a relatively small atom, can be added to the surface of steels by methods similar to that for carburizing and nitriding.

For example, the process can be carried out in a pack of boron-containing salts, by use of a plasma and by gaseous environment. The process can be carried out in the temperature range of the stability of ferrite and carbide (<723°C), or in the higher temperature austenite range. In either case the hardening is associated with the formation of hard, eg, 1400–5000 Vickers hardness, boron compounds.

2. Cleaning

2.1. Alkaline Cleaners. Alkaline cleaners are the most commonly used for metal surfaces. These are typically composed of a blend of alkaline salt builders, such as sodium phosphates, sodium silicates, sodium hydroxide, or sodium carbonate. In addition, they almost always contain detergents, ie, surfactants (qv), and, optionally, wetting agents, coupling agents, chelating agents (qv), and solubilizers. Alkaline cleaners are usually applied in the range of 38–93°C.

The composition of the builders in an alkaline cleaner is dependent on the metal substrate from which the soil is to be removed. For steel (qv) or stainless steel aggressive, ie, high pH, alkaline salts such as sodium or potassium hydroxide can be used as the main alkaline builder. For aluminum, zinc, brass, or tin plate, less aggressive (lower pH) builders such as sodium or potassium silicates, mono- and diphosphates, borates, and bicarbonates are used.

The mechanisms by which an alkaline cleaner removes the soil are saponification, emulsification, and dispersion. These mechanisms can operate independently or in combination. Saponification occurs when alkaline salts react with fatty components of the soil, forming a soluble soap compound.

Emulsification involves the joining of two mutually insoluble materials, such as petroleum oil and water. The surfactant, which usually has a hydrophilic or water-soluble end and a hydrophobic or oil-soluble end, holds the oil and water together in much the same manner that a fastener holds two pieces of material. Often, the emulsion which forms is unstable, subsequently breaking up and releasing the oil from the water. Break-up is actually preferred, because the oil then floats to the surface, whereas the surfactant is free to emulsify more oil.

Dispersion is the process of wetting the surface of the metal, thereby penetrating the oil film. Surfactants can reduce the surface tension and interfacial tension of the cleaning solution at the metal–liquid interface. As the cleaner undercuts and penetrates the oil, the cleaner breaks the oil into small droplets which then float to the surface.

An alkaline sensitive metal cleaning agent has been reported in the patent literature (21).

2.2. Applications. Cleaners are typically applied either by immersion or by spray. Immersion or soak cleaning involves simply immersing a part or panel into a tank containing the cleaner and letting the metal sit for a period of 1–10 min. A simple variation of immersion cleaning is to recirculate the cleaner so that fresh cleaner is continuously passing by the object to be cleaned. Other variations include electrocleaning, ultrasonic cleaning, and barrel cleaning. Variations of spray cleaning include steam cleaning and power washing. Additionally, solvent cleaners can be applied by vapor degreasing, and both solvent and aqueous cleaners can be applied by mechanical methods such as hand wiping or hand brushing the cleaner onto the soiled area. Because of high evaporation rates and toxic fumes, solvent cleaners are not usually applied by spray.

Immersion Cleaning. The simplest method for using an alkaline cleaner is by immersion. A part is placed on a hook or rack and immersed in the cleaner solution so that all of the part is below the liquid level. A typical concentration, temperature, and process time for an immersion cleaner would be ca 75 g/L at 77°C for 5 min. In addition to being the simplest method, immersion is also among the least expensive in terms of equipment. Only a vessel to contain the cleaning solution and a means of heating the solution are needed.

Electrocleaning. Electrocleaning is a specialized variation of immersion cleaning. Electrocleaners are very similar in composition to immersion cleaners, except that the surfactant levels are usually lower and less foaming. The cleaning action of the cleaner is assisted through the use of direct-current electricity. Electrodes are placed on two sides on the inside of the tank, and in most cases they carry a negative charge (making them the cathode). The part to be cleaned carries a positive charge (anode). The oxygen evolving at the part acts as a mechanical scrubber assisting in removal of the soil. The concentration and temperature are usually a little higher than for a straight immersion cleaner: 75–120 g/L at 77–99°C. The d-c current is supplied by a large rectifier, and the current density on the part varies from 27–160 mA/cm^2 (25–150 A/ft^2). Electrocleaning is usually preceded by an immersion or a spray cleaner to remove the bulk of the soil. The part is typically left in the electrocleaner for 1–3 min to produce an exceptionally clean surface.

Ultrasonic Cleaning. Ultrasonic cleaning is another variation of immersion cleaning. Waves of bubbles are generated in the cleaning solution through the use of sound waves. The sound waves are generated by electrically powered devices called transducers, which vibrate rapidly causing the sound waves and bubbles. This is called cavitation. The ultrasonic cleaning action literally vibrates or shakes dirt loose from narrow cracks and crevices. This is aided by the cleaning action of the detergents in solution.

The transducers are typically mounted on an outside wall of the cleaning tank, but may also be mounted on the inside of the tank below the solution level in a sealed container. Alkaline cleaning solutions are typically at the same concentration and temperature as for a normal immersion cleaner, but the time required to clean may be less because of the ultrasonic effect. Like electrocleaning, ultrasonic cleaning produces an extremely clean surface. The main drawback is the relatively high cost.

Barrel Cleaning. Barrel cleaning is a minor variation of immersion cleaning in which parts are placed in a six- or eight-sided barrel the sides of which are perforated, allowing the cleaning solution to enter the barrel. The barrel is immersed in the cleaner and rotated around the long axis by an electric motor. The parts inside tumble and rub against each other, thus aiding in the removal of the soil. Electrodes can also be inserted and hooked up to a rectifier to add electrocleaning assistance. The restriction of barrel cleaning is that it is generally used only for small parts such as fasteners, cabinet handles, and screwdriver shafts.

Spray Cleaning. The other principal method of application of cleaners is by spray. In spray cleaning, the cleaning solution is pumped out of a holding tank into a series of pipes (risers) which have other pipes called headers coming out from the risers. These headers have holes drilled into them and nozzles screwed into the holes. The pipes are configured in such a way that a part going by on a conveyor would be sprayed with cleaner from every conceivable angle. This configuration of pipes is housed in a steel hood which keeps the spray mist confined. The hood is generally over the holding tank so that the excess cleaner drains back into the holding tank. The hood has a narrow slit at the top to permit conveyor parts racks to pass through and at least one exhaust stack to remove the steam. Spray pressures for commercial spray cleaner systems are usually in the range of 70−275 kPa (10−40 psi), concentrations are typically 4−30 g/L, and temperatures vary between 21−88°C. The main difference in composition from immersion cleaners is that spray cleaners contain low foaming surfactants.

Steam Cleaning. In steam cleaning, a machine generates high pressure steam and injects a cleaning solution at the nozzle where the steam is exiting. Cleaner concentration is varied by changing the concentration of the cleaner in the reservoir or the rate at which the cleaner feeds into the exiting steam.

Power Washing. Power washing is similar to steam cleaning, except that the cleaner is injected into a high pressure (6.9−35 MPa (1000−5000 psi)) water blast in power washing. The water can be cold, warm, or hot, because the power washer is fed from a water tap.

Solvent Cleaning. Solvent cleaning employs the natural solubilizing properties of various nonaqueous solvents or blends of solvents. Either 100% solvents or aqueous emulsions of solvents can be used. Application is typically by immersion, hand application, or via a vapor degreaser machine, where the solvents are continuously vaporized and condensed. Solvent cleaners are rarely applied by spray because of excessive loss by evaporation and the subsequent environmental considerations. Solvent cleaning also requires a lot of ventilation and an adequate exhaust system. Whereas solvent cleaning is effective, its cost is usually higher than other cleaning methods.

3. Conversion Treatments

3.1. Phosphating.

Reactive metal surfaces can be chemically treated and covered with inert, amorphous, or crystalline coatings which grow on the base metal. Phosphates represent the most important area of the conversion coatings. These coatings (qv) are applied as preparation for painting, temporary corrosion protection, lubricant carrier in cold forming, friction improver for stamping and drawing, and as insulation on electrical steels (22–24) (see also METALLIC COATINGS, SURVEY; METAL TREATMENTS).

Phosphating processes began with the work of Thomas Watts Coslett. The original patent covered the use of phosphoric acid to which iron filings had been added (25). It took from 2 to 2.5 hours exposure in boiling solution to form a coating on iron and steel articles. Early improvements consisted of controlling the quantity of free phosphoric acid, thus inhibiting attack on the metal, and of accelerating the reaction by using an electric current. Concentrates from which phosphate baths could be prepared by dilution were in use by 1909. The use of zinc in the phosphate bath was patented in 1909 and the use of manganese in 1911 (26). The use of manganese dihydrogen phosphate gave rise to the process which became known as Parkerizing. Reduction in processing time from one hour to 10 minutes came through the addition of copper to the bath. This was the basis for the Bonderizing process. Addition of an oxidizing agent such as nitrate increased the reaction rate by preventing the adsorption of hydrogen on the metal surface. Paint-base phosphate coatings could be applied in two to five minutes. In 1934, this time constraint was shortened even further when phosphate solutions were sprayed onto the metal surface. Processing times as short as 60 seconds became possible.

A crucial development for zinc phosphate coatings came in 1943 when it was found that more uniform and finer crystals would develop if the surface was first treated with a titanium-containing solution of disodium phosphate (27). This method of crystal modification is a prime reason for the excellent paint (qv) adhesion seen on painted metal articles.

Modern phosphating practice involves the treatment of reactive metals with acidic phosphate-containing solutions. This produces a coating which consists mainly of phosphate compounds. Chemically, phosphating processes can be separated into two types. In processes of the first type, the metal ions of the phosphate layer derive almost totally from the substrate. These layers, known as noncoating or iron phosphates, are based on sodium and ammonium dihydrogen phosphate. Processes of the second type, on the other hand, provide metal ions for coating either partially or totally in the phosphate bath. These are the zinc phosphate processes which may contain zinc alone or modifying ions such as nickel, manganese, calcium, as well as several others.

The Iron Phosphating Process. Dissolution and oxidation of iron(II) to iron(III) and coating development result in the formation of an amorphous coating which contains iron phosphate, $FePO_4$, as the principal coating constituent (28). In addition, some iron oxide, Fe_2O_3, which forms from the rearrangement of ferric hydroxide, and some tertiary iron phosphate called vivianite, $Fe_3(PO_4)_2$, are present. The oxidative condition needed for coating formation is provided by accelerators such as chlorate, nitrate, permanganate, and air entrapped during spraying.

Operation and Control. The product concentrates can be supplied either as powders or liquids. Powdered iron phosphates based on dihydrogen phosphates of sodium or ammonium form a popular line of clean-and-coat materials used in three-and four-stage lines. These formulations may also include surfactants (qv), sequestrants, solvents, inhibitors, and accelerators. High temperature iron phosphates are applied at 65.6–76.7°C for 40–60 seconds. The systems operate in the pH range of 4.5–5.5. Total acidity ranges from 6–16 points, ie, 6–16 mL of 0.1 N NaOH for a 10 mL sample of the bath determined by titrating to an end point of pH 8.2, which is faint pink with a phenolphthalein indicator. Low temperature iron phosphate processes operate at 40.6–46.1°C, at a total acidity range of 9–18 points. The optimum pH range lies between 3.7 and 4.4, having measurable free acidity, ie, titration with 0.1 N NaOH to an end point of pH 3.8. These formulations are used at concentrations similar to the high temperature variations. However, these formulations must have increased acidity and increased acceleration to compensate for the lower operating temperature. The formation of Na_2HPO_4 as a by-product of the reaction causes the pH to rise, thus acid replenishment is necessary to keep the bath in the operating range.

The application of this type of conversion coating can be by spray or immersion and is easily tailored to the needs of the user (see COATING PROCESS, SURVEY). The number of stages may vary from two, ie, clean and phosphate then rinse, to as many as five, ie, clean, rinse, phosphate, rinse, and post-treat. The performance requirements dictate the number of operation stages as well as the need for a post-treatment.

Coating Characterization. As indicated, the coatings are amorphous and can therefore be characterized only by coating weight. Coating weights normally range from 0.1 to 0.8 g/m^2, but special formulations may yield coating weights of 1.2 g/m^2. For coating weight determination, coatings may be stripped from steel surfaces with a solution of chromic acid, whereas aluminum or zinc surfaces are stripped with a solution of ammonium dichromate.

Product Utilization. Iron phosphating has been the process of choice for applications where cost considerations override maximum performance needs. Advantages are low chemical cost, low equipment cost, good paint bonding, easy control, and minimal sludge. The disadvantages, thin coatings and poorer corrosion resistance than for zinc phosphating, limit the application of iron phosphating to particular industries. Nevertheless, iron phosphates are the most widely applied conversion coatings when surface preparation for paint application is needed. Most recently developments have been aimed at formulating baths which allow coating deposition on a mixture of metals using the same coating bath. The addition of stronger etchants and the use of different accelerator systems brings these systems closer to zinc phosphates in versatility and performance.

The Zinc Phosphating Process. The zinc phosphating reaction involves acid attack on the substrate metal at microanodes and deposition of phosphate crystals at microcathodes (29). Liberation of hydrogen and the formation of phosphate sludge also occur. The equation for the dissolution of iron together with precipitation of dissolved iron as sludge in a nitrite accelerated system is as follows:

$$2\,Fe_0 + 2\,H_2PO_4^- + 2\,H^+ + 3\,NO_2 \longrightarrow 2\,FePO_4 + 3\,H_2O + 3\,NO$$

The NO_2 is generated when nitrite oxidizes the hydrogen produced by the acid attack on the metal surface to form water. The total reaction uses up hydrogen ions and reduces acidity. The only source of these ions at the interface is the zinc dihydrogen phosphate in solution. The result is that zinc phosphate crystallizes at the surface–solution interface to form a tightly adhering crystal layer according to the following equation:

$$3\,Zn^{2+} + 2\,H_2PO_4^- \longrightarrow Zn_3(PO_4)_2 + 4\,H^+$$

Combining these equations gives a total coating reaction of

$$4\,Fe_0 + 3\,Zn^{2+} + 6\,H_2PO_4^- + 6\,NO_2 \longrightarrow 4\,FePO_4 + Zn_3(PO_4)_2 + 6\,H_2\,O + 6\,NO$$

Hydrogen is prevented from forming a passivating layer on the surface by an oxidant additive which also oxidizes ferrous iron to ferric iron. Ferric phosphate then precipitates as sludge away from the metal surface. Depending on bath parameters, tertiary iron phosphate may also deposit and ferrous iron can be incorporated into the crystal lattice. When other metals are included in the bath, these are also incorporated at distinct levels to generate species that can be written as $Zn_2Me(PO_4)_2$, where Me can represent Ni, Mn, Ca, Mg, or Fe.

Operation and Control. The zinc phosphating process sequence consists of cleaning, rinsing, surface conditioning, phosphating, and final rinsing. Alkaline cleaning is used to remove soils and oils that have accumulated during storage and forming of the parts (30) (see METAL SURFACE TREATMENTS, CLEANING). Rinses between the active stages remove residual chemicals. For zinc phosphates, an effective conditioning rinse before phosphating provides the development of small, tight crystals necessary for improved paint adhesion. Conditioners, dispersions of colloidal titanium phosphate, are formulated to function consistently with equal results in hard and soft water. Finally, improved corrosion performance is most often obtained using a post-treatment or final rinse step. Some of these rinses contain chromium in mixtures of both the +3 and +6 oxidation states. Others contain chromium in the +3 oxidation state alone. Chromium-free post-treatments which match the performance of the chromium-containing post-treatments have been developed. These derive effectiveness from organic polymers which can chelate to the metal surface and to the coating (31).

The bath components for a nitrite–nitrate accelerated bath basic to this conversion coating process are (*1*) zinc metal or zinc oxide dissolved in acid; (*2*) phosphate ions added as phosphoric acid; (*3*) addition of an oxidant such as sodium nitrite; and (*4*) addition of nitric acid. Other oxidants such as peroxide, chlorate, chlorate in combination with nitrate, or an organic nitro compound may also be used.

Conventional practice is to dilute the liquid, which consists of 40–50% solids, zinc phosphate concentrate, having a density ~1.3 times that of water, to a 2–6% concentration with water. Soda ash or caustic soda is added to obtain the correct free acid value and the bath is then heated to the operating temperature. This is followed by addition of $NaNO_2$ to achieve about a 0.02% concentration. The level of free acid is critical. The free acid must be lowered to the point where zinc phosphate starts to precipitate. This is called the point of incipient precipitation (32). If the bath is neutralized too far, valuable zinc dihydrogen phosphate is lost as sludge. As the reaction proceeds and the crystalline coating is formed on the surface, the zinc dihydrogen phosphate in the bath must be replenished. Practical replenishers operate at phosphate to zinc mole ratios between 1.5 and 2.5:1 because an excess of phosphate is required to precipitate dissolved iron as the phosphate. In modified zinc phosphates, the other metals are also restored by the replenisher according to their individual incorporation in the coating.

Application of the zinc phosphate coating can be by spray or immersion. When the coating is applied by spray, the solution is quickly replaced and the coating formation takes place very rapidly. Replacement at the surface of depleted bath solution during immersion application is diffusion controlled. The rate at which the coating develops is somewhat slower. This difference in the rate of coating development is reflected in the composition of the coatings deposited. Those from the immersion application contain a large amount of iron when applied to steel and have better performance qualities than those from spray application (33). Although control parameters for the two application methods do not vary significantly, there is a difference in the replenisher formulations. This is because of a higher drag-out from the spray bath than from the immersion bath.

Coating Characterization. Phosphate coatings cannot be fully characterized by any simple methods. Characteristics such as appearance, coating weight, P-ratio (34), porosity (35,36), coating composition (37), and crystal size combine to define a system's performance. However, measurement of any of these factors individually does not provide a sufficient indication of the coating's efficacy in meeting its intended purpose.

Modified Zinc Phosphates. Coatings on steel have been identified as hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, phosphophyllite, $Zn_2Fe(PO_4)_2 \cdot 4H_2O$, and iron hureaulite, $Fe_5H_2(PO_4)_4 \cdot 4H_2O$. Incorporation is also achieved when nickel, manganese, or calcium are added to the phosphating bath. Similar structures have been identified for these metals (38,39). Modification of the hopeite structure is reflected in an increased resistance to alkalinity and a higher dehydration temperature (40). Both of these properties contribute to improved corrosion and adhesion properties of painted steel (qv), zinc, and zinc alloy surfaces (see ZINC AND ZINC ALLOYS).

Product Utilization. Zinc phosphate coatings form the basis for paint adhesion in a variety of industries. These are used when long-term quality is of concern in applications such as for automotive parts and vehicles, coil-coated products, and appliances.

Testing of Painted Products. The enhancement of paint adhesion is one of the principal functions of conversion coating (41–43). A group of tests based on product deformation is used to test the painted product. The appliance and coil-coating industries use the mandrel bend, the cross-hatch adhesion test, and the direct and reverse impact tests. Adhesion after a water soak is judged using a cross-hatch test performed on the exposed surface.

Several accelerated corrosion tests are also employed to evaluate the effectiveness of the phosphate coating in the performance of painted products (see CORROSION AND CORROSION CONTROL). These tests are designed to duplicate the service environment as well as the corrosion mechanism for the painted article. In the appliance industry the tests used most often include the salt spray test, detergent immersion, water immersion, and humidity resistance. The coil coating industry uses the salt spray test, exposure in the Q-uv cabinet, ie, a test regimen involving uv light and condensing humidity at a temperature of 60°C, and humidity exposure. Testing in the automotive industry is slightly more complicated because each of the car companies has its own cyclic corrosion test. Among the cyclic tests in use are the Ford APGE Test, the GM 9511 Cyclic Corrosion

Test, the GM 9540-P Cyclic Corrosion Test, and the Chrysler Chipping Test. Water immersion, humidity exposure and, to a very limited extent, the salt spray test are also being used. In addition, all industries use outdoor exposure tests for long-term evaluation of corrosion performance. However, test results from both the accelerated and in-service tests function as indicators of relative performance. These are not predictive of application lifetimes.

Other Phosphate Coatings. Phosphate coatings are also used as surface treatments for wire drawing, tube drawing, and cold extrusion. Zinc phosphates of heavy (10–35 g/m^2) coating weights serve as the carrier for drawing compounds and lubricants. It is standard practice to use a manganese phosphate coating as an oil retaining medium on bearings or a sliding surface to eliminate scuffing, galling, and pickup, and to facilitate running in, ie, wear of mating surfaces during initial hours of operation (see Bearing materials). These coatings are usually applied by immersion at temperatures reaching 93°C at times between 5 and 30 minutes.

3.2. Chromating. Chromating or chromatizing has been widely practiced in the metals industry since the late 1940s to improve corrosion resistance and performance of subsequently applied organic finishes (44). Commonly, chromates are used to treat wrought alloys, cast alloys, and coatings comprising aluminum, zinc, magnesium, or cadmium. The aerospace, transportation, architecture, appliance, marine, and electronics industries, among others, utilize chromate coatings extensively (see also Coatings, marine; Electronics, coatings).

Chromate conversion coatings are thin, noncrystalline, adherent surface layers of low solubility phosphorus and/or chromium compounds produced by the reaction of suitable reagents with the metal surface (23,24). The two classes of chromate coatings are chromium phosphates (green chromates) and chromium chrom ates (gold chromates).

Chromium Phosphate. Chromium phosphate treatment baths are strongly acidic and comprise sources of hexavalent chromium, phosphate, and fluoride ions. Conversion coating on aluminum precedes by the following reactions (45):

$$\textit{Oxide removal} \qquad Al_2O_3 + 6\ HF \longrightarrow 2\ AlF_3 + 3\ H_2O$$

$$\textit{Redox reaction} \qquad Cr^{6+} + 3\ e^- \longrightarrow Cr^{3+}$$

$$Al^0 \longrightarrow Al^{3+} + 3\ e^-$$

$$\textit{Chromate reduction} \qquad 8\ H^+ + 2\ HCrO_4^- + 2\ Al^0$$

$$\textit{Phosphate reaction} \qquad Cr_2O_3 \cdot 3\ H_2O + 2\ H_3PO_4 + 2\ H_2O \longrightarrow 2\ CrPO_4 \cdot 4\ H_2O$$

Chromium phosphate coatings can be deposited with very low (0.05–0.15 g/m^2) weights to give colorless coatings for applications such as a paint base or very heavy (2.0–5.0 g/m^2) weights for decorative applications.

Operation and Control. Control of a chromium phosphate conversion coating bath requires monitoring chromium and aluminum concentrations, active fluoride level, and temperature. Coating weight is very sensitive to active, ie, uncomplexed, fluoride. An innovative electrochemical method using a silicon electrode (46) is employed for measuring active fluoride. A special precaution in chromium phosphate bath operation is the formation of whitish, powdery coatings resulting from accumulation of dissolved aluminum. Commercially available proprietary chromium phosphating products typically incorporate sodium fluoride and potassium fluoride. These fluoride additions precipitate aluminum from solution as elpasolite, NaK_2AlF_6.

Typical processing steps in chromium phosphate application by either spray or immersion contact are alkaline cleaning (etching or nonetching), water rinse, chromium phosphate treatment, water rinse, and finally a deionized water rinse because acidified water is often used for paint-base applications. Usually desmutting or deoxidizing is not required for chromium phosphating after alkaline cleaning because of the strongly acidic nature of the treatment bath.

Product Utilization. The principal application for chromium phosphate coatings is as a paint base for painted aluminum extrusions and aluminum beverage can stock. In these applications, extremely demanding performance criteria are met by the chromium phosphate conversion coatings. As an example, the Architectural Aluminum Manufacturer's Association Voluntary Specification 605.2-92 requires humidity and salt spray testing for 3000 hours and allows only minimal incidence of paint failure after testing (47).

Chromium Chromate. Chromium chromate treatment baths are acidic and made up from sources of hexavalent chromium and complex fluoride, fluorosilicate, fluorozirconate, fluorotitanate, and silicofluorides. Optional additional components added to accelerate coating rate are free fluoride, ferricyanide, and other metal salts such as barium nitrate. Conversion coating on aluminum precedes by the following reactions (23,24,38):

$$\begin{aligned} &\textit{Oxide removal} \quad && Al_2O_3 + 6\ HF \longrightarrow 2\ AlF_3 + 3\ H_2O \\ &\textit{Redox reactions} \quad && HCrO_4^- + 7\ H^+ + 3\ e^- \longrightarrow Cr^{3+} + 4\ H_2O \\ & && Al^0 \longrightarrow Al^{3+} + 3\ e^- \\ &8\ H^+ + 2\ HCrO_4^- + 2\ Al^0 \longrightarrow 2\ Al^{3+} + Cr_2O_3 \cdot 3\ H_2O + 2\ H_2O \end{aligned}$$

The coating composition is a combination of hydrated chromium and aluminum oxides and hydroxides, eg, $Cr_2O_3 \cdot xH_2O$, $x = 1, 2$.

Chromium chromate coatings that have very low (0.05 g/m^2) coating weights may be deposited. These give colorless coatings. Moderately heavy (0.8 g/m^2) gold-colored coatings for maximum corrosion protection may also be deposited. Because of the hydrated nature of chromium chromate coatings, the corrosion protective properties are sensitive to elevated temperatures and prolonged heating.

Operation and Control. Control of chromium chromate conversion coating baths is accomplished by controlling chromium concentration and pH. The quality of the conversion coating is sensitive to aluminum accumulations in the coating bath as well as to rinse water purity. Sulfate contamination is a particular problem.

Typical processing steps in chromium chromate application by spray or immersion contact are alkaline cleaning (etching or nonetching), water rinse, acid deoxidize/desmut, water rinse, chromium chromate conversion coat, and a final water rinse. The performance of chromium chromate conversion coatings is strongly affected by the presence of oxides and alkali-insoluble alloying elements (smut) on workpiece surfaces. For most applications, an acidic deoxidizing–desmutting operation is required before the conversion coating stage.

Product Utilization. Applications for chromium chromate coating are extensive. Aircraft components, aluminum castings, zinc castings, magnesium castings, galvanized steel passivation, and aluminum sheet passivation are example applications for chromium chromates. In aerospace applications, the performance criteria for chromium chromate conversion coatings are extremely demanding. The Mil-C-5541E Specification includes performance criteria for salt spray resistance of 168 hours for unpainted conversion coated aluminum alloys without significant signs of corrosion. At the same time, the conversion coating must comply with a low electrical resistivity criteria to perform well in resistance spot-welding operations and electrical and electronic uses (48).

A nitric acid and chromic acid-free cleaning composition and process for cleaning aluminum and aluminum alloys has been reported (49).

3.3. Anodizing.

Whereas many metals can be anodized, aluminum is by far the most widely anodized metal. The anodizing process is comprised of several pre- and post-treatment steps. The anodizing step consists of placing the part to be anodized in a tank where a controlled direct current charge can be applied for a predetermined length of time. At the anode, ie, the part, the aluminum is oxidized to aluminum oxide. The hydrogen ion migrates to the cathode, where it is reduced, forming gas bubbles that are given off to the atmosphere. As this process continues, a uniform porous oxide film is formed on the part (50). The resulting material having the anodic film can be used for structural purposes, such as aircraft parts, or for decorative purposes, such as windows or picture frames.

Operation and Control. The amount of current applied to the part determines the speed of which the anodic film is formed. Generally, a current density of 12.9–25.8 mA/cm^2 (12–24 A/ft^2) is applied to produce a coating thickness of 10–20 μm (0.4–0.8 mils) per 20 minutes. Most coatings range in thickness from 5–50 μm (0.2–2.0 mils).

The temperature of the anodizing solution also has an effect on the anodic film structure. Thus chillers are used to maintain a consistent temperature in the bath while the part is being anodized, and air agitation is continuously applied to ensure a uniform temperature. The result is a consistent anodic film density of uniform pore size.

Several different acids can be used for anodizing. Phosphoric acid is employed primarily to produce a very porous film. During the anodizing step, the phosphoric acid attacks the growing anodic film, etching a portion of it away. The resulting film can be used as a paint base or adhesive bonding preparation having excellent adhesion properties. Chromic acid is used when high corrosion and abrasion resistance is needed. Most aircraft parts receive this type of anodic coating because any residual acid does not corrode the metal. The anodic film has a distinctive dull green color when chromic acid is employed. Oxalic acid is rarely used but produces a very hard, wear-resistant coating. The anodic film has a grayish yellow color. Some movable aluminum engine parts receive this type of anodizing. Sulfophthalic acid, otherwise known as duranodic or integral coloring, is used to produce a decorative anodic film ranging in color from bronze to black. This process was used extensively from 1950 to 1970 for the color of window and building fascia parts. This process consumes large amounts of electricity, however, and has become too expensive to use. Sulfuric acid is the most widely used acid for anodizing. It produces a hard, clear anodic film which can be subsequently colored using inorganic or organic coloring solutions. Sulfuric acid anodizing is used for both wear-resistant coatings and decorative purposes.

Typical processing steps in anodizing are precleaning, alkaline etching, desmutting, anodizing, two-step coloring or dyeing, and sealing. Water rinses are generally interspersed between stages. The precleaning step is critical in anodizing because it removes the shop soils and cutting lubricants before etching. Precleaning solutions are nonetching and nonsilicated cleaners, and usually contain borates to inhibit the etch. If the part to be anodized is not completely cleaned, the subsequent etching step leaves undesirable patterns on the aluminum.

In the alkaline etch step, the aluminum is given the desired appearance by either etching the surface or chemically polishing it. The alkaline etch gives the aluminum a matte finish which has a satin appearance. The desmutting step is used to remove any of the alloying elements left on the surface after the etching process. Many alloying elements, such as copper, iron, magnesium, and silicon, are not soluble in alkaline solutions. Thus these are left behind on the aluminum surface as a smut.

In the anodizing stage electrolytic reactions produce a uniform aluminum oxide layer across the aluminum surface. This anodic film is transparent and porous. The underlying matte or bright surface can be seen. After anodizing, the aluminum part can be colored or sealed.

The two-step coloring method, sometimes called electrolytic coloring, is the most popular coloring method for architectural purposes. The process involves placing the unsealed anodized parts in a bath constructed similarly to the anodizing tank. The two-step bath chemistry contains a metal salt dissolved in an acid. When alternating current is applied to the part, the metal ions are attracted to the anodic film and precipitate in the anodic pore. As the precipitation continues, the anodized part gradually increases in color until a black color is achieved showing complete saturation of the anodic pores. This coloring process can be stopped at any time during the coloring process with varying shades of color.

The use of dyes for coloring is becoming more popular because of the almost infinite range of colors that can be produced. Moreover, dyes do not need to be electrically deposited. Anodized parts are simply placed in a heated dye solution until the pores become saturated with the pigment (see DYES AND DYE INTERMEDIATES; PIGMENTS, INORGANIC).

As a final step, anodized parts must be sealed to ensure corrosion resistance of the anodic coating. Sealing involves plugging the anodic pores completely so contaminants cannot reach the base metal. A variety of sealing methods are used by anodizers (see SEALANTS).

4. Pickling

4.1. Introduction. Pickling is a term used to describe metal-cleaning operations designed to remove oxides from metal surfaces. These oxide films may be the result of in-process operations such as heat treating, hot rolling, forging, chemical passivation and etching, or simply environmental corrosion. Among the terms commonly used to describe these oxide layers are scale, rust, smut, white corrosion, and black or blue oxide. Although in some cases the oxide films may be removed using alkaline solutions of various compositions, pickling solutions are predominantly acidic, and most often very strongly acidic.

A number of pickling formulations are available. The proper choice is dictated by the chemistry of the base metal as well as of the oxide film itself. Whereas no single pickle formula is generally effective on all metal alloys, sulfuric acid is probably the most versatile of all the acids. The mechanism by which the acid solutions attack and remove the oxide film varies with the metal, metal oxides to be removed, and the acid used. In some cases oxides are removed by the acid, such as sulfuric acid, penetrating film imperfections such as cracks in the oxide layer, then attacking the base metal. Hydrogen gas is formed at the oxide–metal interface. The pressures thus generated blow off the oxides. Many acids, eg, hydrochloric acid, dissolve the base metal as well as the oxide layer. Pickle inhibitors are therefore available for most pickling acids. These inhibitors minimize or prevent the acid from attacking the base metal, yet allow effective removal of the oxides.

The speed of the pickle reaction is also dependent on the concentration and temperature of the pickle, the degree of agitation of either the metal part or the pickle solution, the alloy being pickled, and the acid used. Pickling solutions may be applied by either spray or immersion techniques. However, because of the noxious fumes emitted, there must be adequate ventilation. Sometimes, particularly when spraying techniques are used, an enclosure to contain the fumes and mist is employed.

4.2. Metals and Alloys. *Carbon and Low Alloy Steels.* Sulfuric acid and hydrochloric acid are the predominant pickling acids for ferrous alloys and some stainless steels having less than 10% chrome and nickel (see STEEL). However, organic acids, such as citric acid and tartaric acid, are seeing more use because these latter are nontoxic and less hazardous. Sulfuric acid is generally used at 10–15 vol % of 66°Bé acid at 65–83°C; hydrochloric is generally used at 20–40 vol % of 20°Bé acid at ambient up to 55°C. Pickling inhibitors are often used with these acids to minimize base metal loss, severe etching, and pitting without significantly affecting the rate of oxide removal. Metal loss can be reduced by 97–99% by using an inhibitor formulated specifically for the pickling acid.

High Chrome–Nickel Stainless Steels. Probably the most common descaling or pickling solution is a combination of about 10% by volume nitric acid with 1–4% hydrofluoric acid at about 49°C. For heavy oxide films, this mixed acid pickle may be preceded by a 20% by volume sulfuric acid pickle. Because scale is generated upon annealing, a molten oxidizing salt bath is used to condition the scale and minimize the concentration and temperature required for the mixed acid treatment. Hydrochloric acid is rarely used for stainless steels, particularly for descaling or deoxidizing finished parts, because of its propensity to cause localized pitting. Sulfuric acid fortified with chloride salts or organic acids may be used successfully for removal of thin oxides on certain alloys.

Aluminum Alloys. Oxide removal on aluminum is generally accomplished using solutions of nitric (20–25% vol%) or sulfuric acid (5–10 vol%), containing various amounts of fluoride ions to control the etch and speed of oxide removal. Chromic acid has also been used as an etch retardant in sulfuric acid, but for ecological and health reasons use of chromic acid is becoming rare. Nonetching oxide removers, or bright dip solutions, consisting of fluoride compounds such as hydrofluoric acid or hydrofluorosilicic acid, formulated with organic compounds such as tragacanth gum or certain surfactants, are also effective.

Copper and Copper-Containing Alloys. Either sulfuric or hydrochloric acid may be used effectively to remove the oxide film on copper (qv) or copper-containing alloys. Mixtures of chromic and sulfuric acids not only remove oxides, but also brighten the metal surface. However, health and safety issues related to chromium(VI) make chromic acid less than desirable.

Zinc and Zinc Alloys. Zinc metal is highly reactive in acid solutions such as sulfuric, hydrochloric, and nitric dissolving rapidly at acid concentrations normally used to pickle steel and aluminum. Dilute (1–4%) solutions of these acids can be used with caution to remove zinc oxides. Sulfamic acid at concentrations of 2–6%, in conjunction with the proper proprietary inhibitor, can be effective in removing zinc oxides and corrosion by-products without attacking the zinc metal.

Magnesium Alloys. Heavy oxides are usually removed from magnesium alloys by using a concentrated (ca 20–25%) hydrofluoric acid solution. Because of its highly toxic and corrosive nature, extreme care must be taken when handling or using hydrofluoric acid solutions. Chromic acid at about 350 g/L containing small amounts (0.1–0.5 g/L) sulfate and chloride ions effectively removes surface contaminants and oxides without significantly attacking the base metal.

4.3. Alkaline Deoxidizers. In certain applications, and particularly when hydrogen embrittlement caused by acid etching must be prevented, highly caustic alkaline solutions together with complexing agents, eg, gluconates, citric acid, and EDTA, can be used to derust or remove light scale on steel alloys. These solutions are normally operated at concentrations of 120–360 g/L and at temperatures above 93°C. Even under these conditions, alkaline deoxidizers are significantly slower than acids in removing the surface contaminants.

5. Health and Safety Factors

Acids such as sulfuric, hydrochloric, nitric, and especially hydrofluoric as well as strong alkalies such as caustic soda and caustic potash are extremely corrosive to animal and vegetable tissue. Extreme caution must be taken to prevent skin contact, inhalation, or ingestion. Violent reactions may occur when dissolving or diluting many of these chemicals with water.

Proprietary additives used with or formulated into acids and alkalies to impart desirable characteristics such as inhibition, improved wetting, and chelating may also contain toxic or carcinogenic chemicals. Producers of proprietary metal finishing chemicals are researching ways to replace and eliminate hazardous chemicals traditionally used in the pickling industry. The Material Safety Data Sheet (MSDS) for each chemical or proprietary blend used in a process must be thoroughly read and understood before the process is put into practice. Ref. 51 gives data for the individual chemicals.

6. Environmental Concerns

There are three aspects of conversion coating application which impact the environment. First, high operating temperatures for cleaners and phosphating baths make these processes energy intensive. Efforts aimed at formulating systems from cleaning to post-treatment, which can be applied at temperatures ranging from 38–49°C, have had some success for iron and zinc phosphates.

Secondly, because conversion coatings rely on including such metals as zinc, nickel, and chromium, the possibility of discharge of these metals is likely. Some manufacturing locations already fall under legislation prohibiting the use of these metals. Substitutes for Ni-containing phosphates have been developed, but zinc is still part of these sytems. Zinc phosphates and zinc phosphates modified with nickel are coming under scrutiny as contributors to heavy-metal contamination of water supplies. In some locations, the use of nickel is already prohibited and iron phosphates are the alternative choice. Chromium has been eliminated from post-treatment solutions and chromium-containing coatings on aluminum and zinc are being replaced with nonchromium coatings for some applications without any sacrifice of performance.

Lastly, sludge generation is an expected by-product of the conversion coating reaction. Some types of sludge are not considered hazardous waste. In many locations these can be disposed of in open landfill sites. This is expected to change and the disposal of all sludges is expected to be problematic (52). General restrictions on the disposal of sludge generated when aluminum is treated in a conversion coating system have been in place since the early 1980s. No economically feasible way to recycle conversion-coating sludge is available, although this problem occupies research efforts of companies worldwide.

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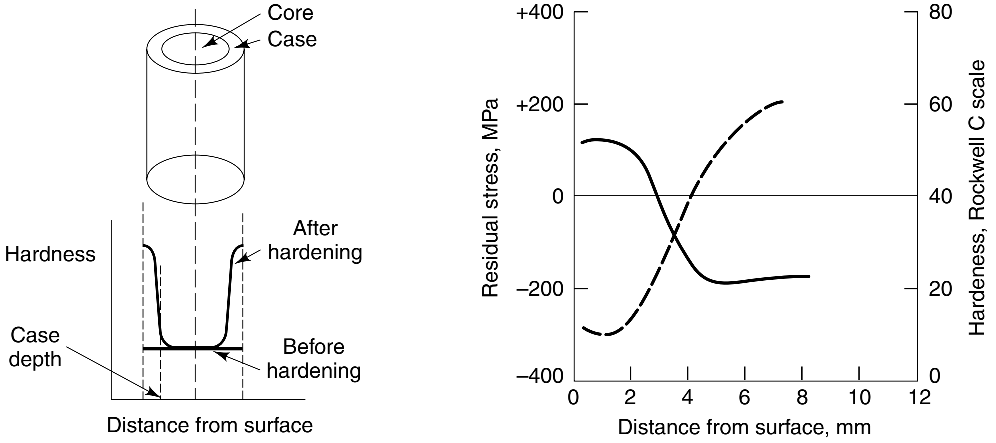


(**a**) (**b**)

Fig. 1. (**a**) Schematic diagram showing definition of case hardening and of case depth where (—) is the diameter; (**b**) residual stress across the radius of a case hardened steel, showing the high compressive residual stress (— — —) at the surface induced by induction heating, as well as the microhardness (—) of the surface (1). To convert MPa to psi, multiply by 145.

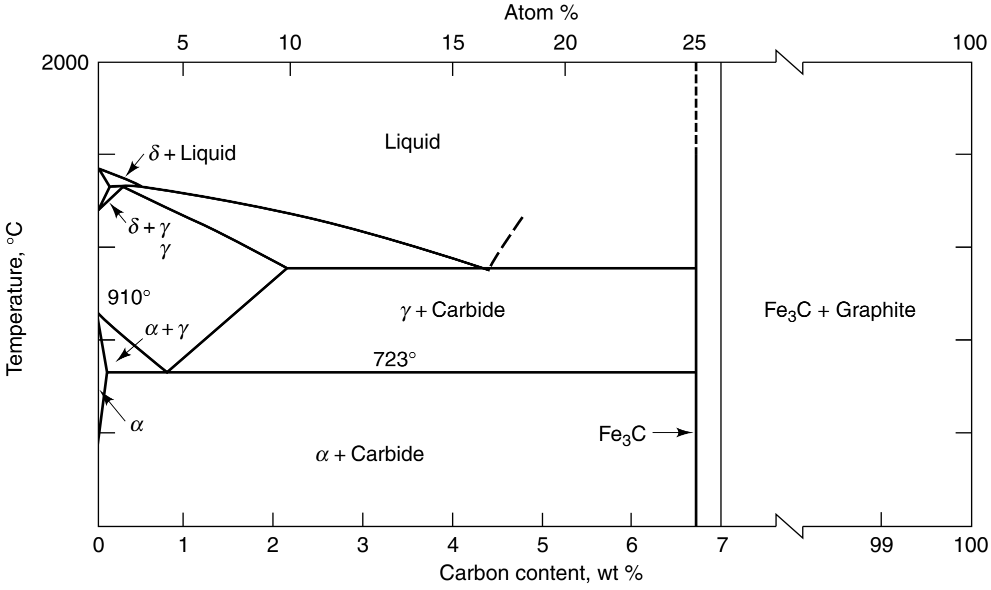


Fig. 2. The iron–carbon phase diagram (3).

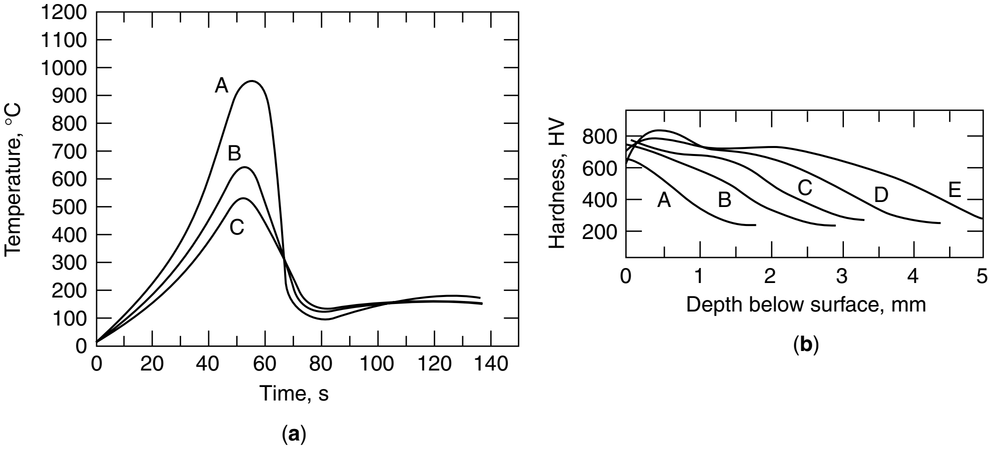


Fig. 3. Flame hardening: (**a**) temperature–time heating curves of a 25 × 50 × 100 mm specimen at a feed of 75 mm/min and burner distance of 8 mm showing temperatures of A, surface; B, 2 mm below surface; and C, 10 mm below surface; (**b**) hardness–depth curves for a 0.50% C steel 25 × 75 × 100 mm specimen at a feed of 50 mm/min, temperatures in °C measured 10 mm below the surface, and burner distances in mm, respectively, of A, 530 and 50; B, 540 and 12; C, 545 and 10; D, 550 and 8; and E, 565 and 6. Flame heating followed by water spray quenching. HV = Vickers hardness. (Courtesy of Butterworths (4).)

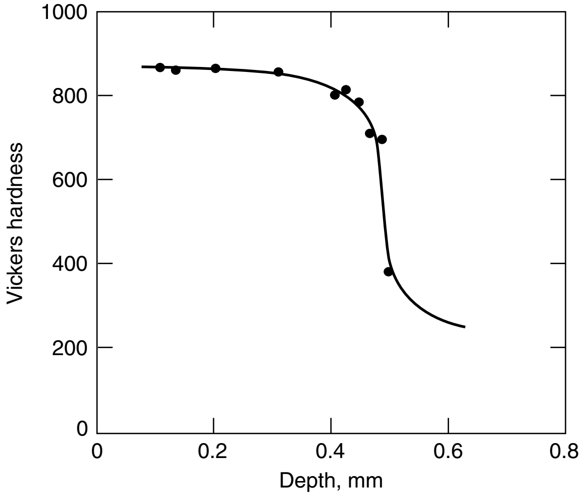
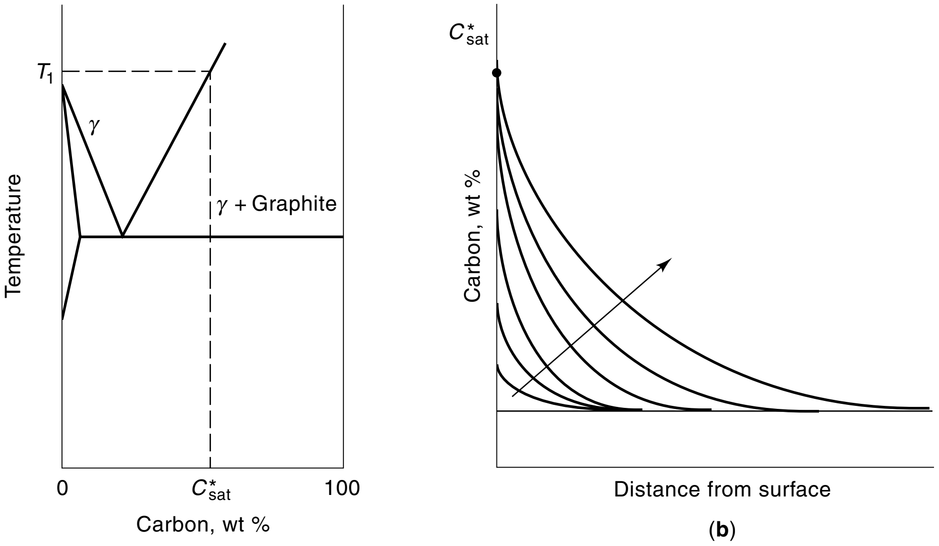


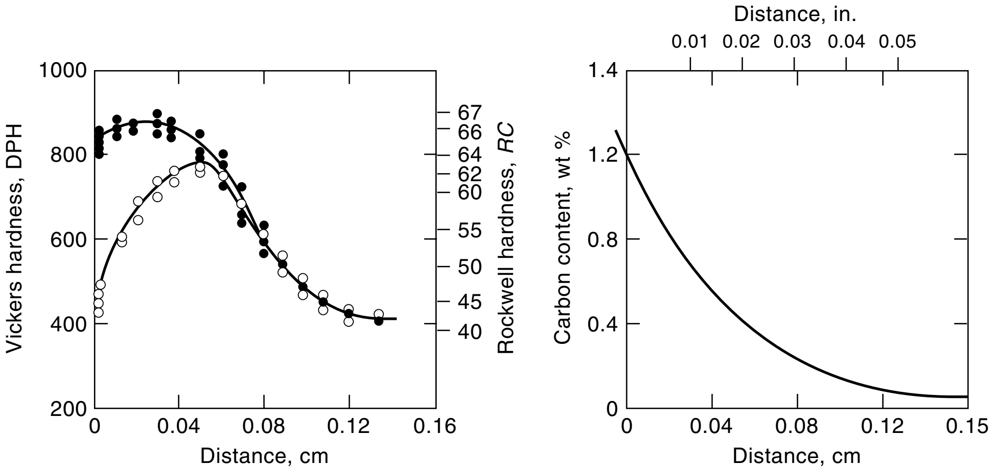
Fig. 4. Hardness–depth curve for case hardening of 0.6 wt% C steel by laser heating (7).



(a)

(b)

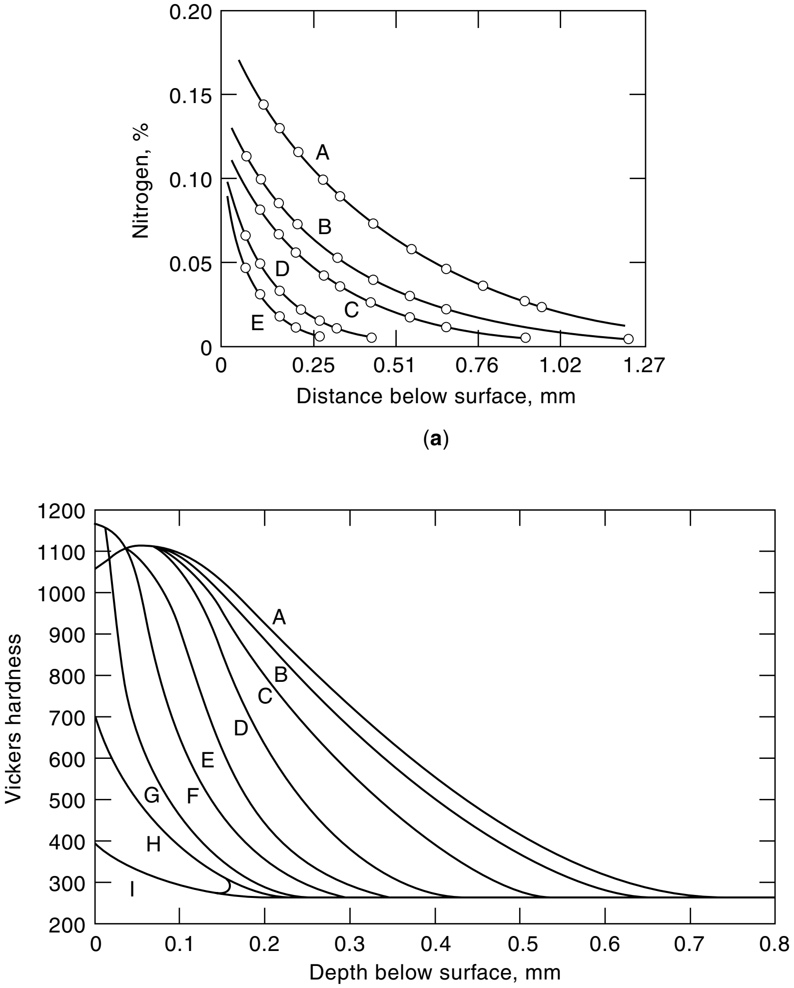
Fig. 5. Schematic illustration of the increase in carbon content with carburizing time. The maximum carbon content at the surface is given by the saturation value, C^*_{sat}. (**a**) Phase diagram; (**b**) plot of carbon content under the surface where the arrow represents increasing time at temperature T_1 (9).



(a)

(b)

Fig. 6. (**a**) The effect of subzero cooling on the hardness gradient in a carburized and quenched 3312 steel where (°) is oil quenched from 925 to 20°C and (●) is cooled to −195°C. The initial quench to 20°C does not convert all of the austenite to martensite because the high carbon content in the surface region lowers the M_f temperature below 20°C. Subsequent cooling to −195°C converts most of the retained austenite to martensite, raising the hardness. (**b**) The carbon gradient for this system (12).



(**a**)

(**b**)

Fig. 7. (**a**) Nitrogen concentration profiles in a 1015 steel nitrided at 566°C using an aerated bath process where A is nitrided 10 h; B, 3 h; C, 90 min; D, 30 min; and E, 10 min (15), and (**b**) hardness profiles in a steel gas nitrided at 510°C where A is nitrided 90 h; B, 60 h; C, 30 h; D, 15 h; E, 10 h; F, 5 h; G, 3 h; H, 1 h; and I, 0.5 h. (Courtesy of Butterworths (4).)

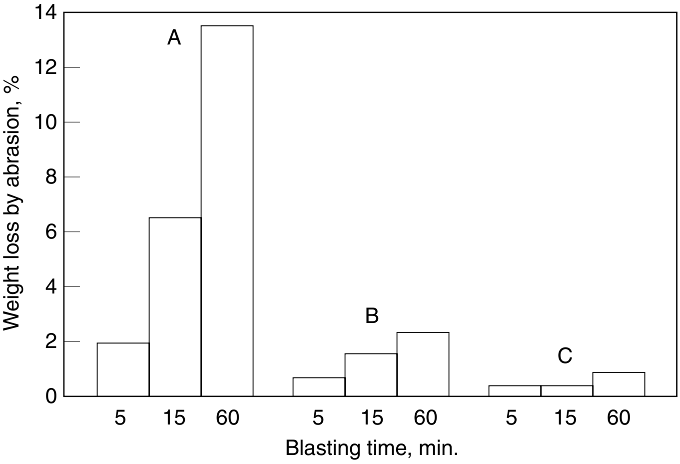


Fig. 8. Illustration of the effect of nitriding on the wear resistance of a steel blasted with steel grit: A, 300 HV steel; B, 750 HV steel case hardened by carburizing; and C, 1100 HV steel nitrided at 500°C for 60 h (17). HV = Vickers' hardness.

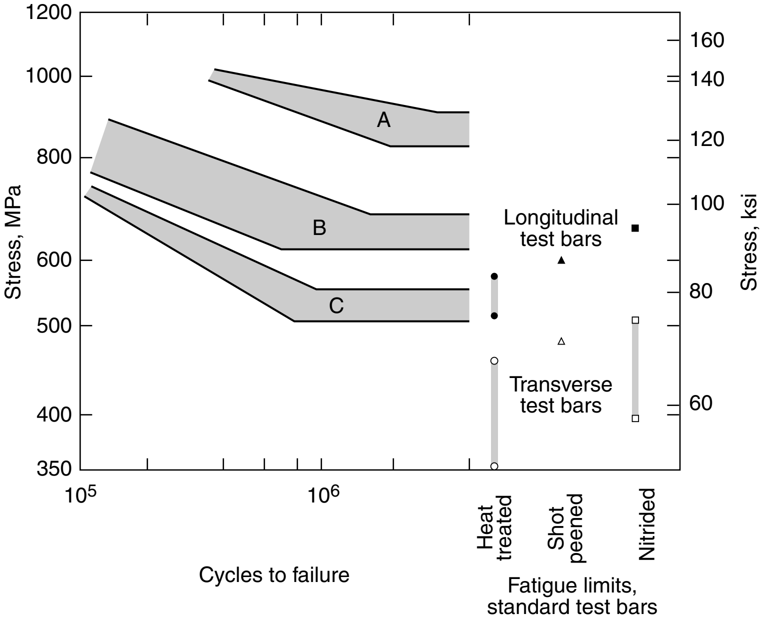


Fig. 9. Effect on fatigue strength of the plastic deformation of a carburized steel surface by shot peening (B) as compared to nitriding (A) and heat treating (C) (18).

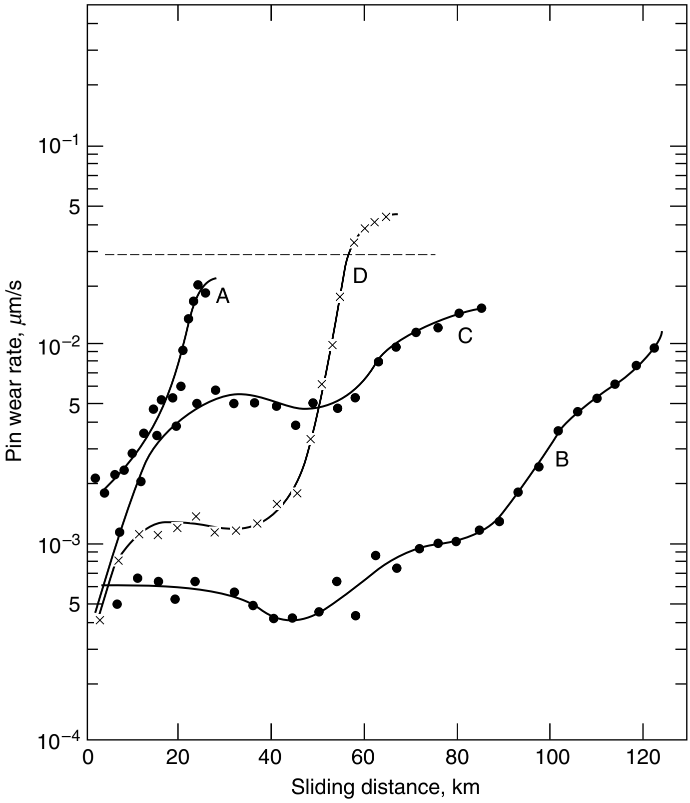


Fig. 10. Wear rates for iron, as measured in a pin-on-disk machine (—) unimplanted and implanted with (●) nitrogen at rates in atoms/cm^2 of A, 7×10^{15}; B, 1.7×10^{17}; C, 1.2×10^{18}; and with (×) neon D, at 1.7×10^{17} atoms/cm^2 (20).

Table 1. **Improvement in Material Life as a Result of Case Hardening**[a]

Steel	Surface hardness, HRC[b]	Method of hardening	Number of shafts tested	Cycles to failure $\times 10^6$
4140	36–42	through-hardened	20	>0.4
4320	40–46	carburized to 1.0–1.3 mm	6	ca 0.8
1137	42–48	induction hardened to 3.0-mm min effective depth and 40 HRC[b]	5	>1.1

[a] Ref. 2.

[b] HRC = Rockwell C hardness (see HARDNESS).