Table 7 Typical applications of liquid carburizing in noncyanide baths

	Weight			Case depth		Temperature					
Part	kg	lb	Steel	mm	in.	°C	°F	Time, h	Quench	Subsequent treatment	Hardness, HRC
Production tools	0.5–2.0	1.1–4.4	1018	0.375	0.015	925	1700	0.5–1.0	Brine	. . .	50–60
Bicycle forks	1.4	3.1	1017(a)	0.05–0.08	0.002–0.003	925	1700	0.085	Brine	Temper at 425 °C (795 °F)	60
Shift lever and ball	~1.5	~3.3	1040, 1017(b)	0.25	0.010	925	1700	0.67	Air cool 30 s in brine	. . .	File hard
Screw machine spindles	0.8	1.8	4620, 8620	0.89	0.035	(c)	(c)	6.0	Molten salt, 205 °C (400 °F)	. . .	60–63
Clock screws and studs	0.005	0.011	1006, 1113	008–0.10	0.003–0.004	955	1750	0.2	Brine	. . .	62–64
Flat head screws	0.015	0.033	1122	0.15	0.006	925	1700	0.33	Molten salt, 290 °C (550 °F)	. . .	56

(a) Partial immersion. (b) Carburizer brass braze. (c) Preheat at 840 °C (1545 °F); carburize at 920 °C (1690 °F)

production basis. For ease of reference, the parts in Table 6 have been separated according to type of steel (carbon, resulfurized, or alloy), and the parts in each group have been arranged in alphabetical order. Tables 6 and 7 also provide details, wherever they were available, regarding case depth, carburizing temperature and cycle time, method of quenching, subsequent treatment, and surface hardness.

The parts listed in Table 6 were carburized in cyanide-type baths. Noncyanide carburizing baths can be used with slight adjustments in operating conditions to do much of the carburizing described in Table 7. Noncyanide carburizing is particularly applicable to parts treated at temperatures above 900 °C (1650 °F). Some specific applications for noncyanide liquid carburizing of production parts are listed in Table 7.

In general, liquid carburizing is best suited to small and medium-sized parts. Very large parts, such as rock-bit drill rods 6 m (20 ft) long and rings 2 m (7 ft) in diameter, are too large to be conveniently processed in salt and are commonly carburized by pack methods. Because of the problems associated with salt removal, carburizing in salt baths is not recommended for parts containing small holes, threads, or recessed areas that are difficult to clean.

Stopoffs and Selective Carburizing

Selective carburizing can be accomplished in liquid carburizing baths by stopping off carbon penetration with either copper plate or copper-base paint. Because cyanide-based salts can dissolve copper, salt baths with relatively low cyanide contents are necessary. One successful formulation operates at 8 to 10% NaCN with approximately 45% $BaCl_2$ energizer. Noncyanide carburizing salts will not dissolve copper.

When copper plate is employed to prevent carbon penetration, the copper layer should be fine-grained, dense, and without pinholes or other porosity. Smooth surfaces require lower plating thicknesses than do rough surfaces. Copper plate thicknesses recommended for protection against liquid carburizing for various times are as follows:

	Copper plate thickness	
Time, h	mm	in.
Low-temperature salts		
<1	0.013	0.0005
1–5	0.020	0.0008
High-temperature salts		
<7	0.025	0.0010
7–15	0.040	0.0015
15–30	0.050	0.0020

Partial Immersion. Another method for selective carburizing in liquid carburizing baths entails partial immersion of the workpiece in the salt bath so that only the immersed areas are carburized. With this method, unless a clean-cut breakoff between carburized and noncarburized areas is required, the use of copper plate or copper-base paint is unnecessary.

Oxidation of the work at the bath surface can be reduced if the parts are initially immersed an inch or two deeper than required, to coat them with salt, and are then withdrawn to the required depth. A piece of plain carbon steel pipe with the bottom closed by welding can be inserted in a corner of the bath to displace salt if a precise adjustment of the bath level is necessary. Typical parts that are well suited to carburizing by the partial-immersion technique are shown in Fig. 11.

Combined Carburizing and Brazing

It is possible to braze and carburize steel parts simultaneously in either a cyanide or a noncyanide liquid carburizing bath, provided that the operating temperature of the bath is high enough to cause the brazing alloy to flow. Initially, the parts are cleaned and degreased and then the components are assembled with brazing alloy enclosed in the joints. One suitable brazing alloy, in the form of wire or thin strip, contains 55% Cu and 45% Zn, melts at 880 °C (1620 °F), and makes a sound joint at 900 to 925 °C (1650 to 1700 °F). No flux is required.

The assembly is immersed in the liquid carburizing bath for a time long enough to produce the desired case depth and at a temperature high enough to cause the brazing alloy to flow. It is then quenched to harden the steel and complete the braze. Press-fit assemblies with carefully designed lap joints are ideal for this application.

Precautions in the Use of Cyanide Salts

Cyanides cause violently poisonous reactions if allowed to come into contact with scratches or wounds (on the hands, for example); they are fatal if taken internally. Also, fatally poisonous fumes are evolved when cyanides are brought into contact with acids. The white deposits that form on hoods and cooler furnace parts consist mainly of sublimed sodium carbonate, with small amounts of sodium, potassium, and barium salts, but may contain some cyanide as the result of splashing.

When cyanide salts are removed from the storage container, the container should be opened in the room in which the cyanide is to be used. The salts should be removed from the container with a metal scoop or gloved hands, or by being dumped out as required. When not in use, the container should be covered with its original cover or with a metal substitute cover.

The precautions that should be observed in handling cyanide-type carburizing salts are the same as for any other cyanide mixture. Work material must be clean and dry, and the bath must be enclosed and well ventilated. Even the slight amount of moisture that may be deposited on parts and fixtures as a result of atmospheric humidity will cause spatter in contact with molten salt. Accordingly, operators should be equipped with long protective gloves, protective aprons, and safety glasses or face shields. Further information is available from OSHA and EPA publications. When adequate precautions are observed, carburizing salts should not present serious hazards to health or safety.

Remelting a frozen cyanide bath in externally heated furnaces can be potentially hazardous because of the expansion of the salt and gases as the salts are heated. This hazard is not encountered with immersed-electrode furnaces because the salts melt from the top down. If remelting is done in externally heated furnaces, however, the following precaution should be

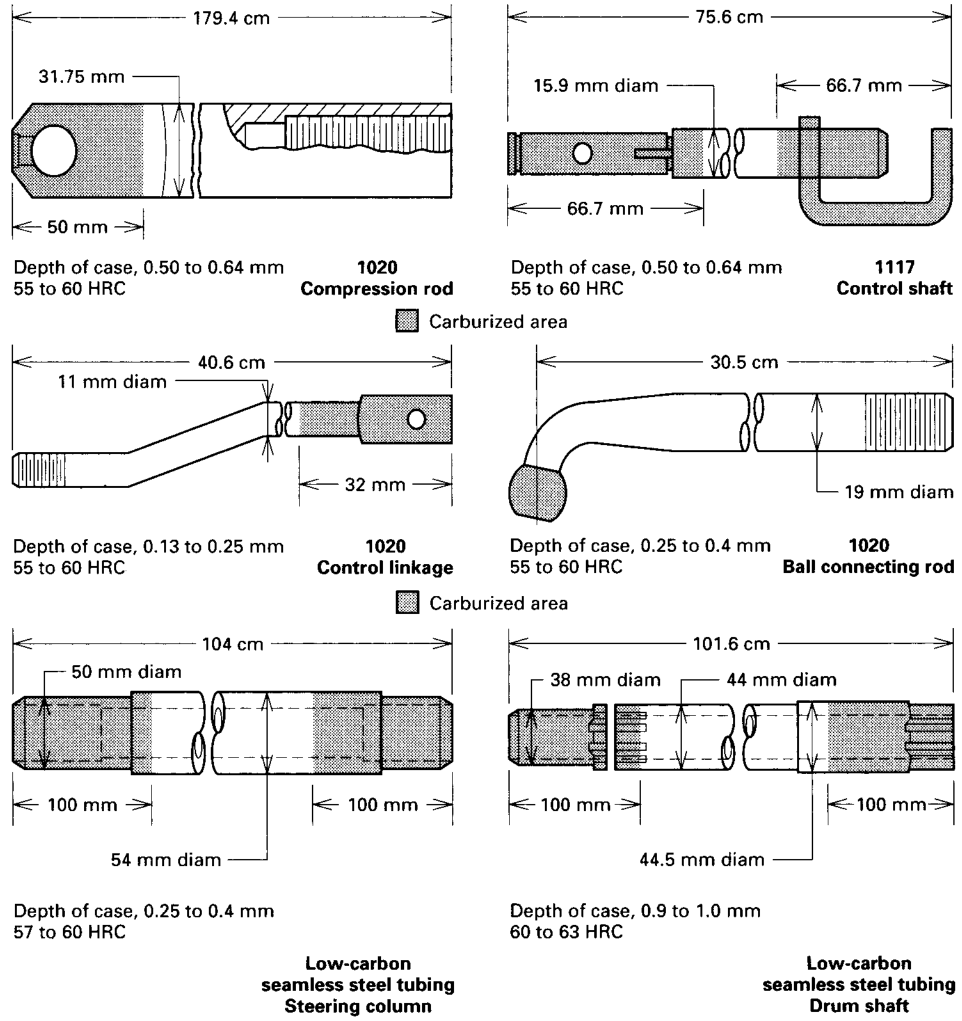


Fig. 11 Typical parts selectively carburized by partial immersion. Only the portion that is to be carburized is immersed in the bath. Area to be carburized is shaded.

observed: a steel or cast iron wedge should be inserted in the center of the bath before the bath freezes. One end of the wedge should make contact with the bottom of the pot; the other end should extend at least 10 cm (4 in.) above the surface of the bath. Before the bath is remelted, the wedge should be tapped with a hammer, loosened, and removed. The space previously occupied by the wedge will provide a vent for expanding salt and gases during remelting. No attempt should be made to remove a wedge from a bath that is not completely solidified, because molten salt may be forcibly blown out through the opening created.

Disposal of Cyanide Wastes

Cyanide wastes, whether dissolved in quench water or in the form of solid salt from pots, pose a serious disposal problem. The cyanide contents of these wastes must be chemically altered to render the material nonpoisonous before it is discharged into sewers or streams. Because of the toxicity of cyanide wastes, local ordinances and pollution authorities must be consulted regarding the proper disposal of wastes.

Chemical Treatment. The simplest treatment consists of oxidizing the cyanide in an alkaline solution to which is added either chlorine gas or its equivalent in the form of a hypochlorite compound, such as sodium or calcium hypochlorite (bleaching powder). The choice between gas or powder depends on the quantity of cyanide to be treated, on the availability of facilities and experienced personnel for handling the oxidizing agents, and on economics. For small quantities of cyanide solutions, it may be more practical to use a hypochlorite compound than to use chlorine gas.

Depending on the oxidizing agent employed, several reactions take place when cyanide is converted into a disposable form. One reaction with chlorine gas is as follows:

$$2NaCN + 4NaOH + 2Cl_2 + 2H_2O \rightarrow (NH_4)_2CO_3 + Na_2CO_3 + 4NaCl \qquad \text{(Eq 18)}$$

This reaction indicates that, for each kilogram (2.2 lb) of sodium cyanide, 1.42 kg (3.13 lb) of chlorine gas and 1.6 kg (3.5 lb) of sodium hydroxide are required. Because of probable side reactions, however, practical experience indicates an actual requirement of slightly more than 2 kg (4.4 lb) of chlorine for each kilogram of sodium cyanide present in the waste solution. When a hypochlorite compound is used, the amount of powder required may be estimated on the basis of available chlorine content in the compound.

Solid cyanide wastes must be dissolved in water before they can be treated. A tank of suitable capacity, equipped with a coarse screen set well above the bottom, will facilitate solution of the solid material. The tank should also have an agitator, and, for chlorine gas, a perforated pipe placed well below the solution level is required.

When cyanide wastes are to be treated with chlorine gas, the cyanide content must first be determined and the proper amount of caustic added. The gas is then introduced slowly while the temperature of the solution is kept below 50 °C (120 °F). If a sodium hypochlorite solution is used, sufficient caustic should be added to raise the pH of the cyanide solution above 8.5. The reaction between cyanide and the oxidizing agent should continue until a slight excess of chlorine is present in the solution. This can be determined by testing with starch iodide paper or with a solution of potassium iodide and starch. Both the iodide paper and starch solution will turn blue in the presence of free chlorine.

Treatment Equipment (Ref 9). The equipment shown in Fig. 12 is used to treat cyanide and barium salts. There is nothing new in cyanide treatment chemistry, and it has been used satisfactorily since the 1930s in batch and continuous treatment processes. It uses sodium or calcium hypochlorite salts. Sodium hypochlorite solutions containing from 10 to 15% available chlorine are available from local chemical suppliers. Calcium hypochlorite, sold in the granular or tablet forms, contains in excess of 70% available chlorine. This is also available from local chemical suppliers. Chlorine gas could also be used, but many wastewater treatment plants prefer to use the hypochlorite salts.

Theoretically, 1.24 kg (2.73 lb) of available chlorine is required to oxidize 0.5 kg (1 lb) of cyanide as CN to the cyanate form. Another way to state this is that 0.66 kg (1.45 lb) of available chlorine is required per 0.5 kg (1 lb) of sodium cyanide. The presence of other oxidizable substances would increase the chemical requirements. The reaction is practically instantaneous; therefore, the allowance of 10 min for completion of the reaction is sufficient. Ferro- or ferricyanides are not removed by this reaction.

The treatment should be performed above a pH of 10 to ensure that the resulting by-product is cyanate and to minimize the evolution of cyanogen chloride. No instances are known where the reaction is required to be conducted beyond the cyanate stage. This reaction results in the evolution of carbon dioxide and nitrogen. It requires in excess of 3.2 kg (7 lb) of available chlorine per 0.5 kg (1 lb) of cyanide (as CN) and two pH adjustments—one above 10 for the first reaction and the other to 6.5.

The aforementioned treatment to the cyanate stage should produce an effluent containing less than 0.2 mg/L of CN amenable to chlorination.

The equipment shown in Fig. 12 can be used for batch treatment of rinses, water quenches, and spent salt. The latter must first be dissolved by placing it in a perforated basket that is immersed in water or a cyanide-rich rinse, while providing agitation. The concentration of sodium cyanide in the solution should not be allowed to exceed 5%, because of the evolution of heat due to the exothermic character of the reaction.

Another procedure for destroying cyanide in higher concentrations is by the use of heat and electrolysis in a plating bath, followed by treatment with sodium hypochlorite to remove the residual cyanide.

Hypochlorination is required for the removal of the cyanide residual because of the reduction in the effectiveness of electrolysis as the cyanide concentration decreases.

The treatment of cyanide solutions should be performed either under a hood or in tanks provided with ventilating ducts.

Figure 13 illustrates a continuous treatment operation with the first rinse being recirculated through cooling coils, with a side stream being treated. The second (still) rinse is also treated. The addition of sodium hypochlorite is controlled by an oxidation-reduction potential electrode assembly through a controller. Maintenance of pH is effected by a pH electrode assembly through a controller that activates metering pumps connected to sulfuric acid and caustic soda solutions. Only one of these solutions is used.

One indirect way to check for the removal of the cyanide amenable to chlorination after treatment is to check for residual chlorine by immersing a paper strip of potassium iodide starch indicator, which turns purple when chlorine is in excess of 10 mg/L.

The final result of the treatment is a treated liquid and a sludge. The latter is dewatered by filtration and carted to a suitable disposal site. The filter cake should not be hazardous, according to the tests prescribed by the EPA. Because the quantity of the sludge should be relatively small, it can be stored and periodically filtered.

The treatment effluent may not pass the test for total cyanides due to the presence of ferro- or ferricyanides, because these cannot be destroyed by chlorine compounds at ambient temperature. If the treated wastewater contains total cyanide in excess of 1.2 mg/L on any one day or a monthly average of 0.65 mg/L, an application can be made to the regulatory agency for approval of a limitation of, respectively, 0.86 and 0.32 mg/L as amenable cyanide. Ferrocyanides that are not amenable to chlorination do not show in this test; therefore, even if the limits on the concentration of cyanide are lower, they are less restrictive than the larger figures because they do not include the ferro- or ferricyanides that are not removable by chlorine treatment at room temperature.

Electrochemical Treatment. Although chemical treatment may be entirely adequate to meet local regulations, an electrochemical process has been used to destroy free cyanide. In the electrochemical process, cyanide wastes in aqueous solution are circulated through an electrochemical reactor. Within the reactor, an applied direct-current potential oxidizes the

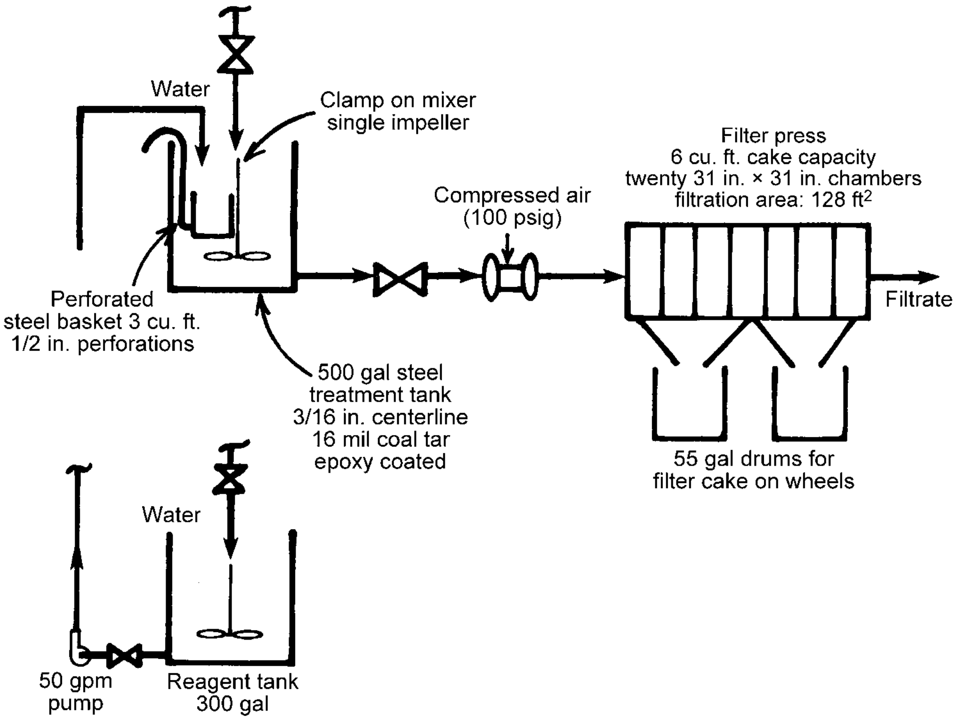


Fig. 12 Basic system for batch treatment of waste water containing cyanide or barium salts Ref 9

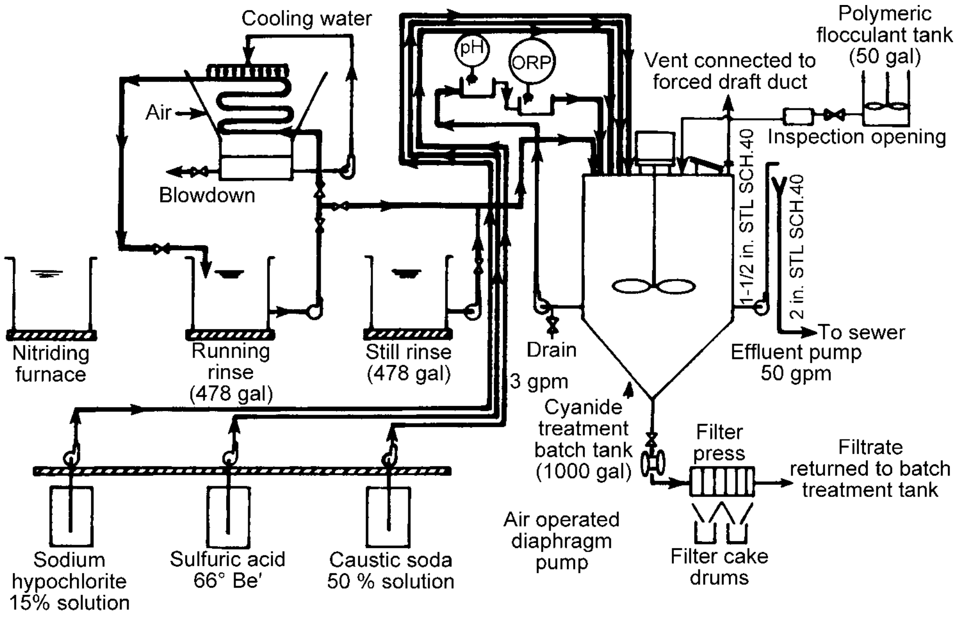


Fig. 13 Treatment of rinses from nitriding operations. ORP, oxidation-reduction potential Ref 9

free cyanide and cyanate according to the reactions:

$$2CN^- + 8OH^- \rightarrow 2CO_2 + N_2 + 4H_2O + 10e^- \quad \text{(Eq 19)}$$

$$2CNO^- + 4OH^- \rightarrow 2CO_2 + N_2 + 2H_2O + 6e^- \quad \text{(Eq 20)}$$

Free cyanide and cyanate are converted to the nontoxic gases carbon dioxide and nitrogen, which are allowed to escape freely from the vented storage tank into which the reacted solution is circulated.

The electrochemical process is most effective at high cyanide-ion concentrations. With continual recirculation between storage tank and reactor, cyanide can be reduced to 1 ppm or less in approximately 100 to 150 h. By combining electrochemical and chemical treatments, effective treatment can usually be achieved at minimum cost. Electrochemical removal is used to reduce cyanide concentration to ≈200 to 500 ppm, and then chemical treatment is used to complete the reduction.

Electrochemical treatment offers the following advantages:

- The process uses only electricity—no chemicals are required.
- Cost per unit weight of cyanide treated is low, depending only on the cost of electricity (approximately 6.6 kW · h/kg, or 3 kW · h/lb of free CN^-).
- Capital investment is higher than alkaline chlorination.
- The process is simple to control, requiring only periodic determination of cyanide concentration.
- There are no toxic or otherwise harmful reaction products.
- Upon reaching a concentration of 1 ppm cyanide, the oxidized effluent usually may be drained and further diluted by plant effluent.
- The process can also be used to convert nitrite into nitrate.

The only significant disadvantage is that the process is time-consuming when levels of cyanide below 200 ppm must be achieved. Increasing the number of reactors decreases process times.

REFERENCES

1. "Pure Case Noncyanide Carburizing Process," Technical Data Sheet, Heatbath Corporation
2. F.W. Eysell, Regenerable Salt Baths for Carburizing, Carbonitriding, and Nitrocarburizing: A Contribution to Protecting the Environment, *FWP J.*, Oct 1989
3. L.S. Burrows, Durofer—A Low-Toxicity Salt-Bath Carburizing Process, *Heat Treat. Met.*, Vol 4, 1987
4. P. Astley, Liquid Nitriding: Development and Present Applications, *Heat Treatment '73*, Book 163, The Metals Society, 1975, p 93–97
5. P. Astley, Tufftride—A New Development Reduces Treatment Costs and Process Toxicity, *Heat Treat. Met.*, Vol 2, 1975, p 51–54
6. H. Kunst and B. Beckett, Cyanide-Free Regenerator for Salt Bath Carburizing, *Heat Treatment '84*, Book 312, The Metals Society, 1984, p 16.1–16.5
7. R. Engelmann, Paper presented at the 39th Heat Treatment Colloquium, Oct 5–7, 1983 (Wiesbaden, West Germany)
8. C. Skidmore, Salt Bath Quenching—A Review, *Heat Treat. Met.*, Vol 13, 1986, p 34–38
9. W. Zabban, Technical Note: Environmental Regulations and Treatment for Salt Baths, *J. Heat Treat.*, Vol 6 (No. 2), 1988, p 117

ASM Handbook, Volume 4A, *Steel Heat Treating Fundamentals and Processes*
J. Dossett and G.E. Totten, editors

Low-Pressure Carburizing

Volker Heuer, ALD Vacuum Technologies GmbH

LOW-PRESSURE CARBURIZING (LPC) has been established over the past few years as one of the most popular case-hardening processes. Low-pressure carburizing is often referred to as vacuum carburizing. As with all case-hardening processes, the goal is to obtain a part with a solid, tough core and a hard, wear-resistant surface. It is applied to increase the fatigue limit of dynamically loaded components. Typical applications include gear parts, machine components, bearing components, as well as injection systems for engines. Case hardening essentially consists of three steps. First, the parts are austenitized, then carburized, and once the required carbon profile is reached, they are quenched. The microstructure in the surface layer (the case-hardening layer) of a case-hardened part is specified for functional surfaces (e.g., tooth flanks of gear wheels) as follows:

- Martensite is present, with a maximum of 20 to 30% retained austenite.
- Bone carbides or carbide networks are not permitted; finely dispersed carbides are permitted.
- Structure is free of bainite up to a depth of 70% of the case-hardening layer from the part surface.

Process

Figure 1 depicts a typical carbon profile, and Fig. 2 shows a typical hardness profile after a case-hardening process. In this example, the surface hardness is 750 HV, the core hardness is 350 HV, and the case-hardening depth (CHD) is 0.8 mm (0.03 in.). The common definition of case-hardening depth is the distance from the surface in which the hardness is still above the hardness limit of 513 HV (50 HRC).

The LPC process takes place in a pressure range between 5 and 15 mbar (4 and 11 torr) and a temperature range between 870 and 1050 °C (1600 and 1920 °F). In most cases, the carburizing temperature is between 920 and 980 °C (1690 and 1800 °F). During the complete process, the treated components are not exposed to any traces of oxygen. The typical CHDs of components processed with LPC are specified between 0.3 and 3 mm (0.012 and 0.12 in.), depending on the size and the application of the component.

Figure 3 shows the LPC process in a schematic diagram. First, the charge enters the furnace chamber under vacuum, followed by convective heating under a nitrogen atmosphere close to 1 bar (750 torr). Convective heating offers a quicker and more homogeneous heating of the load compared to vacuum heating alone. Subsequently, another heating phase under vacuum takes place. The actual carburizing and diffusion starts after all parts have reached the specified carburizing temperature. Carburizing takes place by applying a routine of alternating pulses and diffusion steps.

Oxygen-free hydrocarbons such as acetylene C_2H_2 (ethyne) are used as a carbon source. The hydrocarbons are injected into the furnace chamber, creating a pressure of a few millibars. On the surface of the treated parts, the hydrocarbons dissociate thermally. Subsequently, the surface carbon content rises to the point of saturation within a short time, which results in a high mass flow of carbon into the material. Before carbide formation may take place, the supply of carburizing gas is stopped, and the carbon diffuses into the material. Once the surface carbon content is sufficiently reduced, the carburizing gas is injected into the furnace chamber again. These so-called pulses are repeated until the part has absorbed a sufficient amount of carbon. After completion of the carburizing pulses, a longer diffusion step takes place. This final diffusion step is used to obtain the required surface carbon content. Depending on the steel type and the desired amount of retained austenite, the target for surface carbon content is typically between 0.65 and 0.85% (Fig. 1).

In addition to acetylene, other carbon sources such as propane (C_3H_8) or cyclohexane (C_6H_{12}) can be used. However, acetylene is by far the most commonly used carbon source for LPC.

Depending on the furnace size and geometry of the treated components, the surface area of a carburized load can be between 0.5 and 21 m^2 (5 and 225 ft^2).

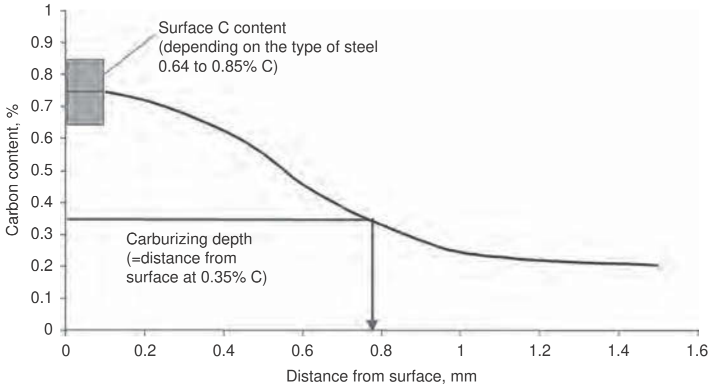


Fig. 1 Example of a carbon profile after case hardening

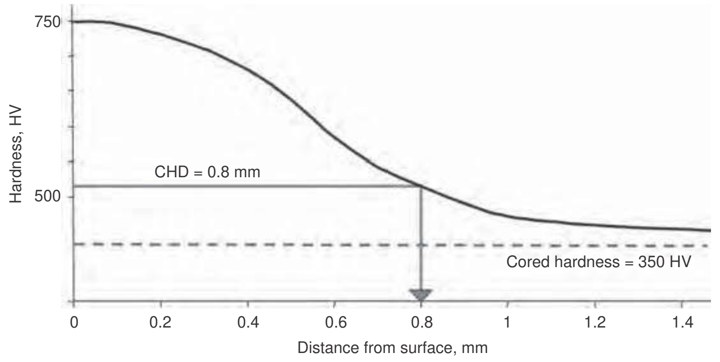


Fig. 2 Example of a hardness profile after case hardening. CHD, case-hardening depth

Once the targeted carbon profile is obtained, the parts are quenched. Quenching can be initiated either from carburizing temperature or from a lower hardening temperature. In most cases, high-pressure gas quenching (HPGQ) with either nitrogen or helium is applied after LPC. In some applications, oil quenching is applied after LPC. Details regarding the HPGQ process can be found in the article "Gas Quenching" in this Volume.

Contrary to atmospheric gas carburizing, where the case depth is achieved by control of the carbon potential, LPC is a recipe-controlled process. The process parameters of temperature, flow rate of carburizing gas, time, and pressure are defined in the heat treating recipe and controlled throughout the process to achieve the specified carbon profile.

The high mass transfer of carbon into the components during LPC leads to significantly shorter treatment times compared to conventional gas carburizing (Table1).

When combining LPC with HPGQ, the process provides the following advantages compared to gas carburizing combined with oil quenching:

- Excellent carburizing homogeneity, even for components with complex shapes
- Intergranular oxidation (IGO) and surface oxidation are avoided.
- Shorter cycle times
- Potential for further reduction of cycle time when applying high-temperature LPC (see the section "High-Temperature LPC" in this article)
- Possibility to integrate heat treatment into the production line
- Conditioning of the equipment is not necessary.
- Parts after heat treatment are clean; washing of parts is not necessary.
- Environmentally friendly process (small consumption of resources; no disposal of oil, salt bath residues, or detergent residues)
- Potential to reduce heat treatment distortion (unwanted changes in form and size of the part geometry during heat treatment)

The disadvantages include the higher equipment cost and the somewhat limited quench intensity of HPGQ, compared to oil quenching. Very large components cannot be quenched in gas successfully, unless they are made of a steel grade with excellent hardenability.

A detailed introduction into the technology of vacuum heat treatment including LPC is given in Ref 1.

Physical Principles

When acetylene comes in contact with the surface of the steel at temperatures above 870 °C (1600 °F), it dissociates thermally. The acetylene molecules dissociate into carbon and hydrogen:

$$C_2H_2 \rightarrow 2C + H_2 \qquad \text{(Eq 1)}$$

However, the real chemical reactions that take place are much more complex and can be reduced into nine main reactions, as illustrated in Fig. 4.

Detailed literature about the pyrolysis of acetylene and the surface reactions during LPC can be found in Ref 2 to 5. The kinetics of the LPC process were analyzed in an extensive study, with the help of a special thermobalance (Ref 6, 7). The height of the carbon mass transfer into the material is a function of steel grade, process temperature, and the number, length, and timing of the carburizing pulses. When working at a pressure range between 5 and 15 mbar (4 and 11 torr), the process pressure has no influence on carbon mass transfer.

The carbon yield that is absorbed by the load is approximately 65% when using acetylene. This value was determined empirically in industrial application. The carbon yield is defined as the amount of carbon absorbed by the load in relation to the total amount of carbon injected into the furnace chamber.

Once the carbon is absorbed into the material, the same diffusion laws apply as in conventional gas; that is, the diffusion of carbon in austenite follows Fick's law.

Low-pressure carburizing provides an oxygen-free surface after treatment. The process gases and the furnace atmosphere are free of oxygen. Therefore, IGO and surface oxidation of the components are safely prevented. Figure 5 shows a comparison of the surfaces after LPC and after atmospheric gas carburizing.

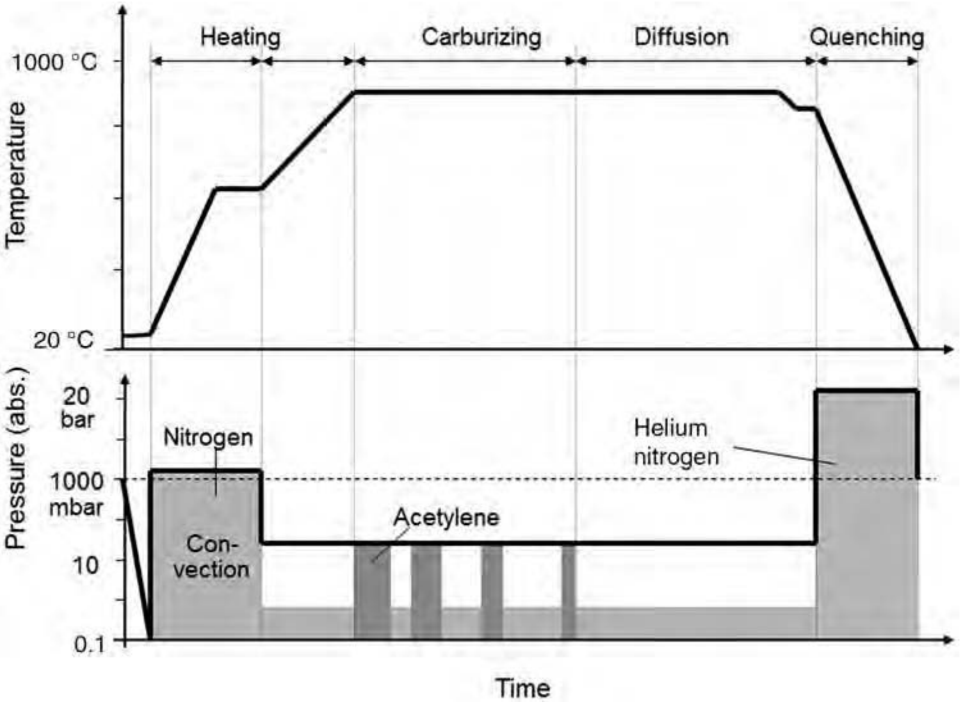


Fig. 3 Schematic diagram of the low-pressure carburizing and high-pressure gas quenching process

Table 1 Comparison of treatment times for low-pressure carburizing and atmospheric gas carburizing

Application	Material	Treatment temperature		Case-hardening depth		Treatment time(a), h	
		°C	°F	mm	in.	Low-pressure carburizing	Gas carburizing
Internal gear	28Cr4 (ASTM 5130)	900	1650	0.3	0.012	0.75	1.5
Gear	16MnCr5	930	1705	0.6	0.024	2	2.75
Shaft	16MnCr5	930	1705	0.8	0.032	2.75	4
Gear	18CrNiMo7-6	960	1760	1.6	0.063	7.5	9.5

(a) Treatment time = Carburize + Diffuse + Lower to hardening temperature

Figure 6 depicts the distribution of alloying elements close to the surface after LPC and after atmospheric gas carburizing. During LPC in some applications, the surface content of manganese is reduced by evaporation of manganese. During gas carburizing, metal oxides are formed at the surface due to IGO, which cannot be avoided in gas carburizing. The formation of metal oxides leads to a depletion of chromium, manganese, and molybdenum at a depth between 5 and 15 μm (0.2 and 0.6 mil).

In recent years, the use of acetylene has been steadily established in industrial practice, substituting for propane, which was the favorite carbon source. The carbon yield of propane is approximately 25% compared to acetylene at approximately 65%. Compared to propane, acetylene is better suited to homogeneously carburize parts with complex shapes, such as injection nozzles. Even bulk loads can be carburized successfully with acetylene.

Injection nozzles have blind holes with a length-to-diameter (*L*/*D*) ratio of up to 15. When using propane, blind holes with an *L*/*D* ratio of up to 2 can be carburized homogeneously; when using acetylene, *L*/*D* ratios up to 20 can be treated successfully (Ref 8).

Equipment for Low-Pressure Carburizing

The LPC process can be run in two different types of equipment. In single-chamber furnaces, the LPC and the HPGQ processes are performed in the same chamber. As an alternative, treatment chambers are dedicated for LPC only. These treatment chambers are part of multichamber systems, where HPGQ is performed in specific cold chambers. The applied carburizing strategies are identical for both types of equipment.

For both types, the vacuum vessel is water cooled. In single-chamber furnaces, the inner insulation typically consists of hard felt made of graphite. In treatment chambers, the inner insulation typically consists of layers of ceramic-fiber modules (e.g., $Al_2O_3 + SiO_2$) and hard felt made of graphite on the inside. Because the ceramic fiber is hygroscopic, it cannot be used in single-chamber furnaces, which are opened to atmosphere after each furnace cycle.

In multichamber systems, the treatment chambers are always at temperature and under vacuum, whereas single-chamber furnaces are cooled down and ventilated with air at the end of each furnace cycle. Therefore, multichamber systems are more energy efficient and have a longer service life.

The work zone is typically heated electrically by graphite elements. The carburizing gas enters the work zone through small tubes made of ceramics or nickel-base alloys (e.g., Inconel). The flow rate of carburizing gas is precisely controlled by mass flow controllers. Typical tube diameters range from 5 to 10 mm (0.2 to 0.4 in.). The tubes are arranged symmetrically inside the chamber to achieve a homogeneous distribution of the carburizing gas. A vacuum pump set is connected to the chamber to control the process pressure, which is usually chosen at a level between 5 and 15 mbar (4 and 11 torr).

Formation of soot or tar in the chamber occurs if the process pressure is too high. The

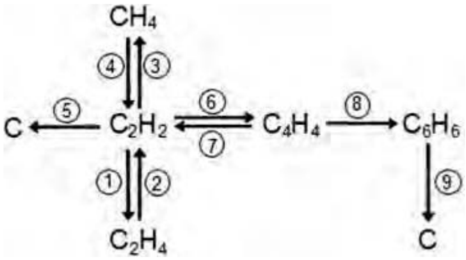
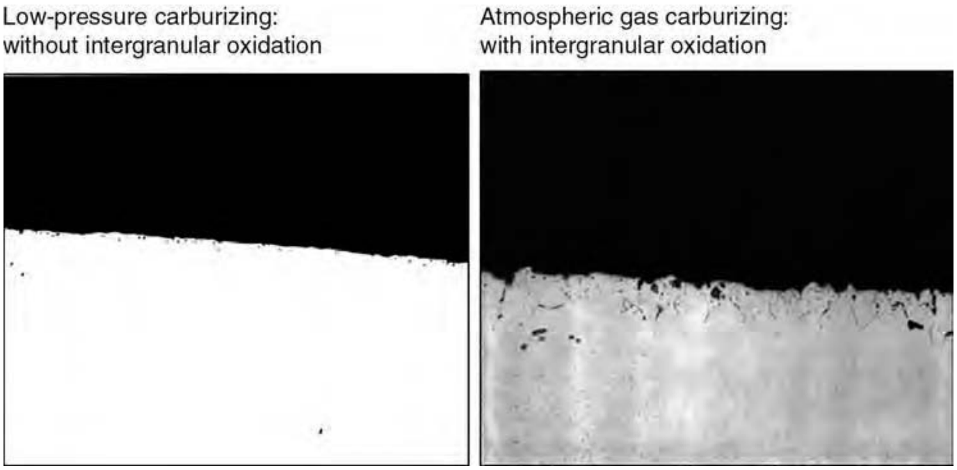


Fig. 4 Dissociation reactions during acetylene pyrolysis. Source: Ref 2


Low-pressure carburizing: without intergranular oxidation

Atmospheric gas carburizing: with intergranular oxidation

Fig. 5 Surface layer after carburizing to a case depth of 0.7 mm (0.03 in.). Material is SAE 5115; scale is 1000:1.

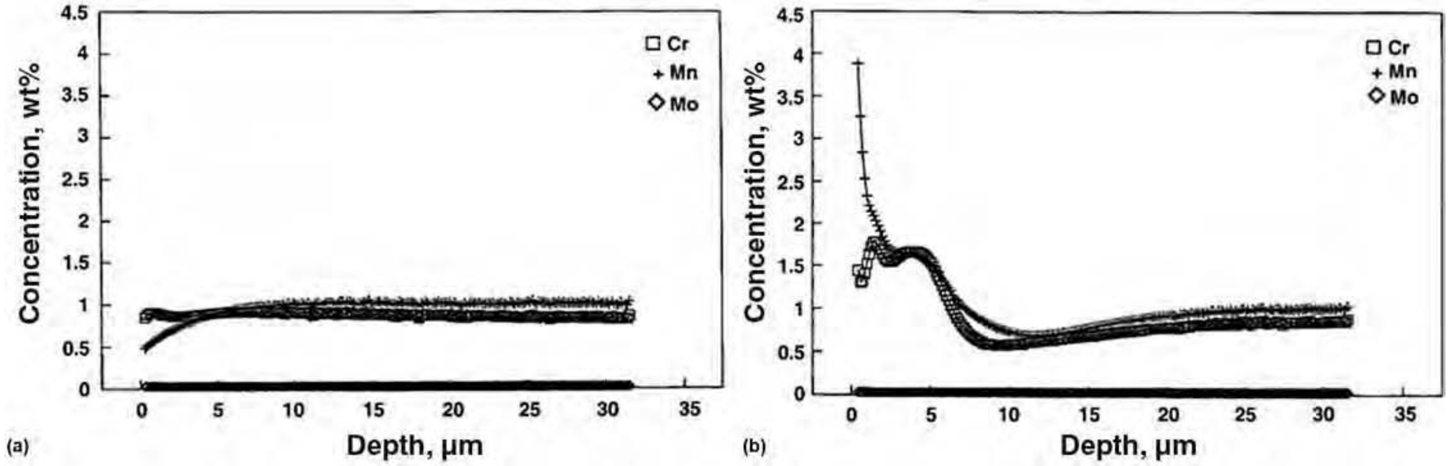


Fig. 6 Distribution of alloying elements close to the surface after (a) low-pressure carburizing and (b) atmospheric gas carburizing. Material is SAE 5115.

same applies for the flow rate of carburizing gas. If the flow rate is significantly above the rate necessary to carburize the given surface area of the load, formation of soot or tar occurs. However, when choosing the correct process parameters and when undertaking regular maintenance, soot and tar is not a threat for applying LPC in mass production.

The load sits in the chamber on a charge support made of graphite and silicon carbide. Fixtures for treatment of loads with LPC are made of either alloy with high nickel content or carbon-fiber-reinforced carbon material. More details regarding fixtures used for LPC and HPGQ are given in the article "Gas Quenching" in this Volume.

Figures 7 and 8 show examples of vacuum systems used for the LPC process. Figure 7(b) depicts a view into a single-chamber furnace with graphite heating elements, charge support, nozzles for the carburizing gas, and nozzles for the quench gas.

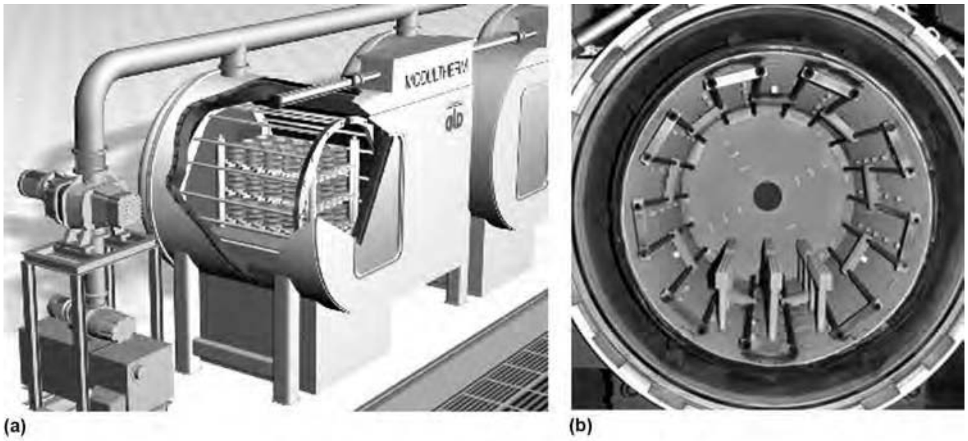


Fig. 7 Vacuum systems for the low-pressure carburizing process. (a) Treatment chamber as part of a multichamber system. (b) View into a single-chamber furnace

Fig. 8 Multichamber system for low-pressure carburizing process in mass production. ModulTherm (ALD Vacuum Technologies) with ten treatment chambers

Carburizing Strategies

The development of the carbon profile during LPC is dictated by the number and the length of the alternating carburizing pulses and diffusion steps. To establish the shortest possible process cycle, the goal is to enrich to the saturation limit the surface of the treated components in each carburizing pulse. This saturation limit is defined as the carbon content where carbides start to be precipitated. Usually, the first pulse is longer than the following pulses, because the component is not enriched with carbon yet and is thus able to absorb more carbon.

Figure 9 schematically shows the alternating carburizing pulses and diffusion steps and the resulting effect on surface carbon content. The length of the final diffusion step depends on the targeted surface carbon content before quenching.

The saturation limit differs from steel grade to steel grade and is a function of temperature. With increasing temperature, the limit of carbide precipitation is shifted to higher carbon contents (Fig. 10).

While the development of the carbon profile is defined by the number, length, and timing of the carburizing pulses, the surface area of the load is accounted for by adjusting the flow rate of carburizing gas during the pulses.

To achieve the desired microstructure of the components after LPC, it is important to examine the development of carbon content close to the surface of the components.

Figure 11 shows an example where the sequence of carburizing pulses and diffusion steps was defined incorrectly. This example shows an LPC process for 18CrNi8 material at 940 °C (1725 °F). The diffusion steps between pulses were too short, thus leading to a carbon content above 1.18% during the course of the process. As a result, the components were oversaturated with carbon, resulting in precipitation of massive carbides. The length of the final diffusion step was chosen correctly, resulting in a surface carbon content of 0.69% C, thus avoiding the formation of excessive amounts of retained austenite.

Figure 12 depicts an example where the diffusion steps between pulses were defined correctly. Therefore, the carbon content was below 1.17% during the course of the process, and thus, the precipitation of carbides was avoided. However, the final diffusion step was too short; therefore, the final surface carbon content before quenching was too high. This resulted in the formation of large amounts of retained austenite.

An optimized carburizing strategy is shown in Fig. 13. A proper sequence of pulses and diffusion steps and the correct length of the final diffusion step are used. As a result, the microstructure is free of any carbides and large amounts of retained austenite.

The proper sequence of pulses and diffusion steps can be easily determined by the use of simulation software for prediction of carbon profiles; see the section "Prediction of Carbon Profiles" in this article.

Table 2 shows an example of the carburizing strategy for material 8630 processed with LPC using acetylene and targeting a case depth of 0.6 mm (0.02 in.). The length of the heating phase (convective and vacuum heating) before the first carburizing pulse depends on the size of the treated components and the size of the load. The flow rate of acetylene during the pulses is adjusted according to the surface area of the load.

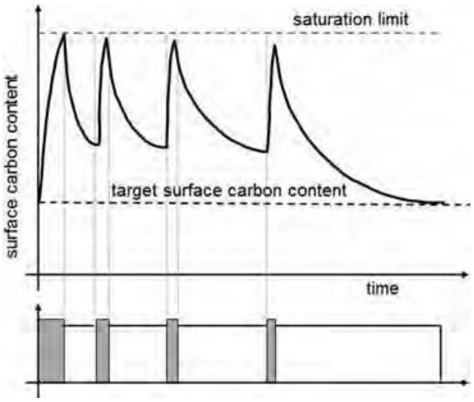


Fig. 9 Schematic of change of surface carbon content during low-pressure carburizing defined by alternating carburizing pulses and diffusion steps

Prediction of Carbon Profiles

The mass transfer of carbon and the diffusion into the material during LPC can be simulated by means of commercially available software. Such programs are based on a mathematical description of the carbon dissociation and adsorption of the carbon at the surface of the parts and equations that describe the diffusion of the carbon into the material (Ref 6). While the carbon transport to the surface in LPC differs significantly from that in atmospheric gas carburizing, the same diffusion laws apply for the carbon transport within the material. The function and the results of simulation software are exemplarily described in Ref 10. To calculate the carbon profile, the following data are entered as input parameters into the simulation program:

- Chemical composition of the steel grade of the components
- Saturation limit of the carbon content for the steel grade
- Carburizing temperature
- Targeted carburizing depth
- Targeted surface carbon content
- Surface area of the load

The program calculates the number and duration of carburizing pulses and diffusion steps as well as the required flow rate of the carburizing gas for each carburizing pulse. Furthermore, it is possible to calculate in reverse and to determine the expected carburizing depth for a given process with given temperature, carburizing pulses, and diffusion steps. In most cases, these calculations are one-dimensional, not taking possible edge effects into account.

In addition, the simulation program is a powerful tool to achieve the targeted microstructure after LPC. The program shows the formation of the carbon profile as a function of time for different distances from the surface. Therefore, it is possible to optimize carburizing strategies

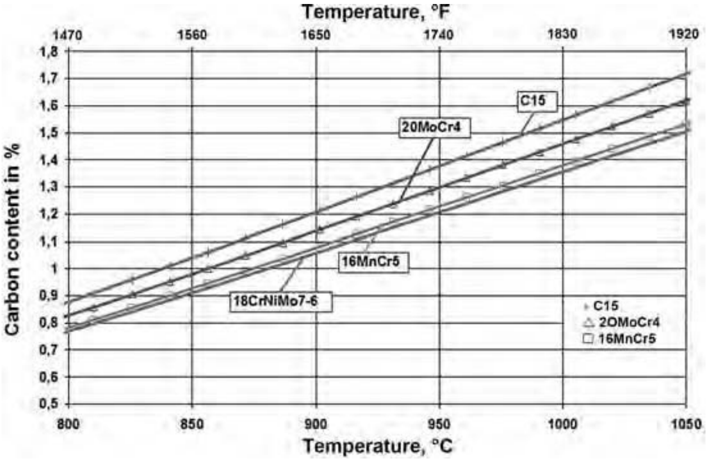


Fig. 10 Limits of carbide precipitation for different case-hardening steels (calculated according to Ref 9)

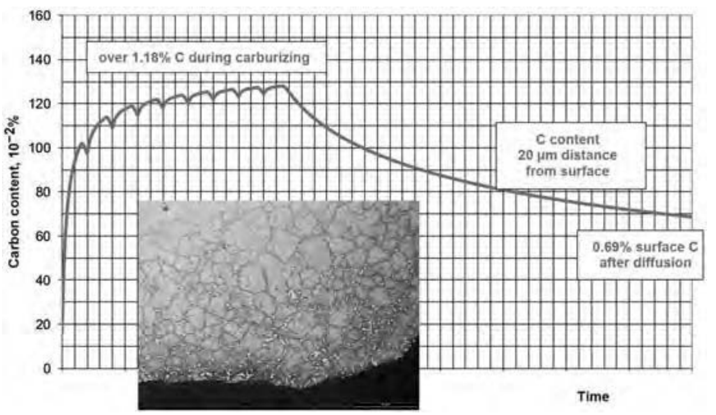


Fig. 11 Carburizing strategy resulting in unwanted carbide formation. Carburizing temperature is 940 °C (1725 °F); material is 18CrNi8.

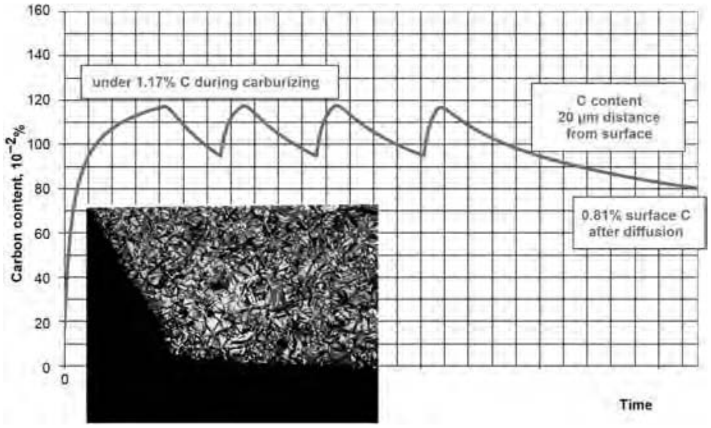


Fig. 12 Carburizing strategy resulting in unwanted formation of retained austenite. Carburizing temperature is 940 °C (1725 °F); material is 18CrNi8.

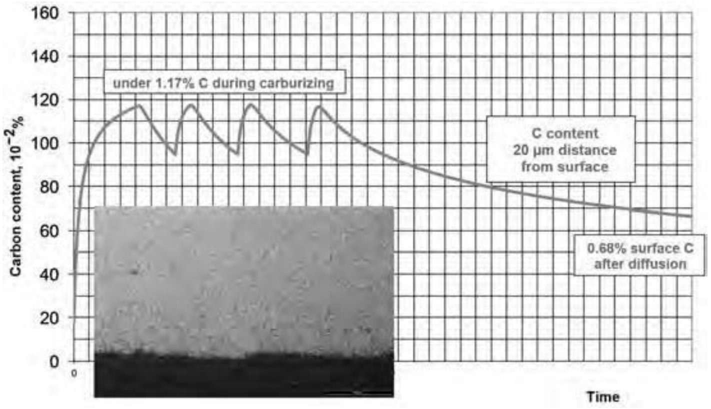


Fig. 13 Optimized carburizing strategy to achieve an optimized microstructure. Carburizing temperature is 940 °C (1725 °F); material is 18CrNi8.

in order to meet the microstructural specification, that is, the absence of large quantities of carbides or excessive amounts of retained austenite.

With the help of more complex finite-element method simulation programs, it is possible not only to simulate carbon profiles but to predict microstructures as well as the resulting core hardness after quenching (Ref 11). In special cases, heat treatment distortions are numerically simulated as well (Ref 12). However, due to the extensive effort in setting up the model and defining the boundary conditions, and due to the large required computing times, the simulation of heat treatment distortion has not yet become established as a standard tool in industrial practice.

Table 2 Example of carburizing strategy for material 8630 at 960 °C (1760 °F) and targeting a case-hardening depth of 0.6 mm (0.02 in.)

Low-pressure carburizing process with acetylene; heating phase before carburizing must be customized according to the size of the treated components and the load size.

Sequence	Temperature °C	Temperature °F	Time
Convective heating	960	1760	80 min
Vacuum heating	960	1760	30 min
Carburizing pulse (C_2H_2)	960	1760	90 s
Diffusion step (N_2)	960	1760	9 min
Carburizing pulse (C_2H_2)	960	1760	60 s
Diffusion step (N_2)	960	1760	11 min
Carburizing pulse (C_2H_2)	960	1760	60 s
Final diffusion (N_2)	960	1760	25 min
Quenching	...	...	...

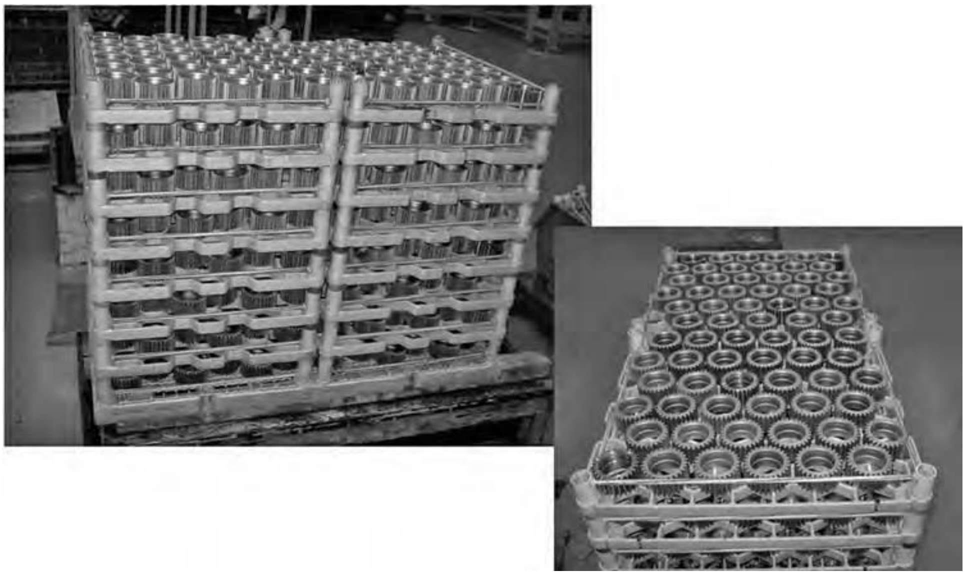


Fig. 14 Load configuration for low-pressure carburizing of sun gears. 20MnCr5HH gear wheel; 576 parts per batch; cycle time, 215 min; carburizing temperature, 945 °C (1735 °F); nitrogen, 8 bar (6000 torr); case-hardening depth, 0.65–0.75 mm (0.026–0.030 in.); core hardness, 35–38 HRC

Applications

Automotive Applications. Figures 14 and 15 show typical examples of loads with automotive gear components processed with LPC.

Another main field of application for LPC is components used for fuel-injection systems, such as nozzle bodies. Figure 16 shows the specification of a nozzle made of 18CrNi8 material after heat treatment. The special challenge during case hardening of this component is to guarantee homogeneous carburizing despite the complex shape of the nozzle (Ref 13). The component requires tight control with carburizing, evident in the blind hole, while at the same time partial overcarburizing must be prevented, for example, in the island.

The nozzles are treated with LPC using acetylene and are gas quenched with nitrogen. Areas that do not require carburizing are covered with mechanical masks. The components are austenitized twice and quenched twice to increase fatigue strength. This is followed by a deep freezing step at −100 °C (−148 °F) to transform any retained austenite into martensite and then followed by tempering. Figure 17 shows the measured hardening profile after treatment at various measuring points (Ref 13).

Aerospace Applications. Figures 18 and 19 depict typical applications of LPC for aerospace components.

For aerospace products, one of the most critical requirements is the geometrical stability of the components during application. It is well known that retained austenite will transform to martensite when subjected to a certain level of stress or to a certain load (stress-induced transformation). Furthermore, retained austenite will transform to martensite when subjected to cold temperatures. This change in microstructure will result in growth of the component. Therefore, the level of retained austenite in the hardened case of the components must be controlled, which is why in many cases the components are subjected to a cryogenic treatment after quenching and before tempering. With such a cryogenic treatment at temperatures below −73 °C (−99 °F) (preferred at −85 or −100 °C, or −121 or −148 °F), the amount of retained austenite is reduced dramatically. The specified time at temperature varies for such a cryogenic treatment, depending on the cross-sectional thickness of the components. However, a minimum of 2 h is often specified.

For example, precision bearings made of material M50NIL are first low-pressure carburized and oil quenched and then subjected to multiple cryogenic/tempering cycles. At a depth of 0.05 mm (0.002 in.) from the surface, the content of retained austenite is determined with an x-ray diffraction method to less than 2% (Ref 15).

As described in the section "Carburizing Strategies" in this article, the LPC process offers a high-flexibility carburizing strategy. This is advantageous for many aerospace applications. For example, to prevent the formation of excessive amounts of retained austenite when treating the material SAE 9310, the carburizing temperature is limited to 930 °C (1705 °F) for atmospheric gas carburizing. With LPC, however, the carburizing strategy can be adjusted to target for a low level of retained austenite. Hence, LPC allows the use of higher carburizing temperatures for this material.

In a few special aerospace applications, the components are treated with multiple-step carburizing, which is used to achieve different carbon profiles on the very same component. To do so, the parts are first partly protected from carburizing (e.g., coated with copper). Then, the first LPC treatment is performed. After cooling with an optional annealing step, the copper is partly removed. Another possibility is to machine additional gear teeth or additional splines. Then, the next LPC treatment is performed. After the final LPC step, the parts are quenched. By applying this multiple-step

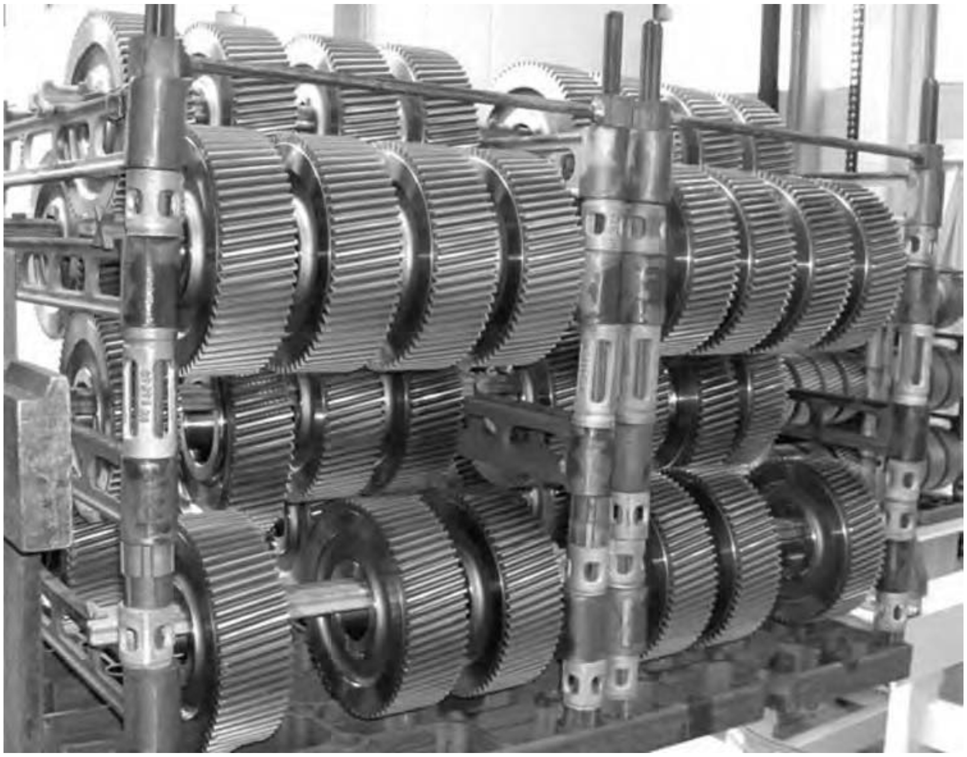


Fig. 15 Load configuration for low-pressure carburizing of ring gears. 16MnCr5 gear wheel; 44 parts per batch; cycle time, 450 min; carburizing temperature, 930 °C (1705 °F); helium, 18 bar (13,500 torr); case-hardening depth, 0.85–0.95 mm (0.034–0.037 in.); core hardness, 27–30 HRC

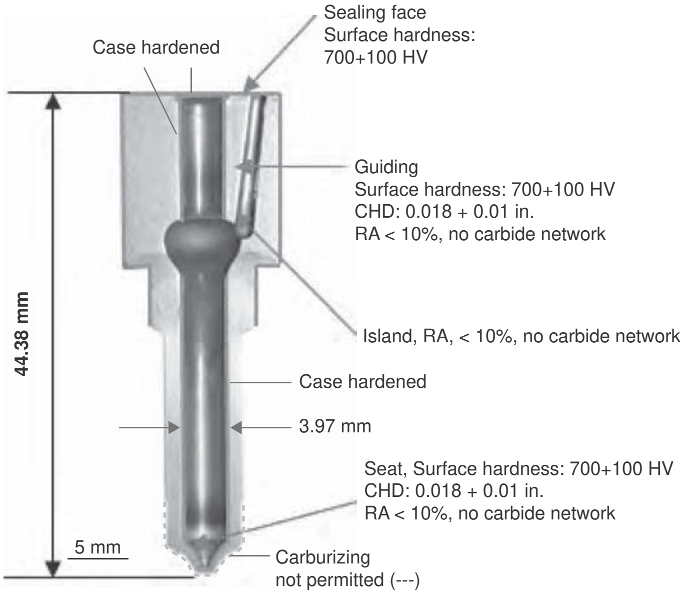


Fig. 16 Specification of a nozzle body for a diesel injection system. Source: Ref 13

carburizing, it is possible to provide uncarburized areas and areas with two different carbon profiles, and consequently two different CHDs, on the very same component.

Other Applications. Besides applications for the automotive and aerospace industry, LPC is successfully used for other components as well. For example, hydraulic components, wear plates, industrial chains, industrial transmissions, axles, die-cutting punches, and components for the agricultural and power tools industries are often processed with LPC.

Quality Control of the LPC Process in Mass Production

To allow the LPC process to be established in mass production, reliable methods of quality control have been developed and implemented in industry over the last few years. Before the start of production of a component, the so-called production part approval process (PPAP) load is treated and analyzed intensively for quality. Components from the corners and the middle of the PPAP load are checked carefully for surface hardness, hardness profile, core hardness, and microstructure. In some cases, the carbon profile and distortion are analyzed and documented as well.

Once the PPAP load is validated and production has started, the frequency of quality checks is reduced.

Modern systems for LPC are equipped with a process-monitoring device. This device controls if the main process parameters deviate from the recipe values. If so, the load is labeled with a "red flag." Depending on the severity of the red flag, the loads are either scrapped immediately or checked very carefully for quality and if they can be released for assembly or not.

Another method often applied in industry is the use of carbon buttons. These are discs, with standardized size and made of standardized material, that travel with the load through the process. The weight increase of the discs is an indicator if the load has indeed absorbed the targeted amount of carbon during the LPC process.

Table 3 shows the ways and means and the frequency of quality checks as typically applied in industry.

High-Temperature LPC

As shown in Table 1, the high mass transfer of carbon into the components results in significantly shorter treatment times for LPC compared to atmospheric gas carburizing. The advantage of LPC can be further enhanced by increasing the carburizing temperature. With increasing carburizing temperature, the diffusion rate rises sharply, and thus, carburizing time is significantly reduced (Fig. 20).

Furthermore, the limit for carbide precipitation shifts to higher values. According to the iron-carbon diagram, the precipitation limit is increased in unalloyed steel (i.e., C15) from 1.3% C at 930 °C (1705 °F) to 1.65% C at 1030 °C (1885 °F) (Fig. 10).

Consequently, high-temperature carburizing allows the targeting of higher surface carbon content in each carburizing pulse. The now higher concentration gradient leads to a further reduction of treatment time. (This additional reduction of carburizing time is not reflected in Fig. 20.)

Table 4 illustrates the treatment times for LPC of 18CrNiMo7-6 at different temperatures