

Gas Carburizing

C.A. Stickels, Ford Motor Company, Manufacturing Development Center

CARBURIZING is a case-hardening process in which carbon is dissolved in the surface layers of a low-carbon steel part at a temperature sufficient to render the steel austenitic, followed by quenching and tempering to form a martensitic microstructure. The resulting gradient in carbon content below the surface of the part causes a gradient in hardness, producing a strong, wear-resistant surface layer on a material, usually low-carbon steel, which is readily fabricated into parts. In gas carburizing, commercially the most important variant of carburizing, the source of carbon is a carbon-rich furnace atmosphere produced either from gaseous hydrocarbons, for example, methane (CH_4), propane (C_3H_8), and butane (C_4H_{10}), or from vaporized hydrocarbon liquids.

Carbon Sources

Low-carbon steel parts exposed to carbon-rich atmospheres derived from a wide variety of sources will carburize at temperatures of 850 °C (1560 °F) and above. In the most primitive form of this process, the carbon source is so rich that the solubility limit of carbon in austenite is reached at the surface of the steel and some carbides may form at the surface. (In earlier editions of *Metals Handbook*, the carbon gradient produced by maintaining saturated austenite at the surface of the steel is referred to as the normal carbon gradient.) Such atmospheres will also deposit soot on surfaces within the furnace, including the parts. While this mode of carburizing is still practiced in parts of the world in which resources are limited, the goal of current practice in modern manufacturing plants is to control the carbon content of furnace atmospheres so that:

- The final carbon concentration at the surface of the parts is below the solubility limit in austenite
- Sooting of the furnace atmosphere is minimized

Controlled carburizing atmospheres are produced by blending a carrier gas with an enriching gas, which serves as the source of

carbon. The usual carrier, endothermic gas, is not merely a diluent, but plays a role, described below, in accelerating the carburizing reaction at the surface of the parts. The amount of enriching gas required by the process depends primarily on the carbon demand, that is, the rate at which carbon is absorbed by the work load.

Endothermic gas (Endogas) is a blend of carbon monoxide, hydrogen, and nitrogen (with smaller amounts of carbon dioxide, water vapor, and methane) produced by reacting a hydrocarbon gas such as natural gas (primarily methane), propane, or butane with air. Endogas is usually produced in a separately fired retort furnace (Endogas generator) using an air-to-hydrocarbon feed ratio that will produce an oxygen-to-carbon atom ratio of about 1.05 in the Endogas. For Endogas produced from pure methane, the air-to-methane ratio is about 2.5; for Endogas produced from pure propane, the air-to-propane ratio is about 7.5. These ratios will change depending on the composition of the hydrocarbon feed gases and the water vapor content of the ambient air. Table 1 lists typical compositions of natural gas. Propane for atmosphere generation should contain less than 5% propylene ($\text{CH}_3\text{CH}=\text{CH}_2$) and less than 2.5% butane or heavier hydrocarbons, satisfying the requirements in ASTM D 1835 for so-called special-duty propane or the Gas Producers Association specification 2140, grade HD 5.

A carrier gas similar in composition to Endogas produced from methane can be formed from a nitrogen-methanol blend. The proportions of nitrogen and methanol (CH_3OH) are usually chosen to give the same nitrogen-to-oxygen ratio as that of air, that is, about 1.9 volumes of nitrogen for

each volume of gaseous methanol. Upon entering the furnace, each volume of gaseous methanol cracks to form approximately one volume of carbon monoxide and two volumes of hydrogen.

A carrier gas can be generated *in situ* by the direct addition of air and a hydrocarbon gas to the carburizing furnace (Ref 1). Special precautions (low flow rates, high temperatures, and good mixing) must be taken in setting up and controlling such a process to ensure a thorough reaction of the feed gases and uniformity of carburizing. Similar precautions are needed if carrier gases high in either carbon dioxide or water vapor content (such as exothermic gas) are used.

Carburizing Equipment

Gas carburizing furnaces vary widely in physical construction, but they can be divided into two major categories, batch and continuous furnaces. In a batch-type furnace, the work load is charged and discharged as a single unit or batch. In a continuous furnace, the work enters and leaves the furnace in a continuous stream. Continuous furnaces are favored for the high-volume production of similar parts with total case depth requirements of less than 2 mm (0.08 in.).

Batch Furnaces. The most common types of batch furnaces are pit furnaces and horizontal batch furnaces. Pit furnaces are usually placed in a pit with the cover or lid located just above floor level and are often loaded and unloaded with the aid of an overhead crane (Fig 1). Pit furnaces are frequently used for large parts requiring long processing times. If the work is to be direct quenched, the load must be moved

Table 1 Specific gravity and composition of natural gas in selected regions of the United States

State	Specific gravity	Composition, vol %			
		CH_4	CH_3CH_3	N_2	CO_2
New York	0.58-0.59	94.1-96.3	1.8-2.0	0.3-1.8	0.83-0.96
Illinois	0.57-0.61	89-97.5	1.6-4.4	0.31-5.7	0.39-0.75
California	0.60-0.63	92-98.8	3.9-5	1.2-1.24	0.76-3.0

CH_4 , methane; CH_3CH_3 , ethane; N_2 , nitrogen. Source: American Gas Association

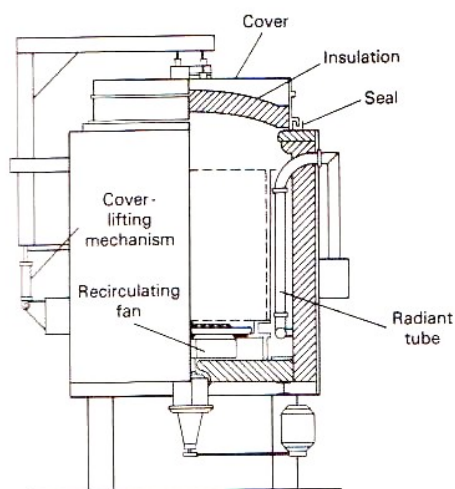


Fig 1 A pit batch carburizing furnace. Dashed lines outline location of workload.

through air before quenching. As a result, parts will be covered by an adherent black scale, which, depending on the needs of the application, may have to be removed by shot blasting or acid pickling.

Horizontal batch furnaces are frequently used for carburizing and direct quenching. Many of these furnaces are so-called sealed quench, or integral quench, furnaces; that is, parts are discharged from the furnace into a vestibule that covers an oil quench tank (Fig 2). Because the furnace atmosphere also flows through the vestibule, parts can be kept free of oxidation prior to quenching. Sealed-quench batch furnaces are capable of processing many different types of loads with widely varying case depth requirements. Like pit furnaces, they can be made quite gas tight, with the result that positive furnace pressures are easily achieved.

Continuous Furnaces. Types of continuous furnaces used for carburizing include mesh belt, shaker hearth, rotary retort, rotary hearth, roller hearth, and pusher designs. Many of these furnaces can be built with sealed oil quenching so that oxide-free parts can be produced. Most of these furnaces can be sealed well enough that positive furnace pressures can be maintained. Some continuous mesh belt furnaces, on the other hand, are open to the air at either end. Because air cannot be positively excluded, carburizing in these furnaces is often difficult to control.

Furnace Atmosphere Parameters. Certain principles of operation apply to all controlled-atmosphere furnaces regardless of design. First, in order to ensure the uniformity of carburizing, the furnaces must be equipped with internal fans so that the atmosphere is well circulated through the work load. In addition, the individual parts within the work load must be well spaced to allow the atmosphere to penetrate the load. Critical parts, such as gears, are usually placed on fixtures to control not only their spacing, but also

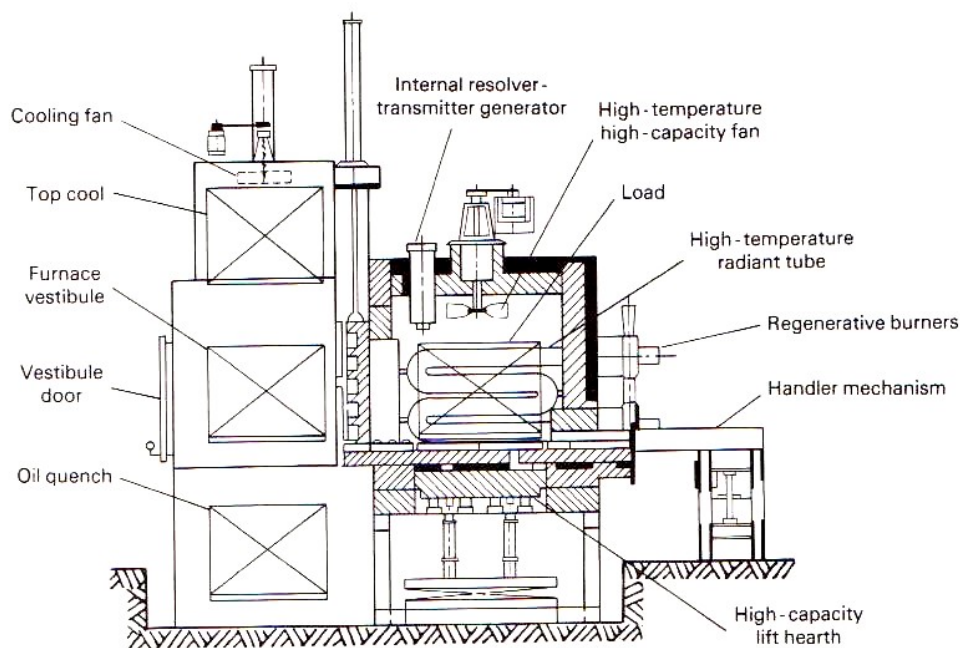


Fig 2 A high-productivity gas-fired integral quench furnace

their orientation entering the quenchant. At times the weight of trays and fixtures in pusher furnaces is two to three times the weight of the parts processed.

Second, the furnace should be operated at a positive pressure so that if the furnace has small leaks, air does not enter the furnace. Pressures of 12 to 37 Pa (0.09 to 0.28 torr, or 0.05 to 0.15 in. water column) are usually satisfactory for carburizing furnaces. The furnace pressure can be controlled by adjusting the orifice size in atmosphere vent lines and the carrier gas flow rate.

Because the hot gases inside a furnace are low in density, the pressure differential (furnace pressure minus ambient pressure, measured at the same height) will have its smallest value at the lowest point in the furnace. The minimum furnace pressure needed (at any height) to maintain a positive differential at all heights (P_{\min}) can be computed from the relation:

$$P_{\min} = H(D_A - D_F) \quad (\text{Eq 1})$$

where H is the internal height of the furnace chamber, D_A is the density of ambient air outside the furnace, and D_F is the density of the atmosphere inside the furnace. Because $D_A \gg D_F$, a suitable minimum value for the furnace pressure in pascals is:

$$P_{\min} = H(0.117) \quad (\text{Eq 2})$$

where H is in centimeters and it is assumed that the ambient air is at 1 kPa (1 atm) pressure and 20 °C (70 °F). Even though the furnace pressure is nominally positive, air can still enter the furnace through small openings if there are local fluctuations in the ambient pressure. A large cooling fan blow-

ing at the furnace might raise the ambient pressure locally by as much as 25 Pa (0.19 torr, or 0.1 in. water column).

Third, the rate at which the furnace atmosphere responds to changes in inlet gas composition depends on the mean residence time of the atmosphere gases in the furnace. The mean residence time (t_{res}) is approximately:

$$t_{\text{res}} = \frac{(V \cdot T_A)}{F \cdot T_F} \quad (\text{Eq 3})$$

where V is the furnace volume; F is the carrier gas flow rate measured at T_A , the absolute ambient temperature; and T_F is the absolute furnace temperature. Residence times in carburizing furnaces vary from about 2 to 15 min. If the inlet gas composition is changed, it takes about three residence times for 95% of the effect of the change to be felt in the furnace. Therefore, batch furnaces, in which the atmosphere composition must be changed during the course of a processing cycle, are usually operated with shorter residence times than are continuous furnaces. It is often considered an advantage to use high flow rates of carrier gas to speed the purging of air that enters the furnace when parts are charged. However, the same result can usually be achieved more economically by using an automatic control system to regulate the flow of the hydrocarbon enriching gas.

Preparation of Parts for Carburizing

Parts, trays, and fixtures should be thoroughly cleaned before they are charged into a carburizing furnace. Often they are

washed in a hot alkaline solution. Some users heat washed parts, trays, and fixtures in an oxidizing atmosphere at 400 °C (750 °F) before carburizing to remove traces of organic contaminants (Ref 2).

Very thin oxide layers on parts (such as those produced by oxidation below 500 °C, or 900 °F) are reduced by the carburizing atmosphere. Heavy oxide layers, such as forging scale, will be reduced to iron flakes, which are not adherent to the part.

Residues from alkaline washer solutions deposited on parts, particularly those with silicates, can cause spotty carburizing, as well as give the parts a blotchy appearance. In addition, alkaline residues can adversely affect the life of heat-resistant furnace alloys. Quenching salts remaining on trays and fixtures can also damage furnace hardware (for example, silicon carbide rails in pusher furnaces). Chlorine- or sulfur-containing residues on parts will release gases that can react with brickwork, the protective oxide films on heat-resistant alloy fixtures, or the work load.

Carburizing Process Variables

The successful operation of the gas carburizing process depends on the control of three principal variables:

- Temperature
- Time
- Atmosphere composition

Other variables that affect the amount of carbon transferred to parts include the degree of atmosphere circulation and the alloy content of the parts.

Temperature. The maximum rate at which carbon can be added to steel is limited by the rate of diffusion of carbon in austenite. This diffusion rate increases greatly with increasing temperature; the rate of carbon addition at 925 °C (1700 °F) is about 40% greater than at 870 °C (1600 °F).

The temperature most commonly used for carburizing is 925 °C (1700 °F). This temperature permits a reasonably rapid carburizing rate without excessively rapid deterioration of furnace equipment, particularly the alloy trays and fixtures. The carburizing temperature is sometimes raised to 955 °C (1750 °F) or 980 °C (1800 °F) to shorten the time of carburizing for parts requiring deep cases. Conversely, shallow case carburizing is frequently done at lower temperatures because case depth can be controlled more accurately with the slower rate of carburizing obtained at lower temperatures.

For consistent results in carburizing, the temperature must be uniform throughout the work load. Temperature gradients through the work load will persist for a substantial period of time while the work is being heated to the carburizing temperature. Because parts at the exterior of the

load reach the furnace temperature first, they will begin carburizing well before parts at the interior of the load. The consequence is variability in case depth from part to part and within a single part. In addition, soot can be deposited on cold parts exposed to a carburizing atmosphere. Therefore, for best results, the work load should be heated to the carburizing temperature in a near-neutral furnace atmosphere. In batch furnaces, parts can be heated in Endogas until they reach the furnace temperature; then carburizing can commence with the addition of the enriching gas. Many new continuous furnaces are being built with separate preheat chambers to ensure that the load is at a uniform temperature before entering the carburizing zone. In continuous furnaces that lack positive separation between heating and carburizing stages, the best that can be done is to:

- Add only Endogas to the front of the furnace
- Establish a front-to-back internal flow of atmosphere gases by adjusting flow rates and orifice size in the effluent lines at either end of the furnace

In batch furnaces, the thermocouple used for temperature control is usually positioned so that it reaches the set-point temperature before the work load does. In continuous furnaces that are not positively separated into zones, the thermocouple in the first zone (used for heating) should be placed near the end of that zone. This prevents overheating of the work load. The control thermocouple is usually positioned near the center of the carburizing zone. If the last zone is at a lower temperature than the carburizing zone, the control thermocouple is usually placed near the discharge end of the zone. However, the features of individual furnaces, such as the location of radiant tubes, must be considered when positioning control thermocouples.

Time. The effect of time and temperature on total case depth is shown in Fig 3. The data given, originally published by Harris (Ref 3) in 1944, are computed assuming saturated austenite at the surface of the workpieces. When the surface carbon content is controlled so that it is less than the saturation value, case depths will be less than they otherwise would be. Figure 4 shows how the carburizing time decreases with increasing carburizing temperature for a case depth of 1.5 mm (0.06 in.). In addition to the time at the carburizing temperature, several hours may be required to bring large workpieces or heavy loads of smaller parts to operating temperature. For work quenched directly from the carburizing furnace, the cycle may be lengthened further by allowing time for the work to cool from the carburizing temperature to about 843 °C (1550 °F) prior to quenching. If the workload is exposed to the carburizing atmo-

sphere during heating, some carburizing will occur before the nominal start of carburizing. Similarly, additional diffusion and interchange of carbon with the atmosphere will occur during cooling prior to quenching. Thus, the actual case depth achieved may differ significantly from the values listed in the table in Fig 3. More complex mathematical models that allow for variations in temperature and atmosphere carbon potential with time can be constructed to allow a better prediction of case depth.

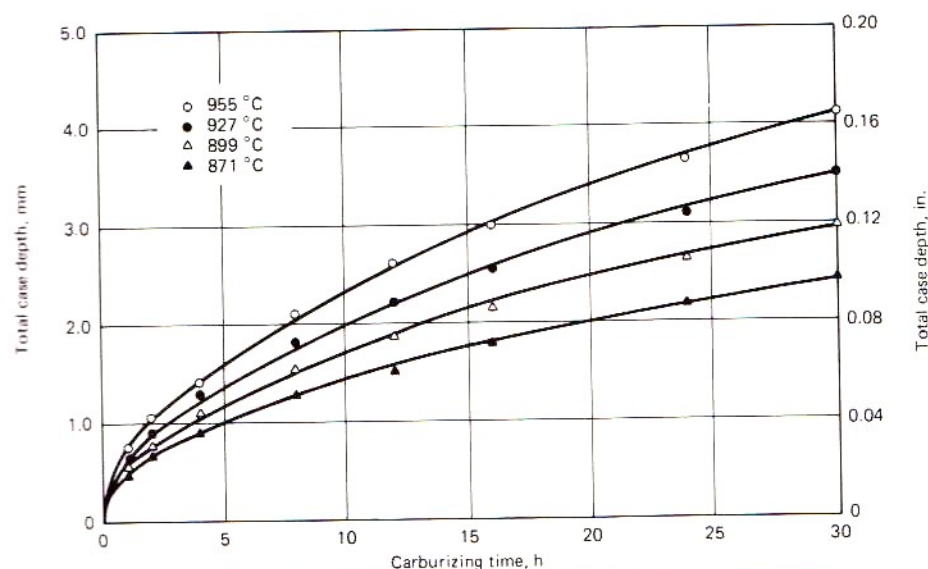
Carbon Potential. The carbon potential of a furnace atmosphere at a specified temperature is defined as the carbon content of pure iron that is in thermodynamic equilibrium with the atmosphere. The carbon potential of the furnace atmosphere must be greater than the carbon potential of the surface of the workpieces in order for carburizing to occur. It is the difference in carbon potential that provides the driving force for carbon transfer to the parts.

Carbon Diffusion. The combined effects of time, temperature, and carbon concentration on the diffusion of carbon in austenite can be expressed by Fick's laws of diffusion. Fick's first law states that the flux of the diffusing substance perpendicular to a plane of unit cross-sectional area is proportional to the local carbon gradient perpendicular to the plane. The constant of proportionality is the diffusion coefficient D , which has the units (distance)²/time. Fick's second law is a material balance within an elemental volume of the system; the flux of carbon into an elemental volume of iron minus the flux of carbon out of the elemental volume equals the rate of accumulation of carbon within the volume. Combining the two laws leads to a partial differential equation that describes the diffusion process. Reference 5 provides solutions to the diffusion equation for a variety of boundary conditions and part configurations, for example, plate, rod, sphere, and so on. With these solutions and values of the diffusion coefficient, it is possible to predict the carbon gradient and depth of penetration occurring for any combination of time, temperature, and surface carbon concentration.

The diffusion coefficient for carbon in austenite is a function of carbon content and temperature. The following expression, proposed by Tibbetts (Ref 6) summarizes the experimental data:

$$D = 0.47 \exp \left[-1.6 C - (37\,000 - 6600 C)/RT \right] \quad (\text{Eq 4})$$

where D is in cm²/s, C is the weight percent carbon, T is temperature in degrees Kelvin, and R is the gas constant. Exact solutions to the diffusion equation when the diffusion coefficient depends on composition are available for steady-state diffusion (Ref 5), but for time-dependent solutions, numerical methods must be used. Figure 5 lists a BASIC computer program for finding the



Time, h	871 °C (1600 °F)		899 °C (1650 °F)		927 °C (1700 °F)		955 °C (1750 °F)	
	mm	in.	mm	in.	mm	in.	mm	in.
1	0.46	0.018	0.53	0.021	0.64	0.025	0.74	0.029
2	0.64	0.025	0.76	0.030	0.89	0.035	1.04	0.041
4	0.89	0.035	1.07	0.042	1.27	0.050	1.30	0.051
8	1.27	0.050	1.52	0.060	1.80	0.071	2.11	0.083
12	1.55	0.061	1.85	0.073	2.21	0.087	2.59	0.102
16	1.80	0.071	2.13	0.084	2.54	0.100	2.97	0.117
24	2.18	0.086	2.62	0.103	3.10	0.122	3.66	0.144
30	2.46	0.097	2.95	0.116	3.48	0.137	4.09	0.161

Fig 3 Plot of total case depth versus carburizing time at four selected temperatures. Graph based on data in table

carbon concentration gradient below a flat surface using the expression above for the diffusion coefficient. In this program, the surface boundary condition is:

$$\text{Carbon flux} = \beta \sigma (CP - C_0) \quad (\text{Eq 5})$$

where carbon flux is in $\text{g/s} \cdot \text{cm}^2$, β is an effective reaction rate constant in s^{-1} , σ is the density in g/cm^3 , CP is the atmosphere carbon potential, and C_0 is the surface carbon content. The value of β may vary depending on the degree of atmosphere circulation within the furnace. Taking β equal to 0.00002 s^{-1} seems to produce results that are in reasonable agreement with experience. However, values of β that are as much as a factor of two larger or smaller may be needed to model carburizing behavior in specific furnaces.

Alloy Effects. The various alloying elements found in carburizing steels have an influence on the activity of carbon dissolved in austenite. A definition of carbon activity (a_C) is:

$$a_C = (\text{wt\% C}) \Gamma \quad (\text{Eq 6})$$

where Γ , the activity coefficient, is chosen so that $a_C = 1$ for an amount of carbon in solution that is in equilibrium with graphite. Chromium tends to decrease the activity coefficient, and nickel tends to raise it. As a consequence, foils of a chromium-bearing steel equilibrated with a specific furnace

atmosphere will take on more carbon than pure iron, and nickel-bearing steels will take on less carbon. It is also true that carbides are produced at lower carbon potentials in chromium-bearing steels than in carbon steels. The primary effect of alloying elements on the diffusion of carbon is due to their effect on the driving force for the surface reaction (Eq 5). To obtain the true driving force, the surface carbon content in an alloy must be converted into the equivalent carbon content in pure iron. Methods of correcting the activity coefficient of carbon for alloy content are available (Ref 7). However, the quantity of experimental data upon which such correlations are based is rather limited. Therefore, predictions should be verified by experiments, particularly when an alloy contains substantial amounts of more than one alloying element.

Gas Carburizing Atmospheres

In the discussion of carburizing atmospheres in this section, it will be assumed that the atmosphere consists of an endothermic carrier gas (produced from methane) that is enriched by a methane addition, which serves as the source of the carbon being transported to the work load. The main constituents of the atmosphere are CO , N_2 , H_2 , CO_2 , H_2O , and CH_4 . Of these constituents, N_2 is inert, acting only as a

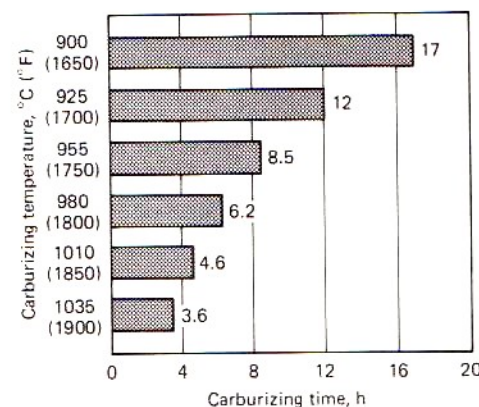
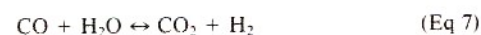


Fig 4 Reducing effect of increased process temperature on carburizing time for 8620 steel. Case depth: 1.5 mm (0.060 in.). Source: Ref 4

diluent. The amounts of CO , CO_2 , H_2 , and H_2O present are very nearly the proportions expected at equilibrium from the reversible reaction:

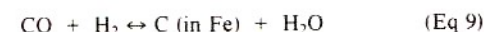


given the particular ratios of carbon, oxygen, and hydrogen in the atmosphere. Methane is invariably present in amounts well in excess of the amount that would be expected if all the gaseous constituents were in equilibrium.

Although the sequence of reactions involved in carburizing is not known in detail, it is known that carbon can be added or removed rapidly from steel by the overall reversible reactions:

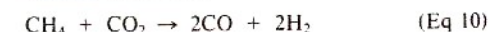


and



A carburization process based solely on the decomposition of CO would require large flow rates of atmosphere gas to produce appreciable carburizing. As an example, the loss of just 0.47 g C from a cubic meter of endothermic gas at 927 °C (1700 °F) is sufficient to reduce the CO -to- CO_2 ratio from 249 to 132 and the carbon potential from 1.25 to 0.8%. The loss of 0.47 g C represents about the same amount present in a steel part of 100 cm^2 (15.5 in.^2) surface area carburized to a depth of 1 mm (0.040 in.).

The methane enrichment of endothermic gas provides carbon for the process by slow reactions such as:



and



which reduce the concentrations of CO_2 and H_2O , respectively. These reactions regenerate CO and H_2 , thereby directing the reactions of Eq 8 and 9 to the right. Because the methane content of carburizing atmo-

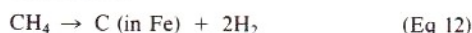

```

10 'Diffusion of Carbon in Austenite
12 'Tibbets' Expression for the Diffusion Constant of Carbon
15 DEF FNDFC(T,WC) = .47*EXP(-1.6*WC - (37000! - 6600*WC)/(1.987*T))
20 INPUT "Temperature in Degrees C ",TC
30 INPUT "Time in Hours ",TH
40 INPUT "Carbon Potential, wt. pct. ",CP
50 INPUT "Surface Reaction Rate Constant ",BETA
60 INPUT "Initial Carbon Content of Steel ",C0
70 T = TC + 273.15 : TSEC = TH*3600
80 DT = 15 : DX = .01
90 DIM C(31), CL(31)
100 L1 = 2*DT/DX : L2 = DT/DX^2
110 NN% = INT(TSEC/DT) : V% = 0
120 FOR I% = 0 TO 31
130 CL(I%) = C0
140 NEXT I%
150 FOR J% = 1 TO NN%
160 WC = (CL(0) + CL(1))/2
170 DB = FNDFC(T,WC)
180 ETA = .75*CL(0) + .25*CL(1) + L1*(BETA*(CP - CL(0))
+ DB*(CL(1) - CL(0))/DX)
190 FOR I% = 1 TO 30
200 IF (V% = 0) THEN GOTO 220
210 C(I%) = C0 : GOTO 270
220 DA = DB
230 WC = (CL(I%) + CL(I%+1))/2
240 DB = FNDFC(T,WC)
250 C(I%) = CL(I%) + L2*(DB*CL(I%+1) - (DA+DB)*CL(I%)
+ DA*CL(I%-1))
260 IF (ABS(C(I%) - C0) < .00005) THEN V% = 1
270 NEXT I%
280 C(0) = 4*(ETA - .25*C(1))/3 : V% = 0
290 FOR I% = 0 TO 31
300 CL(I%) = C(I%)
310 NEXT I%,J%
320 PRINT "Depth, mm.", "Wt. Pct. C", "Depth, mm.", "Wt. Pct. C"
330 FOR I% = 0 TO 15
340 PRINT USING "#.###" " ;DX*I%*10,C(I%),DX*(I%+15)*10,C(I%+15)
350 NEXT I%
360 END

```

Fig 5 Finite-difference computation of the diffusion of carbon in austenite using BASIC computer program

spheres is usually far above the content that is expected at equilibrium, given the CO₂ and H₂O contents present, it is evident that the reactions in Eq 10 and 11 do not approach equilibrium. The sum of the reactions in Eq 8 and 10 and in Eq 9 and 11 is reduced to:



Thus, with constant CO₂ content and constant dew point, the net atmosphere composition change during carburizing is a reduction in methane content and an increase in the hydrogen content. In most commercial operations, atmosphere flow rates are high enough and the rate of methane decomposition is low enough to prevent a large buildup of hydrogen during a carburizing cycle. However, with carburizing loads having high surface area, there is a drop in the CO content of 1 to 3% at the beginning of the cycle when the carbon demand is greatest. This is caused by the dilution of the furnace atmosphere with hydrogen.

Carbon potential control during carburizing is achieved by varying the flow rate of the hydrocarbon-enriching gas, while maintaining a steady flow of endothermic carrier gas. As a basis for regulating the enrichment gas flow, the concentration of some constituent of the furnace atmosphere is monitored:

- Water vapor content by dew point measurement
- Carbon dioxide content by infrared gas analysis
- Oxygen potential using a zirconia oxygen sensor

The first two quantities provide measures of carbon potential according to the reactions of Eq 8 and 9. Oxygen potential is related to carbon potential by the reaction:



When the carbon monoxide content of the atmosphere remains relatively constant, both the carbon dioxide and the oxygen potential provide good measures of the carbon potential. For the dew point to be a valid measure of carbon potential, the product of the hydrogen and carbon monoxide contents must be stable. If the hydrogen content of the furnace atmosphere rises, as a result of either carburizing or sooting, the relationships between CO₂ content, oxygen potential, dew point, and the carbon potential will be altered. For this reason, some process control systems include infrared analysis of CO and the measurement of CO₂ or oxygen potential so that a true carbon potential may be computed for all operating conditions.

Calculation of Equilibrium Compositions.

Gas carburizing is a nonequilibrium process; that is, the gaseous constituents of the atmosphere are not fully in equilibrium with one another, and the atmosphere is not in equilibrium with the steel being carburized. Nevertheless, several important reactions, for example, reactions in Eq 7 to 9, approach equilibrium rapidly enough to permit predictions of the rate of carburizing from the atmosphere composition. Thus, the same case carbon gradient can be expected from different furnaces with different atmosphere gas flow rates when certain factors are held constant:

- Carbon potential, as inferred from CO₂, H₂O, or oxygen potential measurements
- Carburizing time
- Carburizing temperature

To compute the equilibrium gas composition resulting from the reaction of a blend of a hydrocarbon gas and air:

- Six gaseous species are assumed to be present in the reacted gas: CO, CO₂, H₂, H₂O, CH₄, and N₂. The partial pressures of five of these are unknowns to be determined; the sixth can be found by computing the difference after the others are known
- The carbon-to-hydrogen and oxygen-to-nitrogen ratios are fixed by the nature of the hydrocarbon and the composition of air. With the air-to-hydrocarbon ratio fixed, three equations can be found that relate the five unknown partial pressures
- Two equilibrium relationships, for example, the reactions in Eq 7 and 10, provide two additional equations; thus, all the partial pressures are determined

Because explicit expressions for the unknowns cannot be written, trial-and-error computation methods must be used with the aid of a computer (Ref 8). After the equilibrium composition of the gas is known, its carbon potential is found by writing the equilibrium relationship for Eq 8:

$$K_8 = (a_C \cdot P_{\text{CO}_2}) / (P_{\text{CO}})^2 \quad (\text{Eq 14})$$

where P_{CO} and P_{CO_2} are partial pressures of CO and CO₂, respectively; a_C is the activity of carbon ($a_C = 1$ when the atmosphere is in equilibrium with graphite); and K_8 is the equilibrium constant for the reaction in Eq 8.

The constant K_8 can be computed from the Gibbs free energy of formation of CO and CO₂ at the temperature of interest (free energy values are tabulated in Ref 9):

$$\Delta F_{\text{CO}_2}^\circ - 2\Delta F_{\text{CO}}^\circ = -RT \cdot \ln K_8 \quad (\text{Eq 15})$$

where $\Delta F_{\text{CO}}^\circ$ and $\Delta F_{\text{CO}_2}^\circ$ are free energies of CO and CO₂, respectively; T is the absolute temperature; and R is the gas constant.

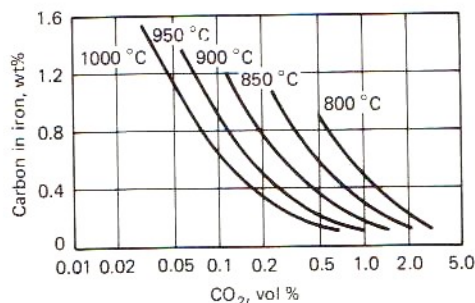


Fig 6 Relationship between CO_2 content and carbon potential for endothermic gas from methane

The carbon activity is related to the carbon content of austenite by the expression (Ref 10):

$$\ln a_C = \ln y_C + (9167 y_C + 5093)/T - 1.867$$

$$\text{where } y_C = (4.65 w)/(100 - w) \quad (\text{Eq 16})$$

where T is the temperature in degrees Kelvin, w is the weight percent carbon in austenite, and y_C is the atom ratio of carbon to iron. Combining Eq 14 and 16 gives a relation between carbon potential (that is, the equilibrium carbon content in austenite) and the carbon dioxide and carbon monoxide contents. As long as the assumptions of the calculation are satisfied, measuring just the CO_2 content suffices to define the carbon potential. However, when carbon is removed from the atmosphere by carburizing, there is a reduction in the carbon-to-hydrogen ratio characterizing the atmosphere. When the carbon-to-hydrogen ratio may vary, it is necessary to measure two constituents of the atmosphere, CO and CO_2 content, to define the carbon potential accurately. However, unless the changes in the atmosphere are large, it is seldom worth measuring both CO and CO_2 because of the effect of the added measuring error on the uncertainty of the computed carbon potential.

Endothermic gas derived from propane has a carbon monoxide content of about 23%, whereas that derived from methane has a carbon monoxide content of about 20%. Therefore, the carbon dioxide contents corresponding to a given carbon potential are higher for atmospheres derived from propane than for those derived from methane. Figures 6 and 7 show the relationship between carbon dioxide content and carbon potential for endothermic gas atmospheres derived from methane and propane, respectively.

The oxygen potential (or oxygen partial pressure), as measured by a zirconia oxygen sensor, is related to the carbon activity by the equilibrium equation for the reaction given in Eq 13:

$$a_C = \frac{P_{\text{CO}}}{K_{13} P_{\text{O}_2}} \quad (\text{Eq 17})$$

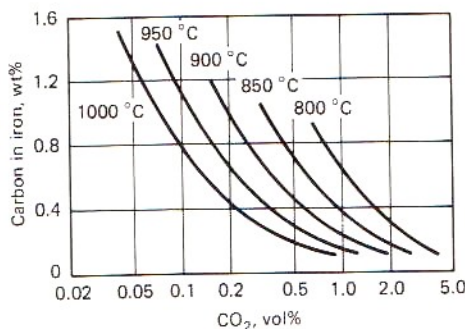


Fig 7 Relationship between CO_2 content and carbon potential for endothermic gas from propane

where P_{O_2} is the oxygen partial pressure and K_{13} is the equilibrium constant. In carburizing atmospheres, the oxygen partial pressure is approximately 10^{-14} to 10^{-20} Pa (10^{-19} to 10^{-25} atm).

The voltage output of a zirconia oxygen sensor, with air as a reference gas, is a function of the absolute temperature (T) and the oxygen partial pressure (P_{O_2}) according to the expression:

$$\text{emf} = 0.00049593 T \log_{10} \left(\frac{P_{\text{O}_2}}{0.209} \right) \quad (\text{Eq 18})$$

where emf is in volts. Combining Eq 16, 17, and 18 yields a relation between carbon potential and emf. Because this relation also depends on the carbon monoxide content of the atmosphere (Eq 18), emf measurements corresponding to a certain carbon potential for endothermic gas atmospheres derived from methane (Fig 8) differ from those for atmospheres derived from propane (Fig 9).

The water vapor content of the atmosphere is related to the carbon potential by the reaction in Eq 11. The equilibrium relation is:

$$a_C = \frac{K_{11} P_{\text{CO}} P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \quad (\text{Eq 19})$$

where K_{11} is the equilibrium constant.

For atmospheres derived from a particular hydrocarbon, the product of the carbon monoxide and hydrogen contents varies lit-

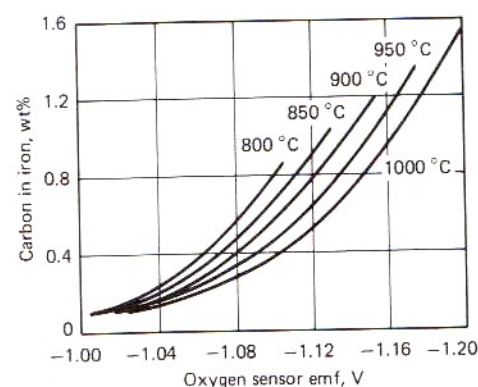


Fig 9 Measurements of the emf of endothermic gas from propane

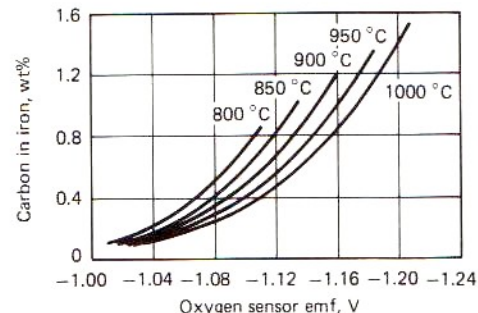


Fig 8 Measurements of the emf of endothermic gas from methane

tle for large changes in water vapor content. The water vapor content of the atmosphere is usually measured by determining its dew point. An equation relating dew point in degrees Celsius and $P_{\text{H}_2\text{O}}$ in atmospheres is:

$$\text{Dew point} = \frac{5422.18}{14.7316 - \ln P_{\text{H}_2\text{O}}} - 273.16 \quad (\text{Eq 20})$$

Equations 16, 19, and 20 can be combined to produce the relations between dew point and carbon potential plotted in Fig 10 and 11 for endothermic gas atmospheres derived from methane and propane, respectively.

Sooting. If the carbon potential of a furnace atmosphere is allowed to become very high, sooting will occur. As carbon is lost from the atmosphere, hydrogen is produced. One symptom of a sooting condition is a pronounced drop in the CO content due to hydrogen dilution. When a furnace becomes sooted, it is found that the carbon potential of the furnace atmosphere is no longer controllable; that is, changes to the flow of enriching gas no longer produce the expected changes in atmosphere composition and carbon potential. The only practical solution is to empty the furnace of parts, introduce air, and burn out the soot.

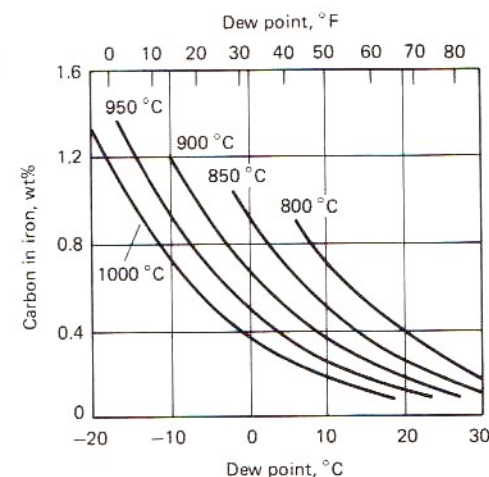


Fig 10 Relationship between dew point and carbon potential for endothermic gas derived from methane

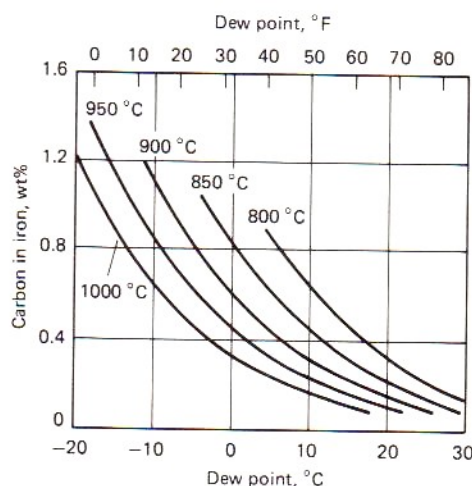


Fig 11 Relationship between dew point and carbon potential for endothermic gas derived from propane

Some care is necessary in burning out accumulated soot to prevent local overheating in the furnace. Typically, the furnace temperature will be set at about 815 °C (1500 °F) for burnout, and air will be admitted to the furnace, by either opening doors or introducing a flow of air. The rise in temperature due to the combustion of soot should be monitored. The air supply can be reduced if the temperature rise is excessive.

Modern automatic atmosphere control systems minimize sooting by maintaining a constant atmosphere composition, thereby matching carbon supply to carbon demand. However, even with the best system, a furnace can be sooted up if the control carbon potential is set too high.

Furnace Conditioning. When a carburizing atmosphere is introduced into an empty furnace that has been idle for some time or that has just been burned out to remove soot, it is found that the amount of enriching gas needed to maintain a given carbon potential is much higher than would be expected. As time passes (typically, 12 to 24 h), the amount of enriching gas needed to maintain the carbon potential decreases to a steady-state value. This process is called conditioning a furnace.

During the time in which conditioning is occurring, carbon is deposited in the crevices of the brickwork and at other locations where the temperature is low. This occurs because the carbon potential of a carburizing atmosphere increases as the temperature falls. An atmosphere with a carbon potential of 1% at 927 °C (1700 °F) is capable, thermodynamically, of depositing soot at or below 843 °C (1550 °F). Eventually, the crevices will be filled with carbon, and the exposed carbon will be at a high enough temperature that further carbon deposition cannot occur. However, there will be some locations, such as sight ports and gas sample lines, where soot will continue to be

deposited as the furnace is used. Soot may also form in unheated furnace vestibules as the furnace atmosphere gas cools upon entering the vestibule.

Process Controllers. A process controller compares the output of a sensor with a set point and generates a control signal intended to reduce the difference between these two values. The sensor can be a thermocouple, if the temperature is to be controlled, or an oxygen sensor or infrared gas analyzer, if the atmosphere composition is to be controlled. In the case of atmosphere control, the device being controlled is usually a valve on the enriching gas line. Valves are of two types:

- Those in which the flow through the valve is proportional to the motion, linear or angular, of the valve stem
- Those simply used to switch the flow on and off

In the first case, the control signal is translated into the position of the valve stem. In the second case, time proportioning is used: The fraction of the time that the valve is open is proportional to the control signal.

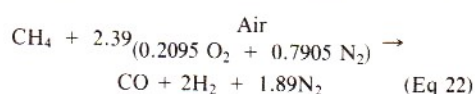
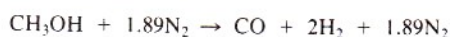
Most controllers used with furnaces employ proportional, integral, and derivative (PID) modes of feedback control (Ref 11). The controller converts an error signal (E) (the difference between the actual output of the sensor and the desired output) into a control signal (M) using the logic:

$$M = K \left(E + \frac{1}{T_i} \int E \cdot dt + T_d \cdot dE/dt \right) \quad (\text{Eq 21})$$

where K is the proportional gain, T_i is the integral time constant, and T_d is the derivative time constant. M can be thought of as the fraction of maximum possible flow through the valve. The quantity $100/K$ is often called the percent proportional band. The quantity $1/T_i$ is often called the reset rate. Derivative control is often called rate control. A process can be controlled using only proportional control (the control signal directly proportional to the error signal), but it will always stabilize at a nonzero value of E . For the process to stabilize at $E = 0$, both integral control and proportional control are needed. The integral portion of the logic effectively generates an offset signal that allows the process to stabilize at $E = 0$. When the set point on the controller is changed, the integral logic must generate a new offset signal for the process to stabilize at $E = 0$. If T_i is too large, the rate of approach to $E = 0$ will be very sluggish; if T_i is too small, the process will overshoot the set point. Finding proper values for K , T_i , and T_d can be quite time consuming, but it is necessary to ensure a controlled process. Fortunately, controller manufacturers have recently introduced self-tuning controllers capable of sensing the response of the system and choosing appropriate values of K , T_i , and T_d .

Nitrogen-Methanol Atmospheres. The *in situ* generation of a carrier gas from a blend of nitrogen and methanol has become more common in recent years. The primary advantage of this approach is that separately fired endothermic gas generators are no longer required. The primary disadvantage is that operating costs are often higher, although this obviously depends on the local cost and availability of natural gas and propane.

Upon entering a heat-treating furnace, methanol cracks to form CO and H₂. The nitrogen-to-methanol ratio is usually chosen so that the nitrogen-to-oxygen ratio is the same as that for air.



The material balances above show that when the nitrogen-to-methanol mole ratio is 1.89, the atom ratios of oxygen, hydrogen, carbon, and nitrogen will be the same as those produced from air-to-methane mole ratio of 2.39. Because Endogas is usually produced with an air-to-methane ratio of about 2.5, it is clear that a nitrogen-methanol carrier gas is richer than conventional Endogas. This poses no special problems when carburizing, but may lead to sooting if the nitrogen-methanol blend is run into an empty furnace for long periods of time. Air is often added to nitrogen-methanol to reduce its carbon potential for neutral hardening applications.

Heat is required to vaporize methanol and the cracking of methanol to CO and hydrogen is quite endothermic. Therefore, successful cracking is favored by higher furnace temperatures and lower rates of carrier gas usage. The presence of lower than expected CO contents in furnace atmospheres is symptomatic of incomplete cracking. However, low CO contents can also arise if the proportions of nitrogen and methanol change with changes in the carrier gas flow.

Because of the similarity in atmosphere composition, a 1.89 mole ratio nitrogen-methanol carrier gas enriched with methane can be controlled using the same control points (Fig 6, 8, and 10) as an Endogas atmosphere produced from methane. The only additional complication is the need for maintaining a constant mole ratio for the carrier gas, particularly when changing the carrier gas flow rate. Rather than invest in sophisticated flow metering, some users have chosen to control their processes by measuring two atmospheric constituents (CO and oxygen potential, for example), rather than just one, to determine carbon potential.

Nitrogen of high purity (about 10 ppm residual CO₂ and water vapor) is produced

by liquifying air and then using the differences in boiling points of the various constituents to effect the separation of nitrogen. In most instances, liquid nitrogen is shipped from an air separation plant to the heat-treating plant and stored in vacuum-insulated vessels. Nitrogen of lesser purity can be produced on site by a variety of means:

- **Combustion processes.** Air is burned with natural gas, and the CO_2 and H_2O are stripped from the gas by absorption and condensation
- **Pressure swing absorption, vacuum swing absorption.** Air separation using zeolite molecular sieves
- **Membrane air separation.** Differences in molecular diffusion rates through thin-walled fibrous tubes are used to separate oxygen and nitrogen

Low-purity less expensive nitrogen can be used with methanol to form satisfactory furnace atmospheres. However, because the oxygen content of the nitrogen should be kept relatively constant, the nitrogen generation process must be designed with this requirement in mind.

Process Planning

Designers usually specify the case hardness, case depth, and core hardness required to meet the service loads they anticipate for a particular part. It is the task of the process engineer to develop the carburizing treatment that will produce the properties desired. Some of the considerations involved in setting up processes include:

- Case microstructure
- Residual stress
- Alloy selection
- Operating schedules
- Quenchants
- Reheating for quenching
- Tempering
- Selective carburizing

Case Microstructure. A carburized case is usually a mixture of tempered martensite and retained austenite. Other microconstituents, such as primary carbides, bainite, and pearlite, are generally avoided. For a particular alloy, the amount of retained austenite in the case increases as the case carbon content increases. An appreciable decrease in case hardness is usually found when the amount of retained austenite exceeds about 15%, but for applications involving contact loading, such as rolling element bearings, the best service life is found when the retained austenite content is quite high, for example, 30 to 40%. In other applications, especially when dimensional stability is critical, the retained austenite content should be low.

Figure 12 shows the dependence of retained austenite content on carbon content

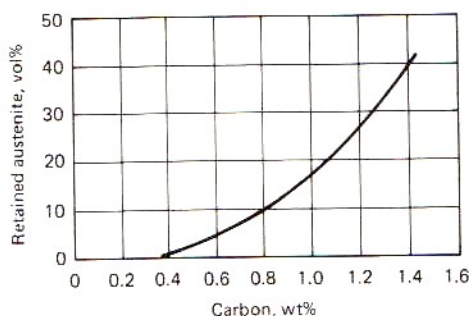


Fig 12 Effect of retained austenite content on carbon content for iron-carbon alloys

for iron-carbon alloys (Ref 12). For a given carbon content, more retained austenite is usually present in alloy steels. Therefore, by controlling the case carbon content, the amount of retained austenite can be regulated. Tempering above 260 °C (500 °F) will also eliminate retained austenite, but at the expense of case hardness.

Residual Stress. Carburized parts have a compressive residual stress in the case that is balanced by a tensile residual stress in the core. The presence of this stress distribution is an advantage for applications in which maximum tensile stresses are experienced at the surface of the part, for example, bending or torsional loading. When other factors are the same, the magnitude of the compressive residual stress at the surface depends on the ratio of case and core thicknesses. When the core is much thicker than the case, compressive stresses at the surface will be high. When the reverse is true, surface compressive stress will be low and core tensile residual stress will be high. Because retained austenite is more dense than is martensite, the former will tend to reduce the magnitude of the compressive residual stress in the surface.

Alloy Selection. Frequently used carburizing steels are listed in Table 2. Carburizing steels are usually selected on the basis of case and core hardenability; comparative hardenability data for these alloys can be found in the SAE specifications J1268 and J1868 (*SAE Handbook*, Volume 1 or the article "Hardenability Curves" in Volume 1 of the 10th Edition of *Metals Handbook*). As a rule, carburized plain carbon steels with less than 1% Mn must be water quenched to form a martensitic case. If an oil quench must be used, adequate case hardenability can usually be obtained by carbonitriding a coarse-grained steel.

Alloy steels are used for most heavily loaded parts, not only because of their increased hardenability, but also because the standards of steel cleanliness are more restrictive. Many of the alloy steels are similar in hardenability but differ in other important respects. For example, nickel-molybdenum alloys provide the most trouble-free processing because the principal

alloying elements are neither strong oxide nor strong carbide formers. However, economic considerations often dictate the use of less expensive steels, such as chromium-manganese alloys, which are prone to alloy depletion (and loss of hardenability) because of the formation of grain-boundary oxides near the surface during carburizing. Chromium-nickel-molybdenum steels, such as SAE 8620 and 8720, provide a balance between cost, hardenability, and ease of processing that leads to their being specified for many parts. More expensive steels, such as SAE 9310 and 3310, are used for critical gearing applications. Some special carburizing alloys, CBS 1000M, for example, have secondary hardening characteristics that provide resistance to softening for temperatures up to about 550 °C (1025 °F).

Operating Schedules. To minimize the total amount of time required for carburizing to a given case depth, most processes are set up in a boost-diffuse mode. The boost step is at a relatively high temperature and high carbon potential to facilitate the rapid development of a deep case; the diffuse step is at a lower carbon potential, allowing the case carbon content to decrease to the level desired. Mathematical models for diffusion, described above, are very helpful in choosing the times and temperatures required for each step.

In practical situations, many considerations, in addition to minimizing processing time, enter into the choice of processing parameters. In continuous furnaces that cannot be separated into distinct zones by means of internal doors, there is a limit to the magnitude of the differences in temperature and carbon potential that can be sustained over the length of the furnace. Similarly, in batch furnaces, the rate at which the temperature can be lowered depends on the thermal inertia of the furnace and load and the magnitude of the heat losses; the rate at which the atmosphere gas composition can be changed depends on the mean residence time of the gas in the furnace. In the absence of a detailed mathematical model incorporating furnace operating characteristics, some trial-and-error experimentation may be required to find the operating set points that produce the desired results. The maximum operating temperature can be limited by the accelerated degradation of fixtures experienced at higher temperatures. Lower processing temperatures are generally favored when the distortion of parts must be minimized.

Thin-cased parts (0.5 mm, or 0.02 in., effective case or less) tend to be processed at 870 °C (1600 °F) or below simply because the processing time at higher temperatures is so short that it is difficult to control the results. For the same reason, thin-cased parts are carburized using a constant carbon potential rather than a boost-diffuse process. Sometimes the available equipment, for example, a continuous pusher furnace,

Table 2 Composition of carburizing steels

Steel	Composition, %					
	C	Mn	Ni	Cr	Mo	Other
Carbon steels						
1010	0.08–0.13	0.30–0.60	(a), (b)
1018	0.15–0.20	0.60–0.90	(a), (b)
1019	0.15–0.20	0.70–1.00	(a), (b)
1020	0.18–0.23	0.30–0.60	(a), (b)
1021	0.18–0.23	0.60–0.90	(a), (b)
1022	0.18–0.23	0.70–1.00	(a), (b)
1524	0.19–0.25	1.35–1.65	(a), (b)
1527	0.22–0.29	1.20–1.50	(a), (b)
Resulfurized steels						
1117	0.14–0.20	1.00–1.30	0.08–0.13 S
Alloy steels						
3310	0.08–0.13	0.45–0.60	3.25–3.75	1.40–1.75	...	(b), (c)
4023	0.20–0.25	0.70–0.90	0.20–0.30	(b), (c)
4027	0.25–0.30	0.70–0.90	0.20–0.30	(b), (c)
4118	0.18–0.23	0.70–0.90	...	0.40–0.60	0.08–0.15	(b), (c)
4320	0.17–0.22	0.45–0.65	1.65–2.00	0.40–0.60	0.20–0.30	(b), (c)
4620	0.17–0.22	0.45–0.65	1.65–2.00	...	0.20–0.30	(b), (c)
4815	0.13–0.18	0.40–0.60	3.25–3.75	...	0.20–0.30	(b), (c)
4820	0.18–0.23	0.50–0.70	3.25–3.75	...	0.20–0.30	(b), (c)
5120	0.17–0.22	0.70–0.90	...	0.70–0.90	...	(b), (c)
5130	0.28–0.33	0.70–0.90	...	0.80–1.10	...	(b), (c)
8617	0.15–0.20	0.70–0.90	0.40–0.70	0.40–0.60	0.15–0.25	(b), (c)
8620	0.18–0.23	0.70–0.90	0.40–0.70	0.40–0.60	0.15–0.25	(b), (c)
8720	0.18–0.23	0.70–0.90	0.40–0.70	0.40–0.60	0.20–0.30	(b), (c)
8822	0.20–0.25	0.75–1.00	0.40–0.70	0.40–0.60	0.30–0.40	(b), (c)
9310	0.08–0.13	0.45–0.65	3.00–3.50	1.00–1.40	0.08–0.15	(b), (c)
Special alloys						
CBS-600	0.16–0.22	0.40–0.70	...	1.25–1.65	0.90–1.10	0.90–1.25 Si
CBS-1000M	0.10–0.16	0.40–0.60	2.75–3.25	0.90–1.20	4.00–5.00	0.40–0.60 Si 0.15–0.25 V
Alloy 53	0.10	0.35	2.00	1.00	3.25	1.00 Si, 2.00 Cu, 0.10 V

(a) 0.04 P max, 0.05 S max. (b) 0.15–0.35 Si. (c) 0.035 P max, 0.04 S max

is larger than the process requires. In this situation the furnace may be run at a lower-than-customary temperature to avoid the frequent door openings, which tend to upset the furnace atmosphere, that would be necessary at higher temperatures.

Quenchants. Carburized parts can be quenched in brine or caustic solutions, water-based polymer quenchants, oils, or molten salt. The more rapid the quench, the lower the requirements for hardenability, but the greater the likelihood of distortion. If a part is used as-heat treated (no finishing operations to control dimensions), mar-quenching into molten salt or hot oil may be used. Rings and shafts are often press quenched, that is, clamped in a fixture while hot and sprayed with oil, to reduce distortion. The choice of alloy and quenchant and the manufacturing-process design are inter-related and must be compatible.

Reheating for Quenching. It has been the practice in some industries to carburize parts at a relatively high temperature (927 °C, or 1700 °F, or above), cool slowly to ambient temperature, then reheat to a lower temperature (843 °C, or 1550 °F, for example), and quench. The advantages of this approach are:

- The final austenite grain size, which controls the size of the martensite plates and

laths, is smaller, and therefore the micro-structure is more refined

- The low reheat temperature places an upper limit on the amount of carbon dissolved in austenite, thereby limiting the amount of retained austenite present in the case

The main disadvantage of this processing, aside from added cost, is increased distortion of the parts. As better controls have become available for regulating furnace atmospheres and as the use of fine-grain steels has become the norm, the need for this practice has diminished.

Tempering. As high-carbon martensite is tempered, carbides precipitate, increasing the density and reducing the hardness of this constituent. The retained austenite, which accompanies the high-carbon martensite, transforms in the temperature range of 220 to 260 °C (425 to 500 °F), reducing the density and increasing the hardness of this constituent. Thus, the response of case hardness to tempering can be complex, affected by the fraction of retained austenite present initially.

Density changes during tempering affect the relief of residual stresses produced by carburizing. Figure 13 (Ref 13) shows the effect on stress relief of tempering for 1 h at

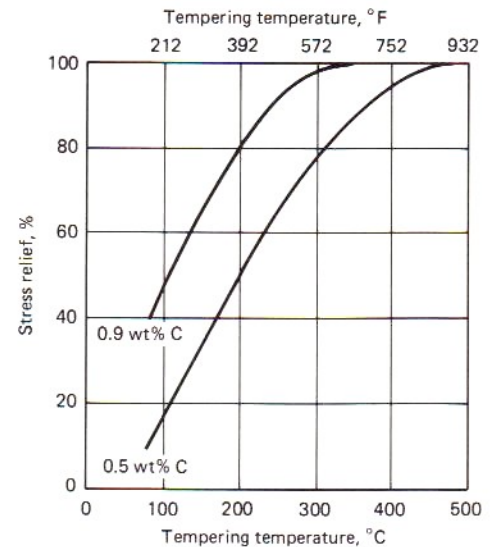


Fig 13 Plot of stress relief versus tempering temperatures held for 1 h for two carbon concentrations in austenite. Source: Ref 13

various temperatures. Stress relief occurs at lower tempering temperatures, as the amount of carbon dissolved in austenite increases. The dependence of stress relief on tempering temperature in carburized parts is qualitatively similar to these results, although more complex behavior can be expected in steels with high levels of retained austenite.

The decrease in hardness with tempering is shown in Fig 14 for four carburized steels. The HRC hardness values shown were converted from Rockwell A for surface hardness and from Vickers microhardness for the subsurface values. It should be noted that the hardness changes very little for tempering temperatures up to 205 °C (400 °F). However, a substantial degree of stress relief will have been experienced as indicated in Fig 13.

Parts that are to be ground after heat treatment should always be tempered. The tempering temperature should be greater than the surface temperature experienced during grinding. If it is not, grinding will produce surface tensile stresses. Tempering in the range of 150 to 205 °C (300 to 400 °F) improves subsequent dimensional stability. If the best possible stability is required, as in some instrument bearings, the treatment should also be designed to eliminate retained austenite. On the other hand, because tempering reduces the compressive residual surface stresses, resistance to bending and torsional fatigue may be best if the parts are not tempered at all. Tempering is omitted on many thin-cased parts (0.5 mm, or 0.02 in., case depth or less) that are not finished after heat treatment.

Selective Carburizing. To function properly, some parts must be selectively carburized,

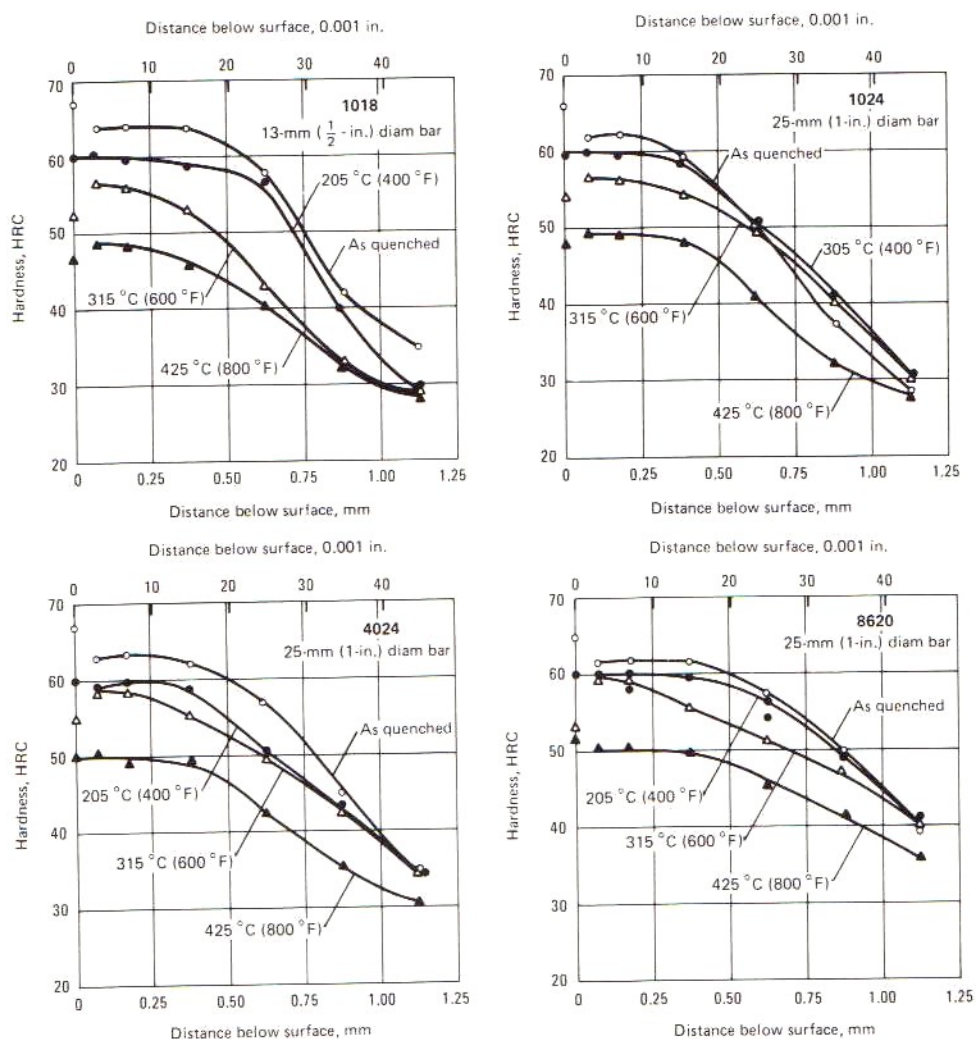


Fig 14 Effect of tempering on hardness in carburized cases for selected steels. Samples were carburized at 925 °C (1700 °F) for 4.5 h, then oil quenched and tempered.

that is, carburized only on certain surfaces. Some gears are carburized only on teeth, splines, and bearing surfaces. In addition to satisfying the performance requirements of a part, selective carburizing may facilitate the machining or welding of noncarburized surfaces in the hardened condition.

Surfaces that are not to be carburized must be protected by a coating or shield that is impervious to the carburizing atmosphere. Various means are employed to protect or stop off selected surfaces from the atmosphere.

Copper plating to a minimum thickness of 13 μm (0.5 mil) is widely used for this purpose because it is relatively easy to apply, is machinable, and does not contaminate furnace atmospheres. Prior to carburizing a large, 915 mm (36 in.) diam, 4620 steel ring gear, for example, the gear is copper plated on the inside diameter flange area only to permit finish machining, after hardening, of the bore and bolt holes located in the flange. Surfaces that are not to be copper plated can be coated with a chemical-resistant lacquer, which is

removed prior to carburizing. After carburizing, the copper can be chemically stripped from the part or removed in subsequent machining operations.

Ceramic coatings in the form of paint can also protect selected surfaces from carburizing. Surfaces must be thoroughly cleaned before ceramic paint is applied, and the first coat is allowed to dry before a second coat is applied. Ceramic paint coatings must adhere tightly in order to be impervious to the carburizing atmosphere. The application of ceramic paint to the bushing and button recesses of a rock bit cutter, for example, has been used in production.

Stopoffs. Blind holes can be stopped off by inserting copper plugs or by filling them with clay. If air is entrapped by the plug, a means of venting must be provided to relieve the pressure buildup during heating. Through holes may be plugged at either end to limit access by the atmosphere, thereby minimizing carburization. Internal threads can be protected by the insertion of a copper screw; external threads by capping with

a copper nut. If a steel screw or nut is used, the threads should be coated with a stopoff material to facilitate removal. The success of all stopoff methods depends largely on the care used in their applications. Seldom are mechanical stopoffs completely effective in production.

If parts are cooled slowly after carburizing, they will be soft enough to permit the removal of the case in selected areas by machining. After subsequent reheating and quenching, these areas will remain lower in carbon and relatively soft. Operations can also be planned so that the case on a hardened part can be removed selectively by grinding. This practice is usually confined to small areas and generally to cases less than 1.3 mm (0.05 in.) in depth.

A part that has been carburized may be locally softened by induction heating. The heat may just temper the part, or, for steels with low hardenability, may actually normalize the area to be softened. This practice is used to soften threads on carburized shafts in the automotive industry.

Dimensional Control

Parts should be as near to final dimensions as possible before carburization so that heat treating times may be kept short. Nevertheless, some growth and distortion will be encountered in all carburized parts. Part size and shape strongly influence distortion, but a host of other factors can play a role as well, such as:

- Residual stresses existing in parts prior to heat treatment
- Shape changes induced by heating too rapidly
- Method of stacking or fixturing parts during carburizing and quenching
- Increasing growth as the case depth increases
- Severity of quenching (including variations caused by changing quench temperatures)
- Hardenability, as influenced by variations in steel composition

A variety of methods, to be described, are used to minimize distortion. All of them add to heat treating cost, but they may be cost effective when total production costs are considered.

In the high-volume production of precision components, such as automotive transmission gears, a general objective is to hold constant all of the processing variables affecting growth and distortion and then to compensate for the changes that do take place by adjusting the shape of the green machined (unhardened) part. For example, the lead angle of a helical gear becomes smaller after it has been carburized because the gear becomes longer. Once the change has been documented, the machining operation prior to heat treatment can be adjusted

to compensate for the growth. Trial lots of parts are processed using the intended production process and then measured to determine shape changes. After production has begun, parts may be checked periodically to ensure that processing conditions that affect distortion have not changed.

Fixturing can be used to separate parts, allowing more uniform heating and access to the carburizing atmosphere, and to orient parts so that each part enters the quench bath the same way. Fixturing adds labor cost (fixtures are often loaded and unloaded by hand) and adds operating cost because the fixtures may weigh as much as, or more than, the work load. However, proper fixturing is often effective in reducing variations in growth and lessening distortion, thereby allowing compensation for the changes in the shape of the green part.

Marquenching, or martempering, involves quenching in molten salt or in hot oil; the quenchant temperature is above the M_s temperature (the temperature at which martensite starts to form from austenite upon cooling) of the case, but below the M_s temperature of the core. Consequently, the core transforms, while parts are in the quenchant, to a mixed microstructure of martensite, bainite, and ferrite. The case transforms to martensite while the parts are cooling in air after leaving the quenchant. Distortion is reduced because the transformation strains in the core are reduced, and because thermal gradients are much lower during transformation in the case and core.

Press quenching and other means of quenching in fixtures, such as plug or cold die, are effective for reducing distortion. While quench presses may have automated loading systems, they are often loaded manually, one part at a time. Quenching in fixtures adds significantly to the cost of heat treating, but there may be no practical alternative for limiting distortion of certain parts, for example, thin-walled rings and slender shafts.

Straightening is employed to reduce the distortion of heat-treated shafts. Most straightening is done by flexing the part. There is always a risk of cracking the case when straightening carburized parts, so it is the usual practice to straighten after tempering. Some manufacturers find it best to straighten while parts are still hot from the tempering furnace. In one instance, shafts which cracked upon straightening after tempering could be straightened without cracking immediately after quenching. Many straighteners are equipped with acoustic emission sensors to detect cracking. Selective peening has also been used as a method for straightening parts.

Case Depth Measurement

Case depth is usually specified as the depth below the surface at which a defined

value of some property occurs. A case depth to a hardness of 50 HRC and a case depth to a carbon content of 0.4 wt% are examples of specifications for an effective case depth. Also used is the term total case depth, which is too vague for general use as a specification because of the gradual transition between case and core properties in most carburized parts. However, some carbonitrided parts and induction case hardened parts will have a sharp transition in microstructure clearly separating case and core. Only in these instances is total case depth defined well enough to be useful as a specification. Methods of measuring case depth are described in detail in SAE Recommended Practice J423.

Many parts, such as gears, consist of some surfaces that are convex, some that are relatively flat, and some that are concave. It is usually found that the case depth will be least at the concave surface (the root) and greatest at the convex surface (the tooth tip). The effect of surface curvature on effective case depth is shown in Fig 15. These data are computed for a particular case:

- Surface carbon, 1%
- Core carbon, 0.2%
- Diffusion time/temperature sufficient to produce a case depth to 0.4% of 1 mm (0.04 in.) beneath the flat surface of a slab of infinite thickness

From Fig 15, the same treatment that will produce a case depth of 1 mm (0.04 in.) in a plane slab of 3 mm (0.12 in.) half-thickness will produce a case depth of 1.13 mm (0.0445 in.) in a rod of 3 mm (0.12 in.) radius, a case depth of 1.28 mm (0.0504 in.) in a sphere of 3 mm (0.12 in.) radius, and a case depth of 0.93 mm (0.037 in.) in a circular hole of 3 mm (0.12 in.) radius. The effect of surface curvature is quite pronounced if the radius of curvature of the surface is less than about five times the effective case depth beneath a flat surface. The effect of curvature is small when the radius of curvature of the surface is more than ten times the effective case depth. Surface curvature also affects cooling so that in parts with marginal hardenability there may be a greater difference between convex and concave surfaces when effective case depth is defined in terms of depth to a specified hardness than when it is defined as depth to a specified carbon content. These facts must be kept in mind when comparing case depth at various locations on a part and when comparing case depths on parts with case depths on testpieces.

Effective case depth to a specified hardness value is best measured by means of a microhardness traverse on a polished metallographic section cut normal to the surface. Vickers (diamond pyramid hardness) or Knoop or Rockwell microhardness indenters may be used with loads of 0.5 to 2 kg.

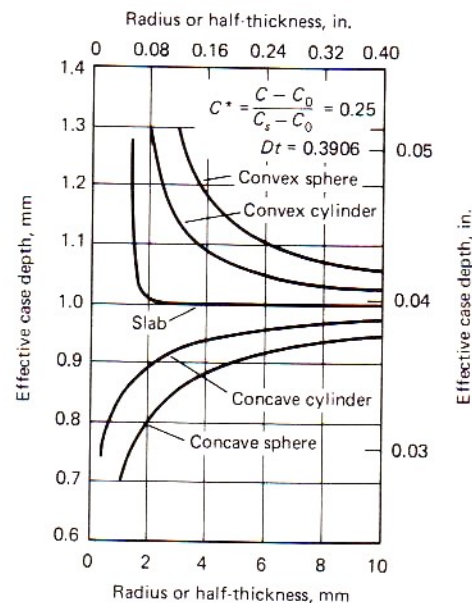


Fig 15 Influence of surface curvature on case depth. C^* , normalized carbon content; C , concentration of diffusing substance; C_0 , base carbon content of the alloy; C_s , surface carbon content (often taken to be the maximum dissolved carbon content in austenite at the carburizing temperature); D , diffusion constant, having units (distance)²/time; t , time

Specifications can be written in terms of a microhardness value or in terms of HRC hardness, where it is understood that microhardness (HV, HK, or HRMF) is converted to HRC using standard tables (50 HRC = 513 HV = 542 HK = 870 HRMF). Surface hardness, which is often a part of carburizing specifications, can be obtained by extrapolating subsurface microhardness values to the surface. Alternatively, the microhardness at a depth of 0.1 mm (0.004 in.) beneath the surface can be defined as the surface hardness. It is difficult to get reliable microhardness readings closer than 0.1 mm (0.004 in.) to the edge of a polished section because of edge rounding, which occurs during polishing.

Effective case depth to a specified carbon content is most frequently measured on testpieces of the same alloy and shape as the workpieces and processed simultaneously with the work load. Typically, a ground bar about 25 mm (1 in.) in diameter is used. If it is quenched with the work load, it must be tempered at about 650 to 700 °C (1200 to 1300 °F) prior to machining. Bars are cut dry, at very slow speeds to avoid burning, and washed between cuts with Freon. Turnings are collected on clean paper, rewashed, and analyzed for carbon. To detect the effect of the final atmosphere exposure on the near surface carbon gradient, three or four initial cuts of 0.025 mm (0.001 in.) thickness should be made. Thereafter, cuts of 0.075 to 0.125 mm (0.003 to 0.005 in.) thickness can be made through the case. The accuracy of the method de-

depends on good machining practice in addition to well-standardized analytical procedures. One user reports repeatability of 0 to 0.03% C at depths greater than 0.075 mm (0.003 in.) and 0 to 0.05% C for samples taken closer to the surface.

As a plant floor test, test bars about 10 to 12.5 mm (0.4 to 0.5 in.) can be processed with the work load, quenched, and fractured. The depth of the case, evident on the fracture surface, can be read with a 10× Brinell glass. Even workpieces can be fractured if their shape (and cost) allow easy fracture. A variant of this test involves reheating a test bar to 780 °C (1440 °F) and then quenching and fracturing. In plain carbon steels, only material with a carbon content of 0.4 wt% or greater will become austenitic at this temperature. Therefore, the line of demarcation between case and core on the fracture surface should occur at a carbon content of 0.4 wt%.

Another test for case depth makes use of the principle that the M_s temperature depends primarily on the dissolved carbon content of austenite. A carburized testpiece or part is austenitized, quenched in a bath at precisely controlled temperature, held for a few minutes to allow tempering of the martensite formed, and then quenched to room temperature. A polished, etched section will show a line of demarcation between the martensite tempered in the salt bath (dark) and the untempered martensite formed during the final quench (white). The location of the line of demarcation corresponds to a specific carbon content. The appropriate quenching bath temperature can be found from a correlation between M_s temperature (in degrees Fahrenheit) and composition (Ref 14):

$$M_s = 930 - 600(\%C) - 60(\%Mn) - 50(\%Cr) - 30(\%Ni) - 20(\%Si + \%Mo + \%W) \quad (\text{Eq 23})$$

If the quenching bath temperature is chosen to be the M_s temperature for 0.4 wt% C in a given alloy, then the austenitizing temperature must be high enough to dissolve at least this much carbon in austenite, typically 830 °C (1525 °F).

Surface hardness is often measured on the plant floor on workpieces using a superficial hardness test, Rockwell 15N, for example. Because of the rather light load, the necessity for supporting pieces well, and the importance of a smooth surface, values tend to be unreliable. However, such checks of surface hardness is often necessary to detect the presence of a shallow, decarburized layer such as might occur if parts experience a delay when transferred from the carburizing furnace to the quench bath.

Safety Precautions

Gas carburizing atmospheres are highly toxic and highly inflammable and form explosive gas mixtures when mixed with air.

A safety program emphasizing furnace operator training and preventative maintenance should be established and adhered to for all heat-treating operations using controlled atmospheres. The installation of alarms and other safety devices cannot substitute for a properly trained operator.

Recommended procedures for safe furnace operation are provided by furnace manufacturers; this information should form the basis for operator training. Safety standards for furnaces and related equipment are also published by the National Fire Prevention Association. Because procedures differ somewhat for furnaces of different design, the discussion in this section focuses on the principles of safe operation, that is, the goal of operating procedures. The three factors of prime consideration are discussed below.

First, all atmosphere gas discharged from the furnace to the operating environment must be burned to ensure that poisonous carbon monoxide is converted to carbon dioxide. Pilot flames should be maintained on atmosphere vent lines at all times, and there must be a flame curtain that ignites automatically whenever a furnace door opens. There should be a thermocouple inserted into each pilot flame and connected to an alarm system to verify that each pilot is ignited. Air-Endogas mixtures that are too lean to support combustion can still contain enough carbon monoxide to be hazardous. The threshold limit value for long-term exposure to carbon monoxide, set by the American Conference of Governmental Industrial Hygienists, is 50 ppm. The short-term exposure limit is 400 ppm. A concentration of 50 000 ppm CO is quickly fatal.

Second, air and Endogas will self-ignite if mixed at a temperature of 760 °C (1400 °F) or above. That is, Endogas may be introduced into an air-filled furnace heated to 760 °C (1400 °F) or above without risk of explosion; the Endogas will simply burn until the oxygen in the furnace is consumed. At temperatures below 760 °C (1400 °F) there is the risk that Endogas will not ignite spontaneously upon entering an air-filled furnace and that the furnace will then fill with an air-Endogas mixture, which may then ignite explosively. Table 3 lists auto-ignition temperatures and composition limits within which combustion can occur for mixtures of several gases and air.

Third, it is very convenient to have available at each furnace a source of inert gas, such as nitrogen, that is available for purging the furnace in the event of power failure or other emergencies. Many operations use cylinders of compressed nitrogen to provide automatic purging whenever the furnace temperature falls below 760 °C (1400 °F) or whenever the pressure in the Endogas line falls below a critical value. Purging with nitrogen can also be used routinely prior to introducing Endogas into a furnace or when

Table 3 Properties of air-combustible gas mixtures

Gas	Autoignition temperature		Flammable limits in air, vol %
	°C	°F	
Methane	540	1005	5.4–15
Propane	466	870	2.4–9.5
Hydrogen	400	750	4.0–75
Carbon monoxide	609	1130	12.5–74
Methanol	385	725	6.7–36

Source: Ref 15

removing the atmosphere from a furnace prior to shutdown. As a rule of thumb, the volume of gas required for effective purging is at least five times the volume of the furnace chamber.

Special precautions are needed to introduce combustible atmospheres safely into furnaces equipped with unheated vestibules. The usual procedure is to raise the furnace temperature above 760 °C (1400 °F), close the furnace door, open the vestibule door, and introduce the atmosphere gas into the furnace while maintaining a pilot flame at the furnace door to ignite gas entering the vestibule. Once a gas flame has been established at the furnace door (one that will continue burning after the pilot flame has been removed), the vestibule door can be closed and pilot flames ignited at the point that gas exits the vestibule. The flame burning at the furnace door will consume oxygen in the vestibule, reducing it to the point at which combustion can no longer be supported. Vestibule explosions can occur during start-up if the flame at the furnace door blows out before sufficient oxygen is consumed in the vestibule. Start-up is simplified if nitrogen is available; thorough purging of the furnace and the vestibule with nitrogen prior to the introduction of the atmosphere gas will eliminate any risk of explosion.

Whenever a furnace must be operated with a flammable atmosphere below 760 °C (1400 °F), the usual practice is to raise the furnace temperature above 760 °C (1400 °F), introduce the furnace atmosphere, and decrease to the operating temperature. Other safe practices have been developed that make use of nitrogen gas for purging air from the furnace before combustible gases are introduced.

ACKNOWLEDGMENT

Preparation of this article benefited from the suggestions and criticisms of Gary D. Keil, Caterpillar, Inc. and Gregory A. Fuller and his colleagues at the Timken Company.

REFERENCES

1. C.A. Stickels, C.M. Mack, and J.A. Pieprzak, *Metal. Trans. B*, Vol 13B, 1982, p 613-623
2. Y. Shimozato, in *Heat Treatment and*

- Surface Engineering: New Technology and Practical Applications*, Proceedings of the Sixth International Congress on Heat Treatment of Materials, G. Krauss, Ed., ASM International, 1988, p 401-404
3. F.E. Harris, *Met. Prog.*, Vol 44, 1943, p 265-272
 4. T.J. Schultz, T.J. Kuhn, and D.E. Goodman, Carburizing—Stepping into the Future, in *Carburizing: Processing and Performance*, Proceedings of an International Conference, G. Krauss, Ed., ASM International, 1989
 5. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, 1975
 6. G.L. Tibbetts, *J. Appl. Phys.*, Vol 51, 1980, p 4813-4816
 7. B. Uhrenius, *Scand. J. Metall.*, Vol 6, 1977, p 83-89
 8. C.A. Stickels, *J. Heat Treat.*, Vol 1, 1979, p 31-41
 9. D.R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., NSRDS-NBS 37, U.S. Department of Commerce, June 1971
 10. D.J. Bradley, J.M. Leitnaker, and F.H. Horne, *High Temp. Sci.*, Vol 12, 1980, p 1-10
 11. B.G. Liptak, Ed., *Instrument Engineer's Handbook*, Chilton Book, 1985
 12. A.R. Marder and G. Krauss, *Trans. ASM*, Vol 60, 1967, p 651-660
 13. R.L. Brown, H.J. Rack, and M. Cohen, *Mat. Sci. Eng.*, Vol 21, 1975, p 25-34
 14. E.S. Rowland and S.R. Lyle, *ASM Trans.*, Vol 37, 1946, p 27-47
 15. J.A. Dean, Ed., *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, 1985