

Special Edition.

Linde Gas

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Furnace Atmospheres No. 1
Gas Carburizing and Carbonitriding

Preface

This booklet is part of a series on heat treatment, brazing and soldering process application technology and expertise available from Linde Gas. The booklet focuses on the use of furnace atmospheres; however, a brief introduction to each process is also provided. In addition to this work on carburizing & carbonitriding, the series includes:

- Annealing & Hardening
- Nitriding and Nitrocarburizing
- Sub-zero Treatment of Steels
- Brazing of Metals
- Soldering of Printed Circuit Boards

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I. Introduction

The purpose of this booklet is to provide an introduction to carburizing and carbonitriding processes. Sections I-III contain a brief introduction to the processes, the properties obtained and the steels used. The remaining sections, IV-VII, deal with the properties and functions of the furnace atmospheres used for these processes.

The highest hardness of a steel is obtained when its carbon content is high, around 0.8 weight % C (Figure 1). Steels with such high carbon content are hard, but also brittle, and therefore cannot be used in machine parts such as gears, sleeves and shafts that are exposed to dynamic bending and tensile stresses during operation. A carbon content as high as 1% C also makes the steel difficult to machine by cutting operations such as turning or drilling. These shortcomings can be eliminated by using a low carbon content steel to machine a part to its final form and dimensions prior to carburizing and hardening. The low carbon content in the steel ensures good machinability before carburizing. After carburizing and quenching the part will have a hard case but a softer core that will assure wear and fatigue resistance. The martensitic case attains a hardness corresponding to its carbon content, as is shown in Figure 1. The case is typically 0.1–1.5 mm (0.004–0.060 inches) thick. The core of the part maintains its low carbon concentration and corresponding lower hardness.

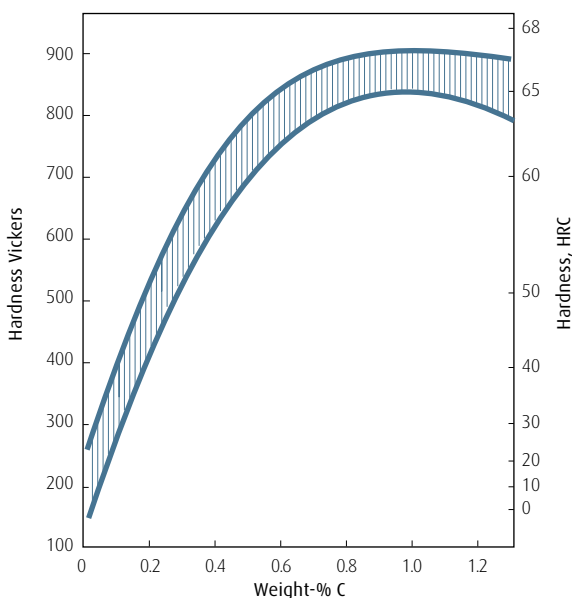


Figure 1: Hardness as a function of carbon content in hardened steel. The shaded area shows the scatter effect of the retained austenite and alloy content of steel [1].

In this booklet we use the term carburizing for a heat treatment process carried out at a temperature where the steel is austenitic, typically in the temperature range 820–950 °C (1510–1740 °F), and which requires a controlled furnace atmosphere at slight overpressure that transfers carbon from the atmosphere to the steel surface. Similarly, the term carbonitriding is used where the aim is to transfer both carbon and nitrogen to the steel surface. The terms carburizing and carbonitriding are normally understood to include hardening, and thus quenching, as the final step. In this step the carburized or carbonitrided case transforms to a hard martensite microstructure constituent. The term of case hardening is sometimes alternatively used to more clearly describe the fact that the process includes the hardening step. The process cycle shown in Figure 2 also includes tempering, which is required to ensure ductility by eliminating internal micro stresses and by somewhat reducing the hardness. After cooling before tempering there is usually a washing step to remove the quench oil that is used in the cooling step.

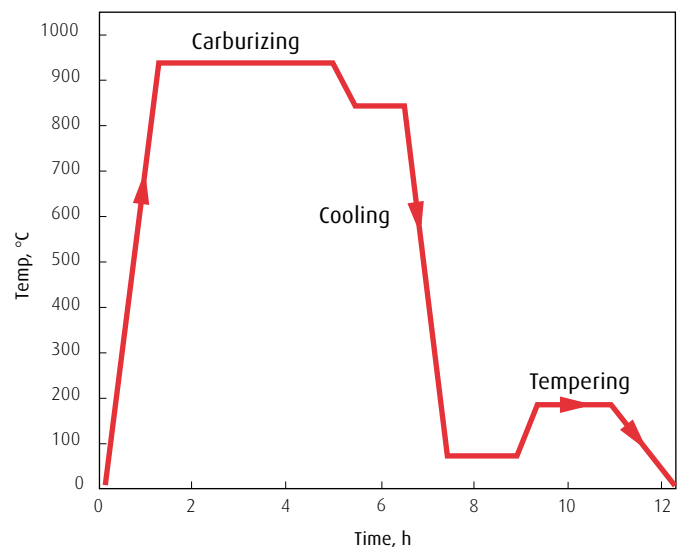


Figure 2: Gas carburizing cycle including the quenching and tempering steps

A carburizing atmosphere must be able to transfer carbon – and also nitrogen in the case of carbonitriding – to the steel surface to provide the required surface hardness. To meet hardness tolerance requirements this transfer must result in closely controlled carbon or nitrogen concentrations in the steel surface. The carbon concentration, as indicated in Figure 3, can be controlled by the ratio $(\text{vol}\% \text{CO})^2 / (\text{vol}\% \text{CO}_2)$ in the furnace atmosphere. The atmosphere nitrogen activity, which plays an important role in carbonitriding,

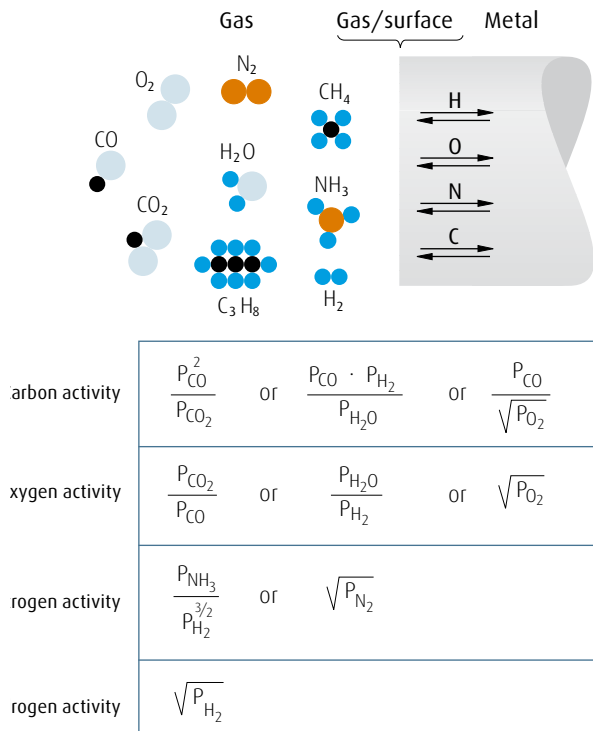


Figure 3: Schematic illustration of atmosphere/metal interaction and expressions for proportionality between atmosphere composition and carbon and nitrogen activities. P is the partial pressure, which at atmospheric pressure is equal to vol% divided by 100.

can be controlled by the ratio $\text{vol}\% \text{NH}_3 / \text{Vol}\% \text{H}_2^{3/2}$. Expressions for the atmosphere oxygen and hydrogen activities are also shown in Figure 3, although they are not of primary interest, but they are related to the oxidation risk for alloying elements and to hydrogen pick up respectively.

The procedure in carburizing is as follows. Ready-machined parts that are to be carburized, for instance gears, are placed in baskets or mounted (hung) on some type of fixture, see Figure 4c. The basket (fixture) is loaded into a furnace, which typically is at a temperature of 820-880 °C (1508-1616 °F) for carbonitriding and 900-950 °C (1652-1742 °F) for gas carburizing. When the charge has reached carburizing temperature, the effective transfer of carbon from gas to steel surface begins. Carburizing is allowed to proceed until the desired depth of penetration is reached, see Figure 9. The charge is then moved from the heating chamber to a gas tight cooling chamber integrated into the furnace. There the load is rapidly quenched in a quench oil bath. After cooling, the charge normally undergoes washing and tempering. The quenching process is important both in order to achieve the correct hardness and also to minimize distortions. Sub zero treatment is sometimes used as a post process after carburizing and quenching to increase hardness. The principles for quenching and sub zero treatment are briefly described in references [2] and [3] and are not described further in this booklet. Dimension-adjusting grinding is normally required before the parts are completely finished.

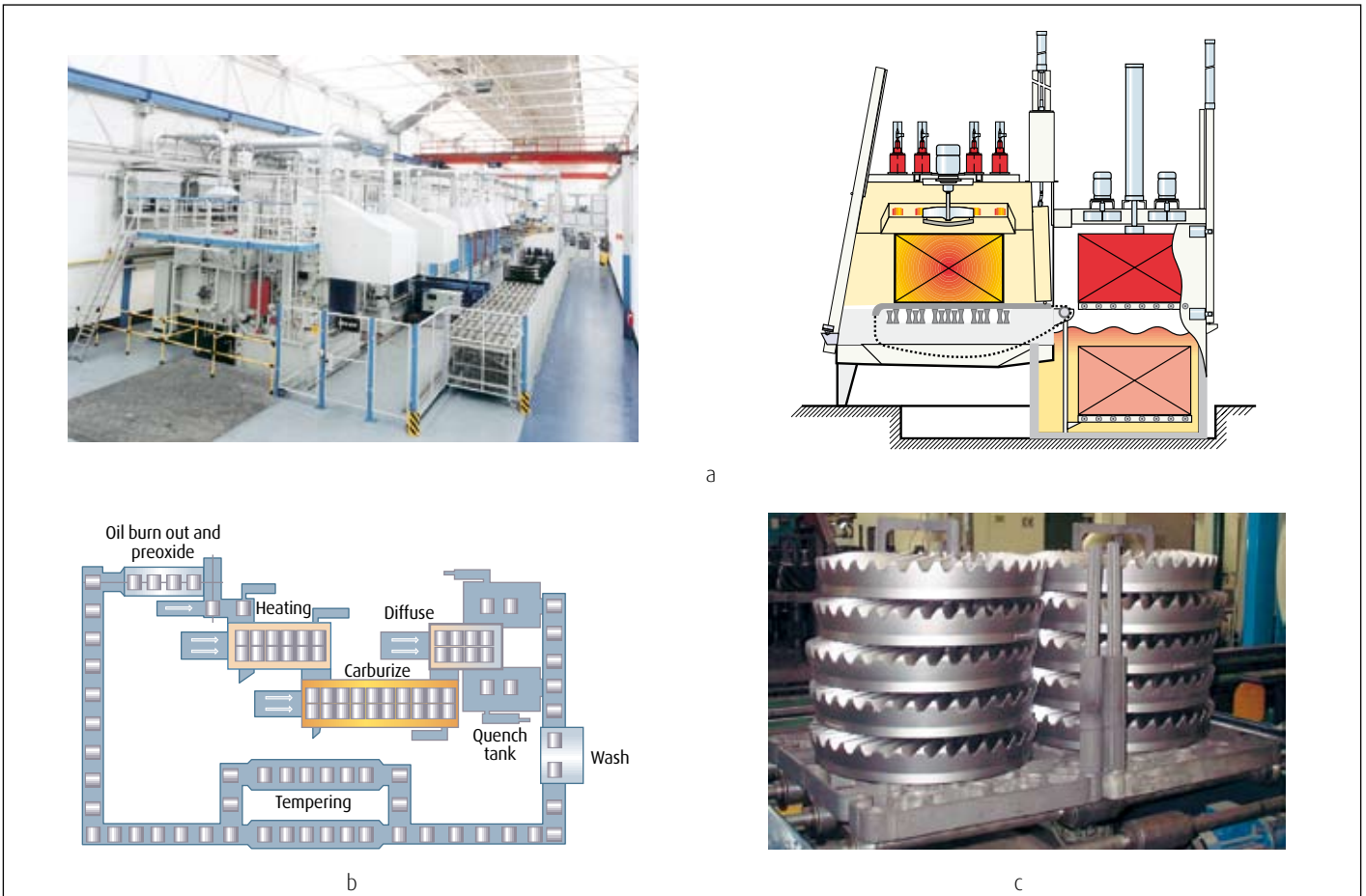


Figure 4: a) Example of a sealed quench furnace line and charging equipment (left) and cross section of a sealed quench furnace showing the heat chamber and the integrated oil quench bath (right) (Courtesy of Ipsen International GmbH.)

b) Layout of a continuous carburizing line with the pusher furnace in the center. c) Example of load.

The sealed quench batch furnace shown in Figure 4a is commonly used within the metalworking industry. In the automotive industry mostly continuous pusher-type furnaces are used that are more suitable for mass production of parts (see Figure 4b). Conveyor-belt furnaces, shaker-hearth furnaces or rotary-retort furnaces are used for small parts, such as screws. Cylindrical batch retort furnaces are commonly used when long parts are to be gas carburized.

The process of carbonitriding is principally performed in the same way as carburizing, only with the difference that both carbon and nitrogen are transferred from the gas to the steel surface. Nitrogen acts in the same way as carbon to increase the hardness of the hardened steel.

Carburizing and carbonitriding are carried out on parts subjected to high fatigue stresses or wear, such as parts for transmissions, car

engines, roller and ball bearings, rock drill parts, etc. The automotive industries and their sub-suppliers are key examples of industries that have carburizing and carbonitriding as steps in their manufacturing processes.

Low pressure carburizing – commonly called vacuum carburizing – is not described in this booklet; however, a detailed description is given in reference [4]. Pack carburizing and liquid drip feed carburizing are rarely used alternatives that are not described in this booklet.

After carburizing quenching is mostly carried out using mineral oils. An alternative, mainly used in vacuum carburizing, is gas quenching. There have also been initiatives to apply gas quenching to atmospheric pressure carburizing. For further information on gas quenching the reader is referred to references [2] and [4].

II. Properties of Carburized and Carbonitrided Steels

The gas-carburized (carbonitrided) part can be said to consist of a composite material, where the carburized surface is hard but the unaffected core is softer and ductile. Compressive residual stresses are formed in the surface layer upon quenching from the carburizing temperature. The combination of high hardness and compressive stresses (Figure 5) results in high fatigue strength, wear resistance, and toughness.

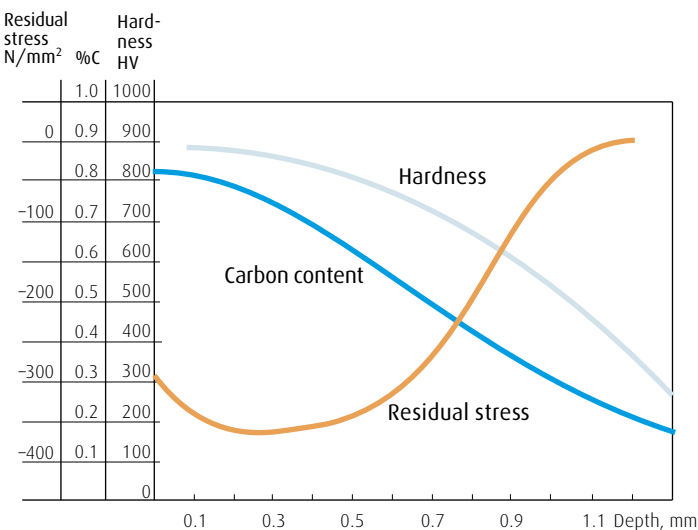


Figure 5: Typical hardness, carbon content and residual stress gradients after carburizing, quenching and tempering

A. Case Hardness and Carbon/Nitrogen Surface Concentration

Maximum hardness for unalloyed steels is obtained when the carbon concentration is about 0.8% C, as was shown in Figure 1. Above that carbon concentration the hardness decreases as the result of an increased amount of retained austenite. The hardness curve therefore often exhibits a drop in hardness close to the surface, where the carbon concentration is highest. Carbon, nitrogen and almost all alloying elements lower the M_s -temperature (see reference [2] for the definition of M_s temperature). This leads to a retained austenite concentration gradient that increases towards the surface after carburizing and quenching. To compensate for this effect, the surface carbon concentration after carburizing that provides maximum surface hardness has to be lowered as the alloy content of the steel increases. Carbide forming elements, such as chromium and molybdenum, can counteract this effect and raise the surface carbon concentration that provides maximum hardness. This is because the formation of carbides leads to a lowered carbon concentration in the austenite, although the average carbon concentration is high. Table 1 gives some examples of the relation between maximum hardness and carbon concentration for different types of steels. Mo-alloyed steels obtain the highest surface hardness and Ni-alloyed steels the lowest.

steels obtain an intermediate surface hardness. (See paragraph IV. D for the relation between carbon concentration and carbon potential.)

Table 1. Surface carbon concentration for maximum surface hardness for some types of case hardening steels [5]

Major alloy elements	Carbon concentration, %C	Surface hardness, HV
Ni (1-4%)	0.60-0.75	620-670
1.5%Cr, 2%Ni, 0.2%Mo	0.65-0.70	840
1.5%Mn, 0.004%B	0.85	815
Mn, Cr	0.70	840
Mo, Cr	1.0	940

The maximum surface hardness after carbonitriding depends on both the carbon and nitrogen surface concentrations. These concentrations are typically in the range 0.6-0.9% C and 0.2-0.4% N. An approximate guideline is that martensite with the same total concentration of the interstitial elements carbon and nitrogen has about the same hardness, irrespective of the relative proportions of the elements carbon and nitrogen.

B. Case and Carburizing Depths

According to European standards [6], the case depth is abbreviated to CHD (case hardened depth) and defined as the depth from the surface to the point where the hardness is 550HV, as shown in Figure 6. Sometimes a hardness other than 550HV is used to define the case depth.

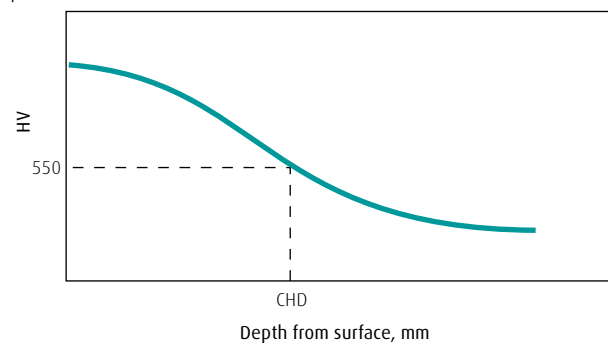


Figure 6: Definition of case depth [6]

The attained case depth depends not only on carburizing depth, but also on the hardening temperature, the quench rate, the hardenability of the steel and the dimensions of the part. This is illustrated in the schematic CCT diagrams in Figure 7. The hyperbolic temperature/time-dependent parts of the transformation curves depict the transformation from austenite to ferrite/pearlite. For a high hardenability steel these curves are located far to the right in the diagram, ensuring that the cooling curves do not cross the ferrite/pearlite transfor-

mation curve. Hardenability increases not only with base steel alloy content but also with increased carbon and nitrogen concentrations. The carburized or carbonitrided case therefore has higher hardenability than the base steel. Some examples of how different parameters will affect hardenability are described in relation to Figure 7 in the following.

In Figure 7a the cooling curves for both “surface” and “center” cross the transformation line for the base steel, the core. This means that the core will transform to ferrite/pearlite upon cooling from hardening temperature. If the cooling curves are related to the “case” instead, it can be seen that the cooling line for the surface passes to the left of the ferrite/pearlite transformation curve. Thus the “surface” cooling line first crosses the M_s (case) line, meaning that the austenite will transform to martensite, as is the intention in case hardening.

The hardenability of steel number 1 in Figure 7b is too low to result in martensite transformation even for the carburized case. As shown in Figure 7c carbonitriding is a method for achieving high enough hardenability to form a martensitic case. (The “surface” cooling line

passes to the left of the carbonitrided transformation curve.) Carbonitriding is a way to make water-quench steels become oilhardening steels.

Figure 7d schematically shows the effect of part dimensions on cooling rate. The bigger the dimensions, the slower the cooling rate. Therefore there is a certain maximum diameter for a certain steel grade that can be hardened to form a martensitic case. When a martensitic case is formed the case depth will decrease with increasing diameter, as shown in Figure 8.

Carburizing depth is not standardized but is nevertheless used in practice, and is defined as the depth from the surface to the point corresponding to a specified carbon concentration. As a guideline, the case depth (CHD) for common steels and part dimensions is approximately equal to the carburizing depth to the point where the carbon concentration is about 0.35% C (cf. Figure 1). The carburizing depth depends on treatment time and temperature. With prolonged carburizing time carbon can diffuse to a greater depth into the steel. Increasing the temperature increases the rate of diffusion and thus increases the carburizing depth. This is illustrated in Figure 9.

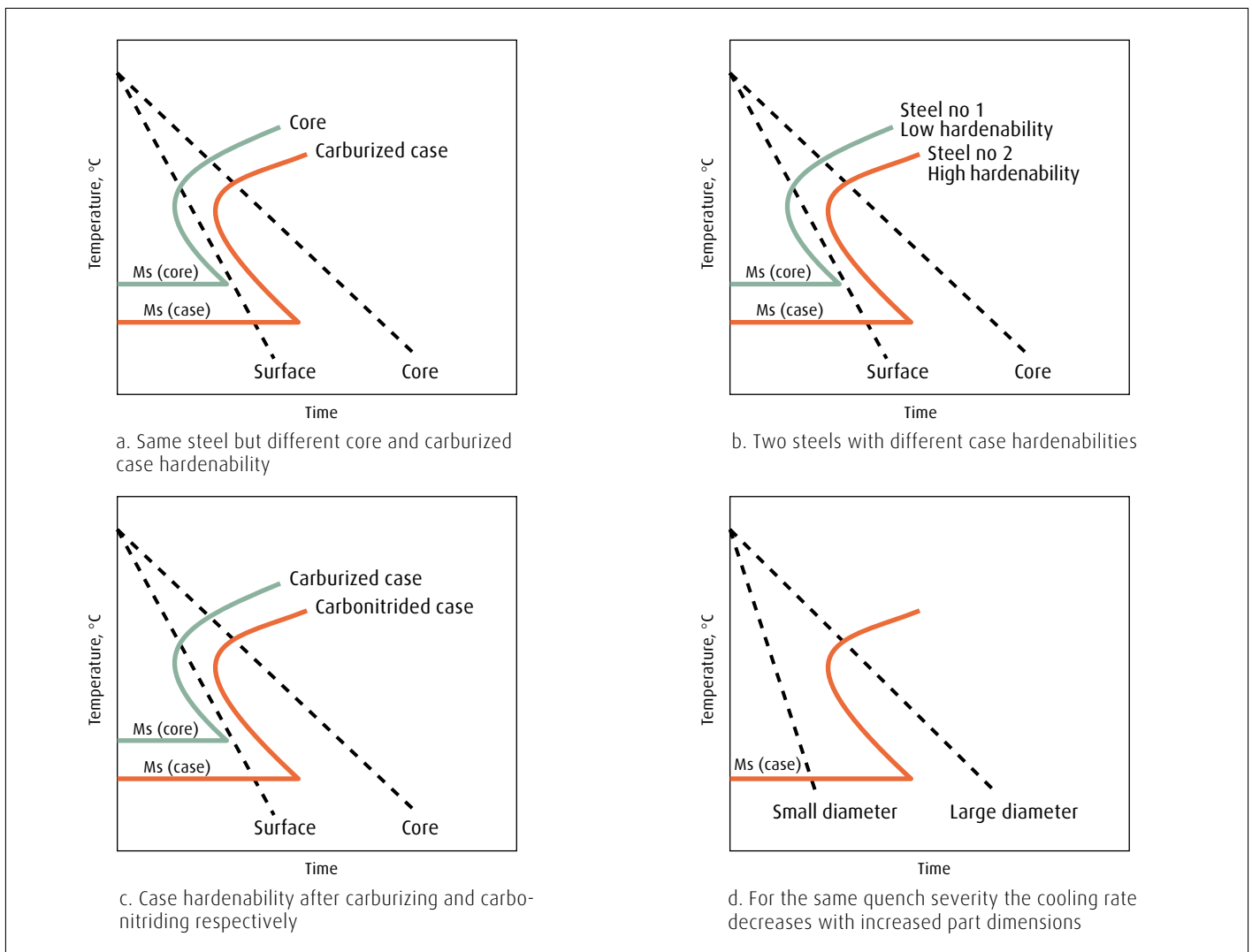


Figure 7: The relation between the cooling rate of the surface and of the center to the hardenability of the carburized case and unaffected core.

- The hardenability of the carburized case, resulting in martensite formation, is higher than for the non-carburized core that transforms to pearlite.
- Upon hardening, the case of steel number 2 will transform to martensite,

whereas the case of steel number 1 will be pearlitic.

- The carbonitrided case will transform to martensite, whereas the carburized case will transform to pearlite.
- The small diameter cools faster, resulting in a martensitic case, whereas the larger diameter will have a pearlitic case.

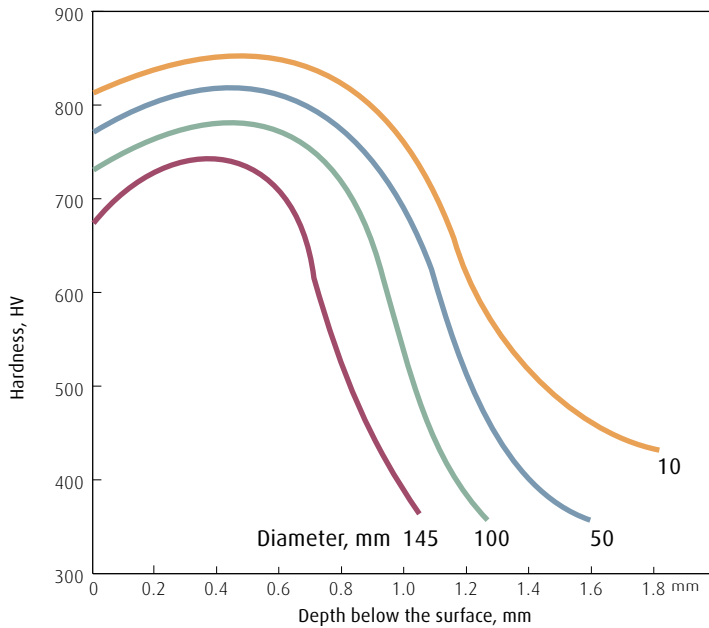


Figure 8: An example of how case depth depends on dimensions [7]

Carbonitriding often yields carburizing depths that are somewhat greater than for pure carburizing. It is an effect caused by the interaction with respect to diffusivity between carbon and nitrogen

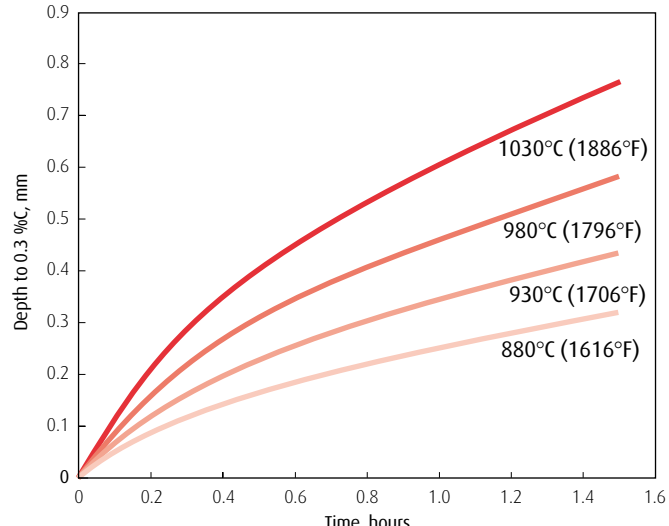
The proper case depth requirements are determined by the surface load, wear conditions, and static and bending fatigue stresses that the finished part will be subjected to in its service life. A limiting factor is the cost of the required process time, which, as Figure 9 shows, increases in a parabolic manner as carburizing depth increases. Some guidelines for case depth specifications are given in Table 2.

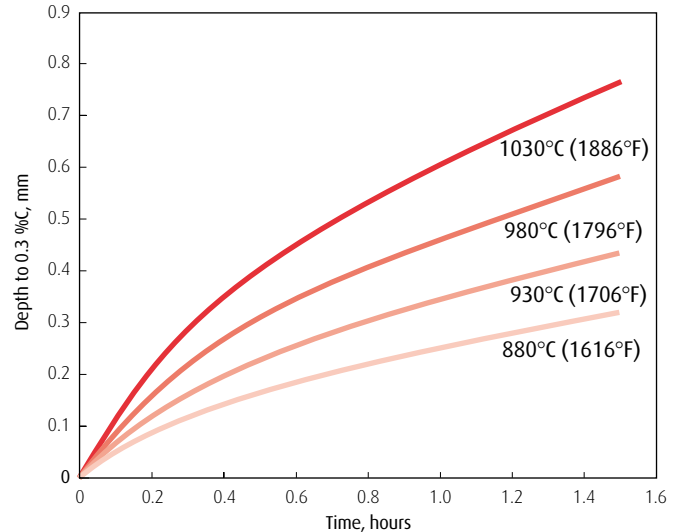
Distortion after carburizing and quenching normally results in the part dimensions not meeting the specified tolerances. The carburizing depth must therefore be high enough to attain the final specified case or carburizing depth after grinding. Grinding allowance is typically of the order of 0.1-0.2 mm.

C. Core Hardness

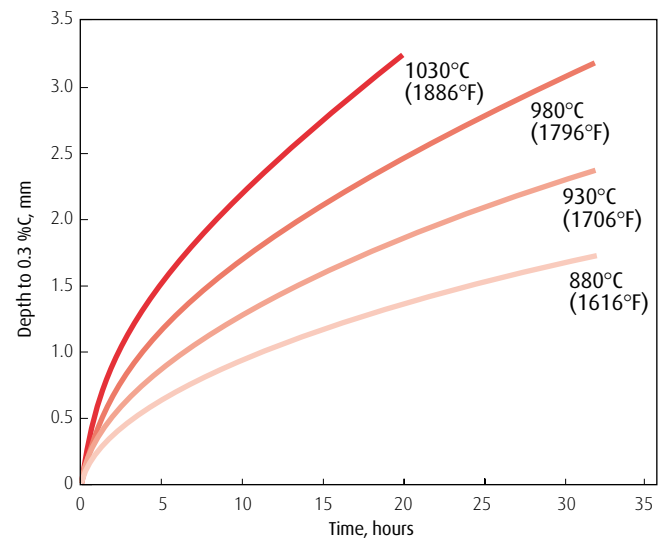
Core hardness is not affected by the carburizing process itself but depends only on the type of steel and its carbon content, hardenability, part dimensions and quenching severity. The best fatigue resistance both for gears and parts subjected to bending fatigue is obtained with a core hardness in the range 400-450HV [5].

Table 2. Simple rules for selection of case depth

Type of part	Case depth	Remark
Parts subjected to surface fatigue		The case depth shall be deep enough to avoid failure initiated below the surface.
Gear	CHD = 0.15 to 0.20 times the gear module	For optimum fatigue life
Thin parts	CHD < 0.2 × thickness	To prevent through-hardening
Parts subjected to surface loads	CHD = 3 to 4 times the depth to maximum stress	



a. Carburizing depth for a carburizing time of 0-1.6 hours



b. Carburizing depth for a carburizing time of 0-25 hours

Figure 9: Approximate relationship between temperature, time and carburizing depth to 0.3%C: Curves are calculated for the following conditions; steel 16MnCr5, carbon potential 0.8%C, atmosphere 40% nitrogen/60% cracked methanol. No account is taken of heating up time or time for atmosphere conditioning.

There is an interdependence between case and core as regards residual stresses. The amplitude of the compressive residual stresses in the case is lowered as core strength increases.

III. Steels for Carburizing and Carbonitriding

When selecting the steel type, the first requirement is that the alloy and carbon concentration meet the requirements for the resulting core hardness after austenitizing, quenching and tempering. For specific core hardness requirements this means that, as the dimensions of the treated parts increase, the required alloy content will also increase. The hardenability of a case hardening steel must be sufficiently good to result in a martensitic surface case to the required depth. Case hardening steels must therefore contain a certain amount of alloying elements. A further requirement is that steels for carburizing should be fine grain treated. This means that the steel should contain an alloy element, usually aluminum, that creates fine precipitates. These precipitates act as barriers to grain growth up to a certain maximum temperature, typically about 950 °C (1742 °F). Examples of some standardized carburizing steels are given in Table 3.

Carbonitriding can be applied to low cost, low alloy steels. The combination of adding nitrogen as well as carbon to the case increases the case hardenability sufficiently to result in a martensitic case that would not be possible with pure carburizing. A few examples of steel types suitable for carbonitriding are given in Table 4.

Some rare applications require carburizing of high alloy steels. The term excess carburizing is used when such steels are carburized to surface carbon concentrations as high as 2-3%C. The aim is not just to produce a martensitic case but also to form high concentrations of carbides and of retained austenite, which has been shown to improve contact fatigue life, as illustrated in Figure 10.

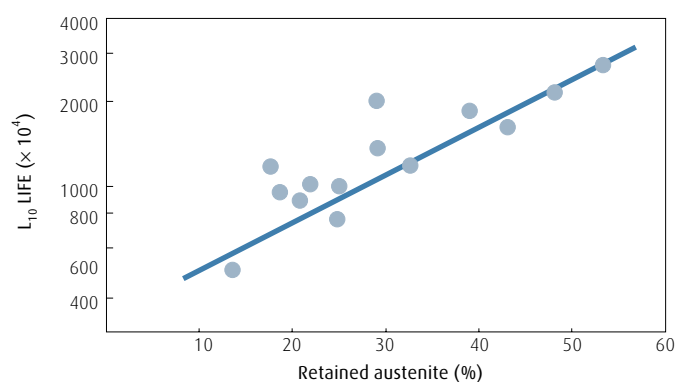


Figure 10: Contact fatigue life of excess carburized steels [8]

Table 3. Composition of selected steel types that can be carburized and hardened

European steel designation	USA ASTM steel designation	Chemical composition					
		%C	%Mn	%S	%Cr	%Mo	%Ni
16MnCr5	5117	0.14-0.19	1.00-1.30	<0.035	0.80-1.10		
16MnCrS5	5117	0.14-0.19	1.00-1.30	0.020-0.040	0.80-1.10		
20MnCr5	5120/5120H	0.17-0.22	1.10-1.40	<[0.035	1.00-1.30		
20MnCr S5	5120/5120H	0.17-0.22	1.10-1.40	0.020-0.040	1.00-1.30		
18CrMo4	4118/4118H	0.15-0.21	0.60-0.90	<0.035	0.90-1.20	0.15-0.25	
18CrMoS4	5120/5120H	0.15-0.21	0.60-0.90	0.020-0.040	0.90-1.20	0.15-0.25	
16NiCr4	8620	0.13-0.19	0.70-1.00	<0.035	0.60-1.00		0.80-1.10
16NiCrS4		0.13-0.19	0.70-1.00	0.020-0.040	0.60-1.00		0.80-1.10
20NiCrMoS2-2	8620/8620H	0.17-0.23	0.65-0.95	0.020-0.040	0.35-0.70	0.15-0.25	0.40-0.70
17NiCrMo6-4		0.14-0.20	0.60-0.90	<0.035	0.80-1.10	0.15-0.25	1.20-1.50
17NiCrMoS6-4	AISI 4317	0.14-0.20	0.60-0.90	0.020-0.040	0.80-1.10	0.15-0.25	1.20-1.50

Table 4. Composition of some steel types that can be carbonitrided

Steel type	% C	% Si	% Mn	% P	% S	% Pb
Steel for cold-rolled strip	0.07	max 0.30	0.25-0.45	max 0.030	max 0.040	-
Free-cutting steels	max 0.14	max 0.05	0.90-1.30	max 0.11	0.24-0.35	0.15-0.35
	max 0.14	max 0.05	0.90-1.30	max 0.11	0.24-0.35	0.15-0.35
	0.12-0.18	0.18-0.40	0.80-1.20	max 0.06	0.15-0.25	-
	0.12-0.18	0.10-0.40	0.80-1.20	max 0.06	0.15-0.25	0.15-0.35
General constructional steel	max 0.20	max 0.5	(1.0-1.6)	max 0.05	max 0.05	-

IV. Interaction between Furnace Atmosphere and Steel

The primary function of the furnace atmosphere is to supply the needed carbon – and nitrogen in carbonitriding – and to provide the right surface carbon content – and surface nitrogen content – in carburized (or carbonitrided) parts. The atmosphere must have a composition that meets these needs and that can eliminate (buffer) the disturbances caused when air enters the furnace via an open door or a leakage. To control the surface carbon content, it must be possible to control the composition of the gas. This is done with a separate enriching gas, a hydrocarbon, usually propane or methane. In order to achieve an even heat treatment result, both temperature and gas composition must remain the same throughout the volume of the charge. This is achieved by forced gas circulation by means of a fan. For the sake of safety, the supplied gas flow should create a positive pressure in the furnace in order to prevent air ingress. To ensure safety it must also be possible to purge a combustible gas out of the furnace in the event of insufficient furnace temperature, a power failure or insufficient furnace pressure.

In summary the functions of the furnace atmosphere are to:

- Supply the necessary carbon (and nitrogen)
- Provide the right carbon (and nitrogen) content
- Buffer from disturbances
- Purge
- Give uniform results
- Maintain a positive pressure
- Permit safety purging

A. Carbon Transfer from Gas to Surface

Possible carbon transfer reactions are



It has been shown that the last of these reactions, illustrated in Figure 11, is by far the fastest and is therefore the rate-determining reaction in carburizing atmospheres with CO and H₂ as major gas

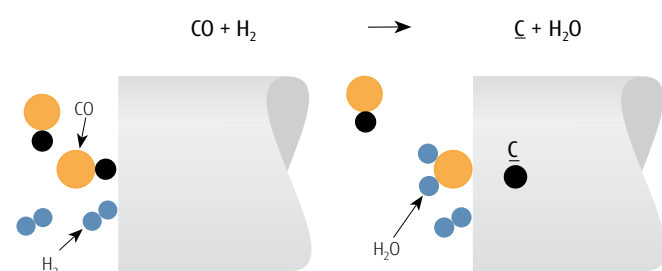


Figure 11: Schematic illustration of the carburizing process

components [9]. The slowest carburizing reaction is from methane, with a rate that is only about 1% of the rate of carburizing from CO+H₂.

In the above reaction, carbon monoxide (CO) and hydrogen (H₂) react so that carbon (C) is deposited on the steel surface and water vapor (H₂O) is formed. The furnace atmosphere must contain enough carbon monoxide and hydrogen to allow the carburizing process to proceed in a uniform and reproducible fashion. The supply of fresh gas must compensate for the consumption of CO and H₂. A higher gas flow is required in cases where the furnace charge area is high, resulting in a high rate of carbon transfer from gas to surface. In the initial part of a carburizing cycle, there is also a high carbon transfer rate, which may be compensated for by increasing the gas supply.

According to the fundamental principles of chemistry, the equilibrium condition for the carburizing reaction 1 is described by an equilibrium constant expressed by:

$$K_1 = (a_c \cdot P_{\text{H}_2\text{O}}) / (P_{\text{CO}} \cdot P_{\text{H}_2})$$

where P_{H₂O} etc. is the partial pressure of the respective gas species. At atmospheric pressure that pressure is obtained from an atmosphere concentration value expressed in vol% divided by 100. The value of K₁ is dependent on the temperature and can be calculated from the relationship:

$$\log K_1 = -7.494 + 7130/T$$

where T is the absolute temperature in Kelvin. a_c is termed carbon activity and is a measure of the “carbon content” of the gas. We see that a_c can be calculated if K₁ and the gas composition are known.

When the carbon activity of the gas, a_c^g, is greater than that of the steel surface, a_c^s, there is a driving force to transfer carbon as expressed by the following equation:

$$dm/dt = k \cdot (a_c^g - a_c^s) \text{ or } dm/dt = k' \cdot (c_c^g - c_c^s)$$

where:

m designates mass, c concentration per unit volume, t time, dm/dt expresses a carbon flow in units of kg/cm² · s or mol/m² · s, and k or k' is a reaction rate constant dependent on temperature and gas composition in accordance

with Figure 12. (Sometimes the notation β is used instead of k'). The maximum value for k' is obtained in a gas mixture with equal parts of CO (carbon monoxide) and H₂ (hydrogen), illustrated at the point marked CARBOQUICK[®], in Figure 12. Section V explains how to make use of this.

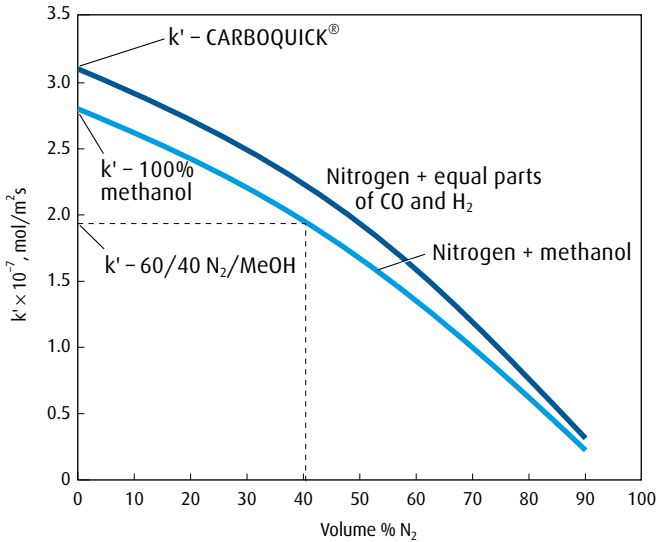


Figure 12: Carbon mass transfer rate coefficient in two types of atmospheres at 930°C (1742°F) and carbon potential 0.8wt%C as a function of nitrogen dilution. The upper curve shows k' for an atmosphere with equal concentrations of CO and H₂ and the lower curve k' for dissociated methanol. k' calculated from data in reference [10].

Fick's first law expresses the carbon flux from the surface into the steel:

$$dm/dt = -D \times dc/dx$$

where D is the temperature dependent diffusion coefficient for carbon, see Table 5 (not taken into account that the diffusion coefficient increases with increased carbon and nitrogen concentrations [11]).

Table 5 Typical values of the diffusion coefficient for carbon and nitrogen in austenite expressed as $D = D_0 \times \exp - Q/RT$ ($R = 8.314 \text{ J/mol} \times \text{K}$) ; $D \{900^\circ\text{C} (1652^\circ\text{F})\}$ is calculated as example.

	$D_0, \text{m}^2/\text{s}$	$Q, \text{kJ/mol}$	$D(900^\circ\text{C}) \text{m}^2/\text{s}$
Carbon	11×10^{-6}	129	20×10^{-12}
Nitrogen	20×10^{-6}	145	7×10^{-12}

Since mass balance must exist between carbon flux by transfer from the gas to the steel surface and by diffusion from the surface to steel interior, the following boundary condition applies at the steel surface:

$$k' \cdot (c_c^g - c_c^s) = -D \cdot dc/dx$$

as illustrated in Figure 13.

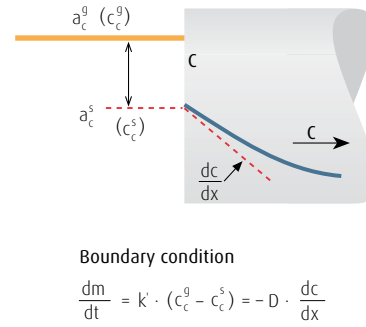


Figure 13: Carbon flux and activities (concentrations) at the gas/steel interface.

The gradient dc/dx has its highest value at the beginning of the cycle when carbon has only diffused to a thin depth. This results in a high driving force for carbon flux by diffusion into the steel. The rate of the carbon transfer from gas to surface will therefore initially be the limiting step. At the start of a carburizing cycle, the term $(c_c^g - c_c^s)$ has its highest value, and accordingly the driving force for carbon transfer from gas to steel has its highest value. The surface carbon concentration c_c^s will increase with increasing carburizing time. The driving force for carbon transfer, $(c_c^g - c_c^s)$, will thus decrease. The carbon concentration gradient, dc/dx , will decrease concurrently as carbon diffuses into the steel. In conclusion, these limitations will lead to a continuous reduction of carbon flux into the steel as shown in Figure 14. About 60 minutes into the carburizing cycle the carbon flux in the example shown in Figure 14 is reduced to about 20 % of the initial rate.

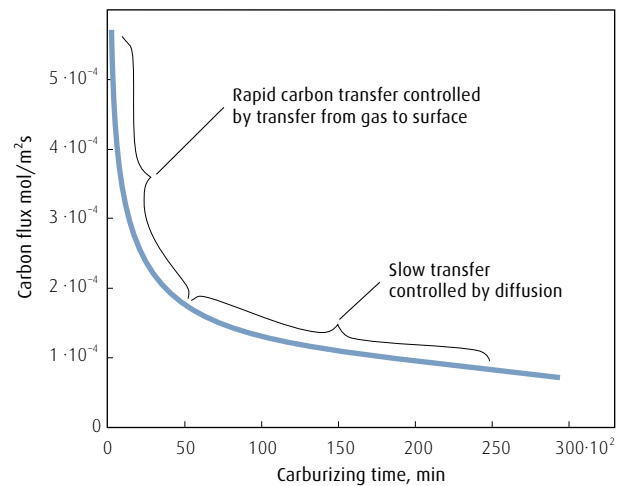


Figure 14: Carbon flux as a function of the carburizing time at 930°C (1706°F) in a 20%CO/40%H₂ atmosphere with a carbon potential of 0.8%C.

From the expression for carbon transfer it follows that there are two fundamentally different ways to increase the rate of carbon transfer. Firstly, the difference $(a_c^g - a_c^s)$ or $(c_c^g - c_c^s)$ can be made as large as possible. This means maximizing a_c^g . The upper limit is given by $a_c^g = 1$, which is the limit for the formation of free carbon or soot. Another upper limit is given by the fact that the carbon activity must not exceed the value that corresponds to carbide formation in the steel. This principle is used in what is called "boost carburizing" or

two-stage carburizing (see Figure 18). Secondly, the reaction rate constant k' can be maximized. k' reaches its highest value when the product $P_{CO} \cdot P_{H_2}$ is greatest, i.e. for an atmosphere with equal parts of carbon monoxide and hydrogen (See Figure 25).

Both the rate of diffusion and the rate of transfer of carbon from gas to the steel surface increase exponentially as temperature increases. Increasing the temperature is therefore one way to shorten the carburizing time, as was shown in Figure 9.

Gas composition and gas flow can be adjusted to obtain the best economy and fastest carburization. During the phase when the transfer of carbon from gas to surface is rate-determining, the carbon activity of the gas should be as high as possible, and the product $P_{CO} \cdot P_{H_2}$ should be maximized.

B. Nitrogen Transfer

Ammonia, NH_3 , is added to the furnace atmosphere as the source of nitrogen in the carbonitriding process. The transfer of nitrogen from the gas to the steel surface takes place via the reaction illustrated in Figure 15.

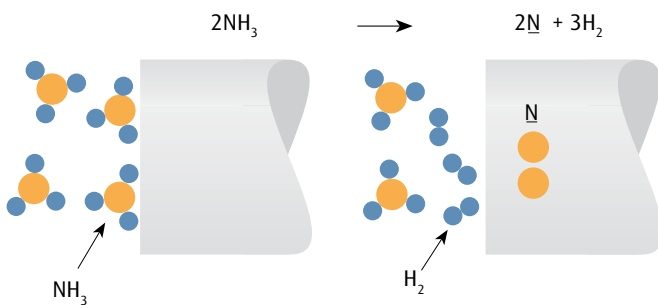
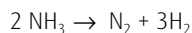
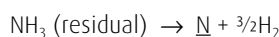


Figure 15: Schematic illustration of the nitriding process

However, most of the supplied ammonia does not actively cause nitriding, but decomposes into hydrogen and nitrogen in accordance with the reaction



It is only the portion that does not decompose – called residual ammonia or NH_3 (residual) – that is the active component for nitriding expressed by the reaction



The same type of equation as given in Figure 13 for the carbon flux is valid for the rate of nitriding. There is, however, limited data on the nitriding rate constant k' and additionally a lack of means to control the atmosphere nitrogen activity. Therefore it is not possible to calculate reliable results for the rate of nitriding.

Similarly to the case of carbon transfer, it is possible to express an equilibrium constant for the nitriding reaction illustrated in Figure 15 with the expression

$$K_4 = (a_N \times P_{H_2}^{3/2}) / P_{NH_3} \text{ (residual)}$$

According to this equation it is possible in principle to control the nitrogen activity by analyzing the NH_3 (residual) and the H_2 content of the furnace gas. However, there is no reliable analyzing technique for closed loop nitrogen atmosphere potential control. The common practice is instead to add ammonia of the order 1-10 vol% to the inlet gas stream. Most of the ammonia is dissociated on entering the hot furnace. Remaining residual ammonia concentrations available for active nitriding are typically in the range 50-200ppm. An example of the relation between ammonia addition and the resulting nitrogen surface concentration is shown in Figure 16. The curves in Figure 16 were established empirically and are valid only for the furnace for which the analysis was conducted. The reason is that the degree of ammonia decomposition depends on the catalyzing effect of the interior surfaces of walls, load baskets, radiant tubes etc. Metallic surfaces on radiant elements, for instance, catalyze the ammonia decomposition to a higher degree than ceramic surfaces. The residual ammonia content, which determines the resulting nitrogen concentration in the steel, will therefore be different for different furnaces, although the ratio of ammonia addition in the inlet gas stream is the same. It is therefore necessary to experimentally establish a curve such as the one in Figure 16 as a guideline for each furnace or furnace type.

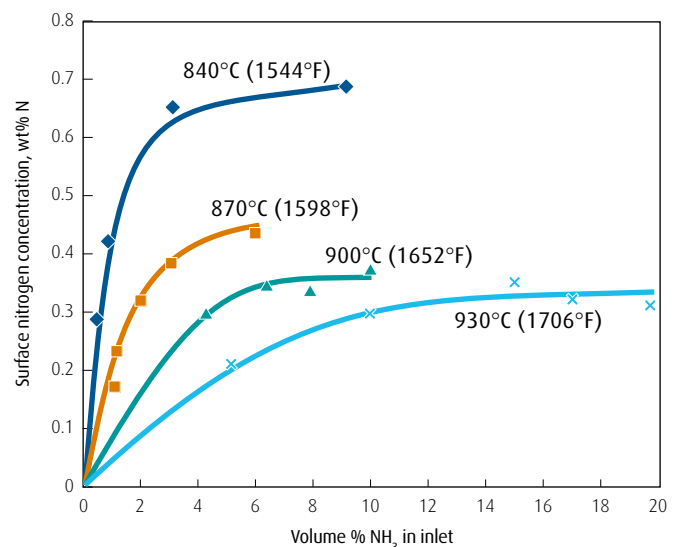
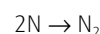


Figure 16: Relation between ratio of ammonia in the inlet gas and resulting surface nitrogen concentration at four temperatures. The relations are valid only for the small laboratory furnace for which the analysis was conducted. Industrial size furnaces require markedly higher ammonia additions than shown here [12].

The % NH_3 curves in Figure 16 are approximately linear for low NH_3 additions but progress in a parabolic arc to reach a constant maximum nitrogen concentration level above a certain ratio of ammonia in the inlet gas. The reason is that over a certain nitrogen concentration denitriding is initiated according to the reaction



During denitriding atomic nitrogen that is dissolved in the steel will diffuse to weak points such as slag inclusions or grain boundaries in the steel microstructure and form gaseous nitrogen. The resulting

equilibrium nitrogen gas pressure is so high that voids and porosities can form. These porosities will form at lower nitrogen concentrations when the temperature is increased. This is the reason why the experimentally determined nitrogen concentration decreases as temperature increases, as shown in Figure 16. The 930°C data indicates that in extreme cases the denitriding may even become higher than the nitriding rate.

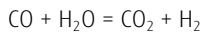
C. Atmosphere Carbon Activity

According to the preceding paragraph, the carbon activity of the furnace atmosphere can be calculated from:

$$a_c = (K_1 \cdot P_{CO} \cdot P_{H_2}) / P_{H_2O}$$

The equation is valid under conditions of equilibrium, i.e. the state the system would assume if it was left undisturbed for an infinite length of time. Practical experience shows that the assumption of equilibrium in the gas phase is reasonable for normal carburizing conditions. It is therefore possible to control the gas composition to the desired carbon activity if the value of the equilibrium constant K_1 is known. From the expression above, we see that the carbon activity can be controlled if P_{CO} , P_{H_2} and P_{H_2O} can be controlled. This is the basis for dew point analysis (a certain value of P_{H_2O} corresponds to a certain dew point) for the carbon activity control.

Atmosphere carbon potential is nowadays preferably controlled by oxygen probe or CO_2 infrared gas analysis. This is based on the assumption of gas equilibrium in the water gas reaction



This in turn leads to the assumption that equilibrium also exists for the carbon-transferring reactions:



We can therefore express the carbon activities in the furnace gas in the following alternative ways:

$$a_c = K_2 \cdot P_{CO}^2 / P_{CO_2}$$

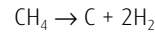
$$a_c = K_3 \cdot P_{CO} / P_{O_2}^{1/2}$$

From this it is evident that the carbon activity of the gas can be controlled by controlling the CO_2 content or the O_2 content, provided that P_{CO} is known. CO_2 control with an infrared (IR) gas analyzer and O_2 control with an oxygen probe are practical ways to do this. See also the tables in the Appendices.

For carbonitriding atmospheres, accurate carbon activity control should take into account the effect of dilution on the gas composition caused by the addition of ammonia.

The accuracy of the carbon potential control depends on how close or how far the atmosphere composition is from equilibrium. The deviation from equilibrium may be expressed by the ratio $P_{CH_4}(exp)/$

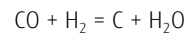
$P_{CH_4}(eq)$, where $P_{CH_4}(exp)$ is the actual empirically measured atmosphere methane concentration, and $P_{CH_4}(eq)$ is the equilibrium methane concentration. The actual methane concentration, $P_{CH_4}(exp)$, is always higher than the equilibrium concentration, $P_{CH_4}(eq)$. The reason for this is the high stability of the methane molecule, which means that the reaction



does not reach equilibrium. The carbon activity expressed by

$$a_c = K_4 \times P_{CH_4}(exp) / P_{H_2}^2$$

is therefore higher than the equilibrium carbon activity, for instance based on the equilibrium



The carburizing rate for the methane reaction increases with increased methane concentration. For high methane concentrations this means that the actual carburizing power will be higher than predicted by the carbon potential gained from oxygen probe, dew point or CO_2 analysis. The deviation will be highest for CO_2 control and smallest for dew point control. The average carbon potential will increase as the ratio $P_{CH_4}(exp) / P_{CH_4}(eq)$ increases, as will the scatter in attained surface carbon concentration.

To achieve a high quality atmosphere carbon potential control, it is thus important to keep the ratio $P_{CH_4}(exp) / P_{CH_4}(eq)$ as close as possible to unity. A rule of thumb as a minimum quality requirement is to assure that the condition

$$P_{CH_4}(exp) / P_{CH_4}(eq) < 10$$

is fulfilled. This can be controlled by analyzing the atmosphere $CH_4(exp)$ concentration and by calculating the equilibrium $CH_4(eq)$ concentration.

D. Atmosphere Carbon Potential

In practice, the concept of "carbon potential" is used instead of carbon activity. The carbon potential of a furnace atmosphere is equal to the carbon content that pure iron would have in equilibrium with the gas. The relationship between carbon activity a_c and carbon potential C_p may be expressed by the following equation:

$$a_c = \gamma^\circ \times x_c / (1 - 2x_c)$$

where x_c is the carbon mole fraction that is calculated from C_p and γ° is a temperature dependent constant expressed by [13]

$$\gamma^\circ = \exp \{ [5115.9 + 8339.9 \cdot x_c / (1 - x_c)] / T - 1.9096 \}$$

A graphical presentation of the relation carbon activity – carbon potential is shown in Figure 17. The carbon activity in an atmosphere should not exceed $a_c = 1$, which is the carbon activity of solid graphite. Over that value soot will form as indicated in the figure.

To calculate the relation between the carbon content in low-alloy case hardening steels, C , and the carbon potential, C_p , the following

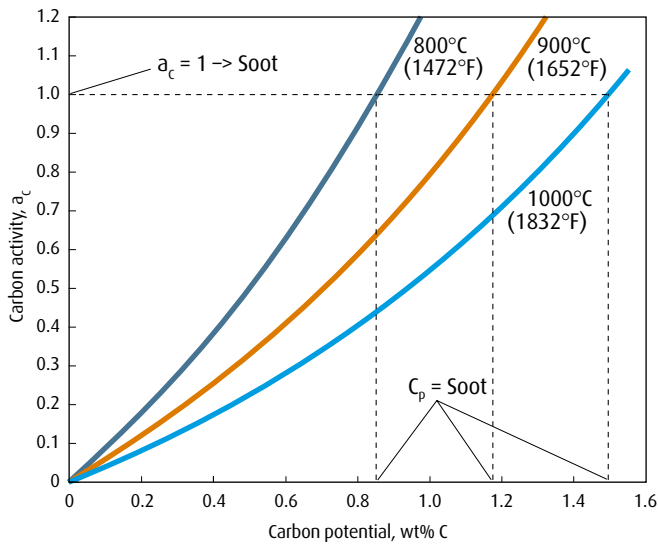


Figure 17: Relationship between carbon activity and carbon potential (= carbon content in pure iron) at different temperatures.

regression formulae developed by Gunnarsson [14] and others [15-16] may be used.

$$\log C_p/C = 0.055 \cdot (\%Si) - 0.013 \cdot (\%Mn) - 0.040 \cdot (\%Cr) + 0.014 \cdot (\%Ni) - 0.013 \cdot (\%Mo) - 0.013 \cdot (\%Al) - 0.104 \cdot (\%V) - 0.009 \cdot (\%Cu) - 0.013 \cdot (\%W) + 0.009 \cdot (\%Co)$$

E. Carbon Concentration Profile Control

Different forms of the carbon concentration profile can be achieved by varying the carbon potential of the gas during the carburizing cycle. The two main characteristic carbon concentration curve forms that can be attained are shown in Table 6. Single stage carburizing uses one constant carbon potential throughout the carburizing cycle and results in a carbon concentration gradient with the concave curvature shown in the upper part of the table. Boost carburizing uses a high carbon potential for most of the cycle time, but at the end of the cycle the carbon potential is lowered to meet hardness requirements. The resulting carbon concentration curve close to the surface is convex, as shown in the lower part of the table. As indicated in the “benefits” column, there are certain advantages of each of these two types of carburizing cycles.

Table 6. Carbon profile characteristics

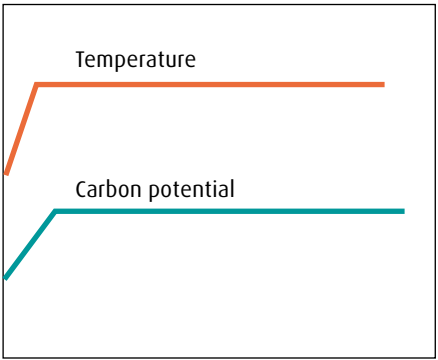
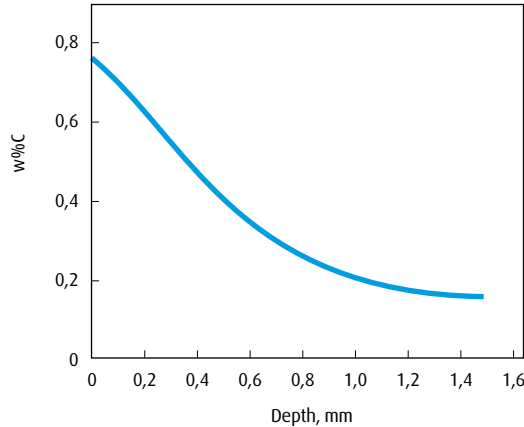
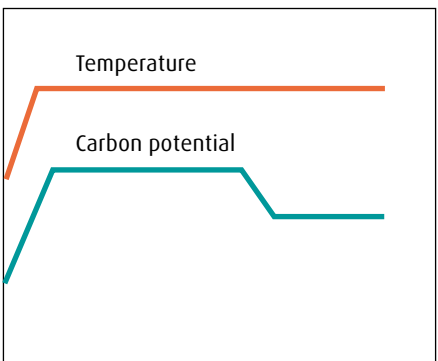
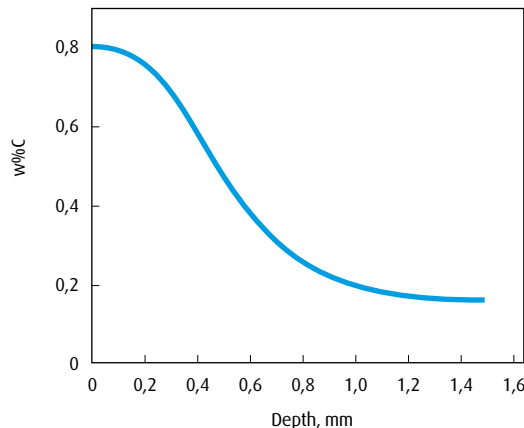
Carburizing cycle	Type of carbon profile	Benefits
Single stage	 	Residual stress distribution that is optimised for certain fatigue properties.
Boost	 	Minimized carburizing time Grinding allowance Wear resistance

Figure 18a shows the calculated carbon concentration profiles for two cycles with the same carburizing time and temperature, but where one run as a “single stage” and the other as a “two stage” “boost” cycle. The boost cycle results in a carburizing depth of about 1.1mm, whereas the single stage cycle results in a depth of about 0.9mm, a difference of 0.2mm. Figure 18b shows two carbon concentration profiles with equal depths but different curve forms due to the fact that one cycle was run as a 206-minute single stage and the other as a 146-minute boost cycle.

If high productivity is preferred, then a “boost” carburizing recipe should be used. The highest possible atmosphere carbon potential

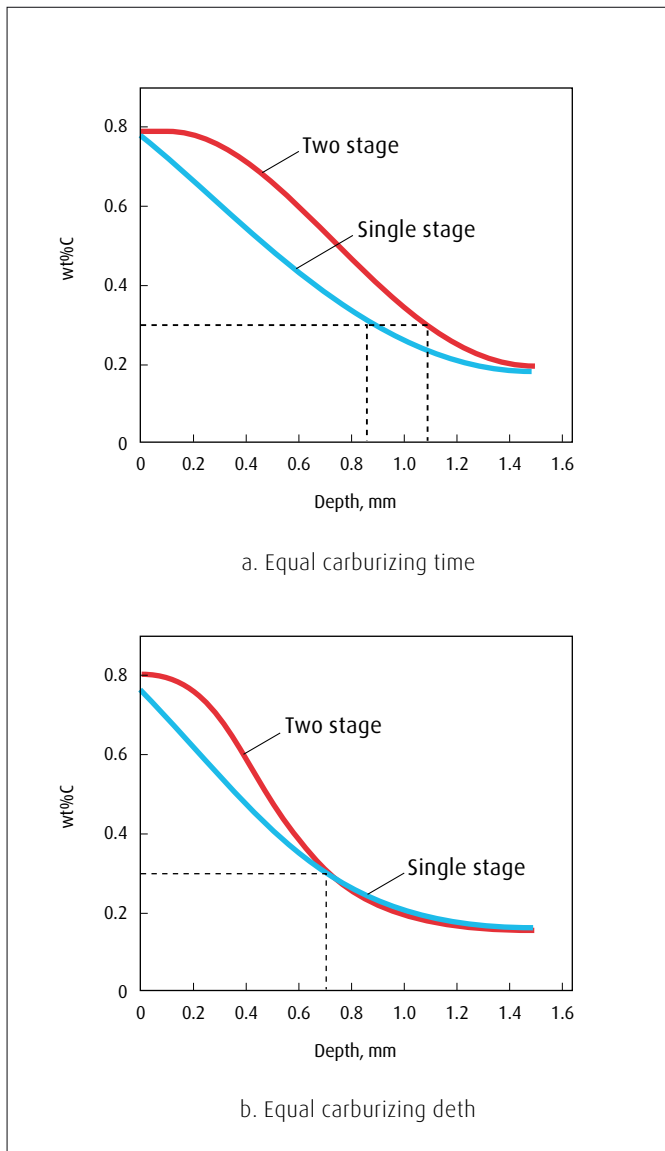


Figure 18: Calculated carbon concentration profiles for “single-stage” and “two-stage” carburizing processes at 930°C (1706 °F) with:
a) identical total carburizing time, 5 hours, and
b) identical carburizing depth of 0.7 mm.

With constant time there is an increase in depth from 0.87 to 1.10 mm, i.e. an increase of 26%. With identical carburizing depths the time decreases from 206 to 146 minutes, i.e. a decrease of 29%.

“Single-stage process” = constant carbon potential.

“Two-stage process” = high carbon potential for the first three hours and low carbon potential for the last hour. (Cycles are idealized and do not include time for ramps for heating and carbon potential change)

should be used in the first part of the carburizing cycle. This gives the fastest carbon transfer. There are two upper limits that the carbon potential must not exceed. First, the carbon potential must not exceed the limit for the creation of soot. Secondly, for parts subjected to impact or bending fatigue, the carbon potential must not result in grain boundary cementite formation in the steel. These two limits are numerically close to each other, with the soot limit being slightly higher, as shown in Figure 19. To ensure best results, the atmosphere carbon potential should not exceed the carbide limit.

Figure 19 shows that both the carbide and soot limit increase with increased temperature. Increased temperature can therefore shorten the carburizing time not only because of the increased diffusion rate, illustrated in Figure 9, but also because a higher carbon potential can be applied, as illustrated in Figure 17.

During the second part of a boost carburizing cycle the carbon potential should be lowered to ensure a final surface carbon concentration with optimum properties and to prevent an excessive amount of retained austenite.

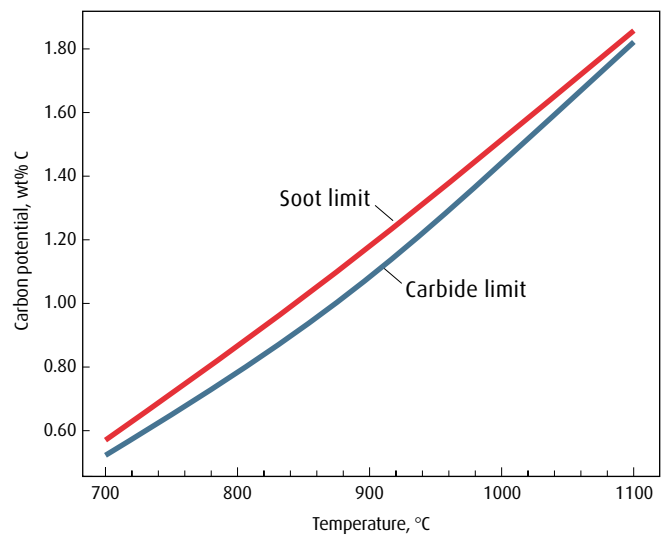


Figure 19: Cementite (lower curve) and soot limits as a function of temperature. Cementite limit is calculated for the steel 16MnCr5

F. Internal Oxidation

The oxygen partial pressure in a carburizing atmosphere is typically of the order of 10^{-20} atm. This low oxygen partial pressure means that the atmosphere is reducing with respect to iron oxide (FeO) that has an equilibrium oxygen partial pressure of the order 10^{-16} atm at normal carburizing temperatures. However, oxides of alloying elements such as Mn, Si and Cr have equilibrium oxygen partial pressures of the order 10^{-24} to 10^{-30} atm, which are thus much lower than the oxygen partial pressure of the carburizing atmosphere. These elements can therefore be selectively oxidized during carburizing. Selective oxidation is normally seen as grain boundary oxidation but also as selective oxidation within the grains, see Figure 20. The selective oxidation depletes the matrix composition with respect to alloy content, leading to lower hardenability. Thus the outermost surface of carburized steels sometimes contain a pearlitic non-martensitic structure, see Figure 20b.

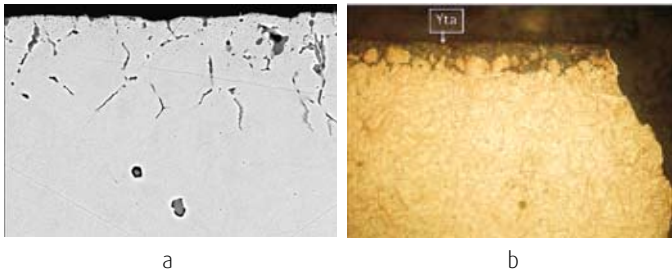


Figure 20: Grain-boundary oxidation as viewed on
a) a polished un-etched surface and
b) an etched surface exhibiting pearlite in the surface zone of internal oxidation [17].

Additional uncontrolled oxidation may occur after furnace door openings when loading and unloading takes place. This is a risk especially during heating. Internal oxides may be the starting points for crack initiation. The formation of surface pearlite results in a tensile residual stress at the surface. Therefore internal oxidation has a detrimental effect on fatigue resistance, as illustrated in Figure 21

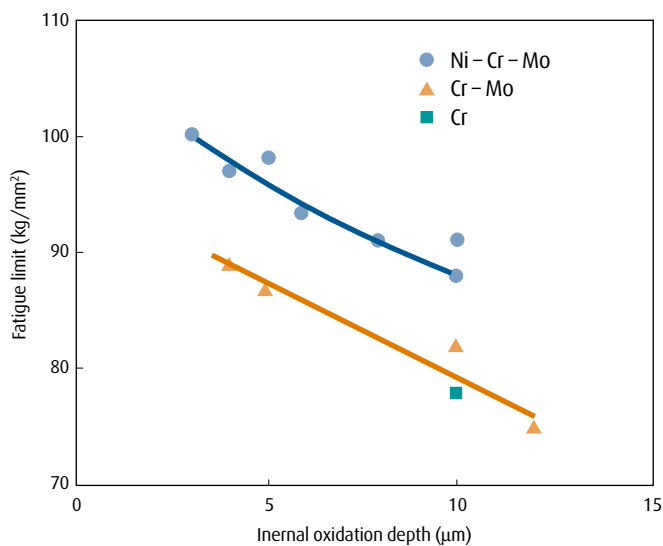


Figure 21: Effect of internal oxidation on the fatigue limit [18]

The negative effects of internal oxidation on hardenability can be compensated for by ensuring that the hardenability of the steel is sufficient to result in full martensite transformation even after loss of hardenability from oxidized alloying elements. Another possibility is to compensate for the hardenability drop by adding nitrogen to the steel surface as a last step in the carburizing process. This is achieved by adding ammonia as in carbonitriding but only for a short time, of the order of 10 minutes, at the end of the carburizing cycle.

Vacuum carburizing completely prevents internal oxidation, as outlined in more detail in reference [4].

G. Hydrogen Pick Up

Some of the hydrogen in the carburizing atmosphere is transferred in atomic form into the surface layer of the carburized steel. Hydrogen solubility increases with increased temperature. Upon quenching, the amount of dissolved hydrogen after carburizing remains in the surface layer, resulting in a supersaturated hydrogen concentration. In some cases this leads to embrittlement, especially for high strength steels and for thick case depths. Upon tempering, hydrogen will leave the surface, but to ensure efficient removal the tempering time or the tempering temperature has to be increased.

The nitrogen/methanol atmosphere technique is a method that offers the possibility to end the carburizing process with a nitrogen purge to remove hydrogen (and other active gas species) from the furnace atmosphere and thereby making the hydrogen to diffuse out of the steel.

H. Surface Passivation

Carburizing can sometimes be blocked because a passive layer is formed at the surface, which prevents or decelerates carbon transfer. The passivation is often local, which leads to some surface areas not being carburized. This may lead to what is called white spots. The reason for passivation is not completely understood, but suggested causes are thin adherent oxide layers or adhered substances left over from operations such as turning or washing before carburizing.

The surface can be activated to eliminate the passivation effect by pre-oxidation at a temperature of about 650 °C (1202 °F) or by pre-phosphating.

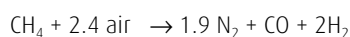
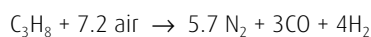
V. Carburizing Atmospheres

There are a number of possible options to produce an atmosphere for carburizing. Naturally, the atmosphere must have a carbon source, which could be carbon monoxide, a hydrocarbon, an alcohol or any other liquid carbon source. To obtain a high quality controllable carbon atmosphere, the options are limited to atmospheres that contain carbon monoxide and hydrogen in order to result in carburizing according to the illustration in Figure 11. In addition a certain part of the atmosphere often consists of nitrogen, which acts as a carrier for the active gases. Nitrogen also dilutes the concentrations of the active and flammable gases to minimize flames and the risk of soot deposits. Nitrogen also ensures safety. The combination of $N_2 + CO + H_2$ is often called the “carrier gas”. Endogas and nitrogen/methanol are the two main options for carrier gas supply, which is briefly described in the following two sections. The fastest carburizing is achieved in an atmosphere consisting of equal parts of carbon monoxide and hydrogen, as was described in section IV.A. One method of producing an atmosphere of this kind is described in section C below.

To control the atmosphere carbon potential an “enriching gas” is also needed. The enriching gas is a hydrocarbon, such as propane or methane, for increasing the carbon potential. Sometimes air is added to decrease the carbon potential. For carbonitriding, ammonia is additionally required.

A. Endogas

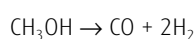
A carburizing atmosphere can be achieved by means of incomplete combustion of propane or methane with air in accordance with one of the reactions:



The mixing and combustion of fuel and air takes place in special endothermic gas generators. See reference [2] for a description of the endogas generator.

B. Nitrogen/Methanol Atmospheres

Introducing nitrogen and methanol directly into the furnace chamber is a common way of creating the furnace atmosphere. Upon entering the furnace, methanol cracks to form carbon monoxide and hydrogen in accordance with the following reaction:



As shown in Figure 22, complete cracking of methanol into CO and H_2 only occurs if the temperature is above 700-800°C (1292-1472°F),

which is why methanol should not be introduced into a furnace at a lower temperature.

The cracking of methanol into CO and H_2 requires energy. This energy is taken from the area surrounding the point of methanol injection. There must therefore be sufficient heat flux towards the injection point to ensure proper dissociation.

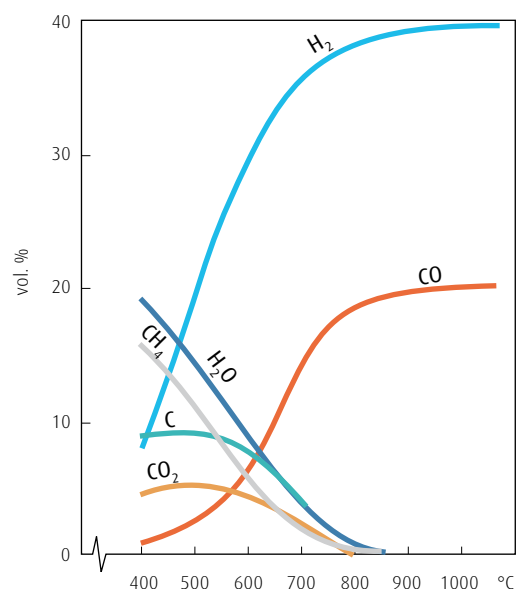


Figure 22: Resulting gas composition upon cracking of methanol in an atmosphere containing 40% nitrogen and 60% cracked methanol.

For every liter of methanol that is added, approximately 1.7m³ of gas is formed, consisting of one part CO and two parts H_2 . Different gas compositions are obtained by varying the mixing ratio between nitrogen and methanol. Compared with endothermic gas, the nitrogen/methanol system offers the advantage that both the gas flow and the gas composition can be adjusted to particular needs at any time. This is illustrated for purging (conditioning) and for atmosphere disturbance from door openings in Figures 23-24.

A high gas flow is desirable in the following cases:

- At the beginning of a cycle when the furnace is originally air-filled or has been contaminated with air after a door opening. The higher the gas flow is, the faster the correct gas composition will be obtained.
- When carbon demand is great, i.e. at the beginning of a process or in cases with a large charge surface area.

Low gas flow can be used in the following cases:

- When the furnace is empty.
- When the carbon demand is low, i.e. at the end of a process or in cases with a small charge surface area.

The need to vary the gas composition parallels to some extent the need to vary flow. A high proportion of methanol, i.e. active portion

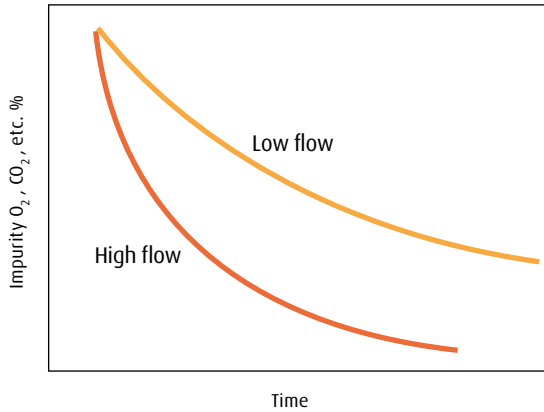


Figure 23: Purging of a furnace with inert gas.

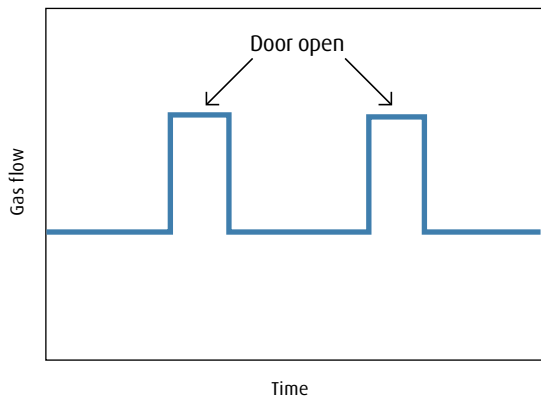


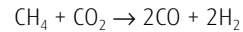
Figure 24: The gas flow can be adjusted to demand

$\text{CO} + \text{H}_2$, is required at the beginning of a cycle when carbon demand is high. High nitrogen content can be used when the furnace is empty during purging and when carbon demand is low.

To allow the benefits of flow and composition flexibility to be exploited to the full, a more advanced flow control system is required than is customary for endothermic gas. Continuous flow control with mass flow meters and motorized valves is the most advanced type of system. Fixed flow combined with solenoid valves is another possibility. Even being able to adjust the gas flows manually is a considerable advantage.

C. 50%CO/50%H₂ Atmosphere

In accordance with section IV.A, the fastest carbon transfer is achieved in an atmosphere consisting of equal parts of CO and H₂. It is technically feasible to create an oxidizing reaction of a hydrocarbon that leads to a ratio of 1:1 between CO and H₂ by oxidizing methane with CO₂ according to the reaction



Generating a reaction gas atmosphere with an optimum k' value in this way is more expensive than generating endothermic or nitrogen/methanol atmospheres. One reason for this is that the reaction between CH₄ and CO₂ to form CO and H₂ is extremely endothermic and therefore requires energy. It is therefore only worthwhile using gases of this kind if it is possible to achieve either cost cuts due to increased productivity or improvements in quality. The absolute time saving increases with increased carburizing depth, but the possible percentage reduction in carburizing time is particularly significant for low carburizing depths, see Figure 25. For a carburizing depth of 0.1 mm the time saving is close to 20%, but falls to about 5% for 1 mm depth. As seen in Figure 25, the absolute time saving effect in minutes is greater at lower carburizing temperatures. These benefits are best utilized in carburizing small components (such as bolts or

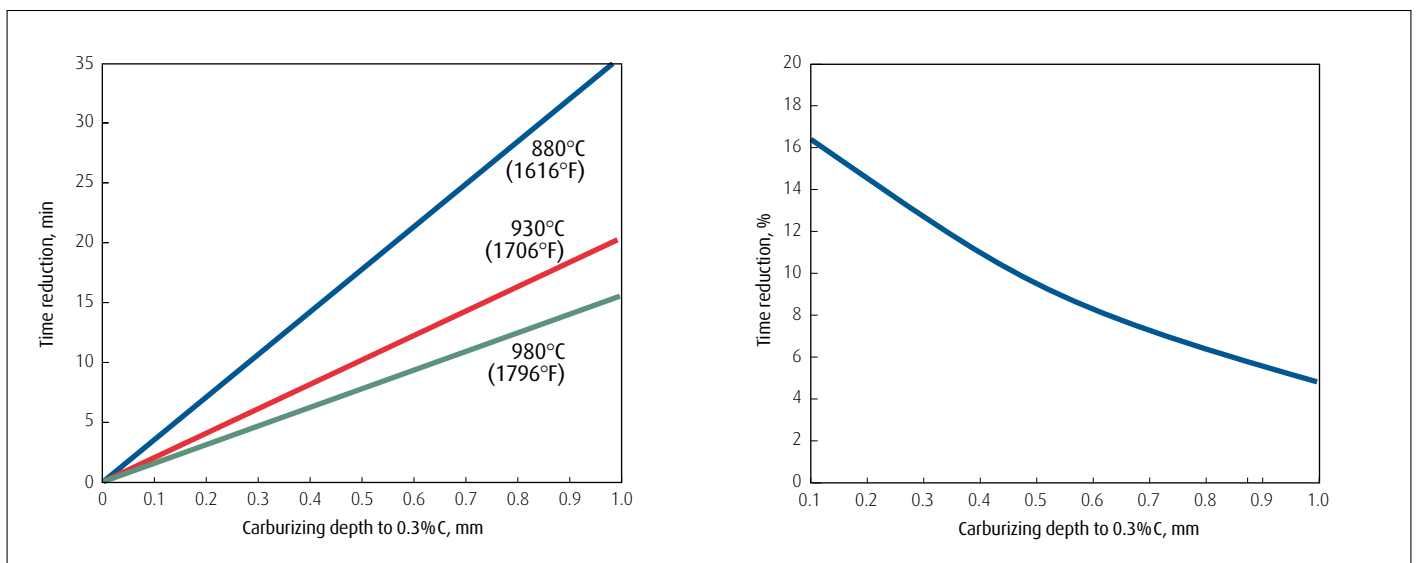


Figure 25: a. Calculated time saving in minutes as a function of carburizing depth and temperature when comparing carburizing in atmospheres containing 50%CO/50%H₂ (CARBOQUICK®) to 20%CO/40%H₂ (40%N₂-60% cracked methanol).

b. Approximate relative time saving in % as a function of carburizing depth. (The calculation was conducted for an atmosphere with 0.8%C carbon potential. Heating up time and atmosphere conditioning time were neglected).

machine components) and thin-walled sheet metal parts to low carburizing depths in continuous furnaces such as belt furnaces.

The results of a production test carried out in order to evaluate the difference in carburizing rate when using three carburizing atmospheres – CARBOQUICK®, endogas from methane, and direct feed of natural gas and air (the Ipsen SUPERCARB process) – is shown in Figure 26. For all three atmospheres the carburizing parameters were the same, temperature 940 °C (1724 °F), carburizing time 180 min., and carbon potential 1.2 %C. The result with CARBOQUICK® reveals a significant increase in the carburizing depth.

Atmospheres that only contain CO, H₂ and traces of CO₂, H₂O and CH₄ also have the advantages of improved heat transfer. The heating-up speed in a chamber furnace was shown to be approximately 4.5 °C/min for endothermic gas and 5.8 °C/min for the CARBOQUICK® atmosphere with the same charge load and dimensions. It appears that the improved emission behavior of the CO contents has a positive effect in that it shortens the heating period and improves heat conduction due to the increased hydrogen contents.

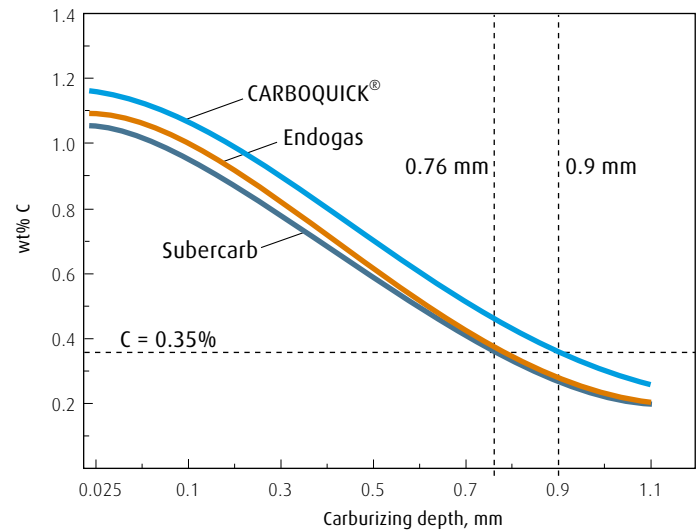


Figure 26: Comparison of carburizing depths [19]

VI. Description of a Nitrogen/Methanol System

A nitrogen/methanol system for heat treatment is set up by media storage, flow control and distribution to furnaces, intake into furnace and atmosphere control as shown in Figure 27. Assurance of safety is an important part that has to be integrated into the system.

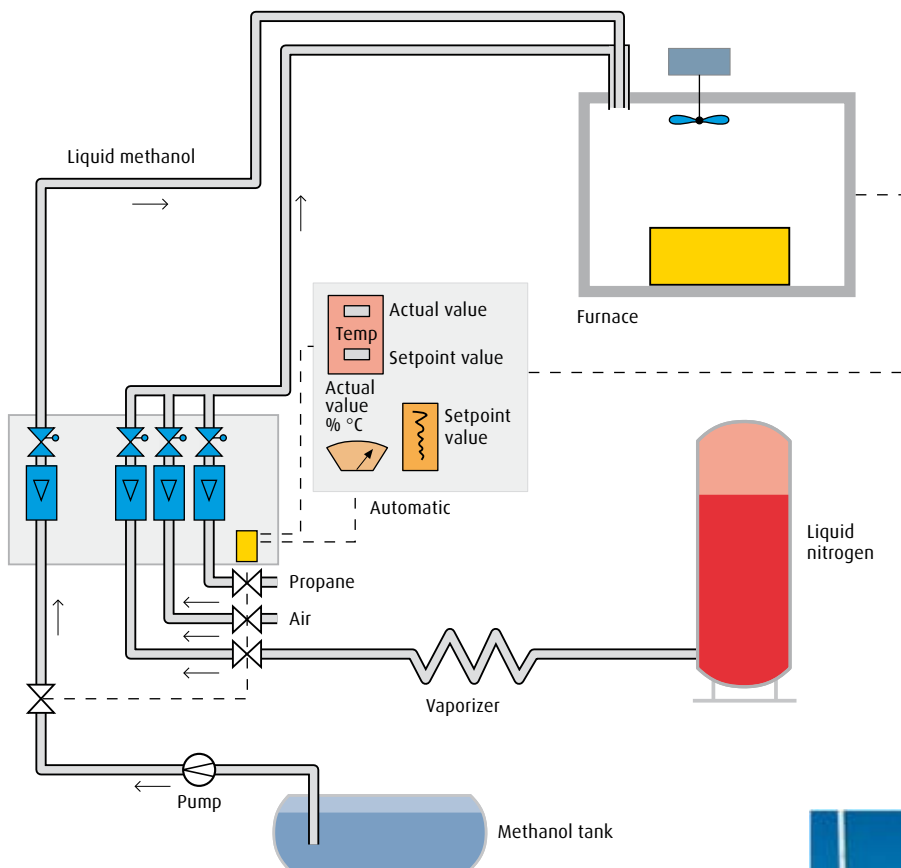


Figure 27: Nitrogen/methanol system

A. Media Storage and Supply

The nitrogen is usually stored in liquefied form in a vacuum-insulated tank. (See description in reference [2]).

Methanol is stored in tanks of varying size depending on the rate of consumption. Small consumers fill their tanks from barrels, while large consumers fill them from road tankers. An example of a methanol tank installation is shown in Figure 28.



Figure 28: Methanol tank installation. The liquid nitrogen tank is seen in the background

For propane and ammonia, small consumers use cylinders or cylinder bundles and large consumers use tanks. Propane and ammonia liquefy at relatively low pressures. These “gases” are therefore also stored in liquid form.

Local safety directives have to be obeyed for all installations.

B. Distribution to Furnace

The nitrogen leaves the storage tank at a medium pressure set on the tank or cylinders. Inside the industrial premises, the pressure is reduced before the gas reaches the furnaces.

Methanol is introduced into the piping system by means of a pump. Propane and ammonia are transported by the pressure in the storage vessels.

C. Intake into Furnace

The gaseous components in nitrogen-based systems are introduced in the same way as gas from other systems, i.e. to ensure optimum mixing and circulation. However, for methanol, which is introduced in liquid form a special technique is required, which uses lances in order to ensure good vaporizing and cracking regardless of the type of furnace, location of intake, or whether a fan is used etc. (Figure 29).

D. On-site Nitrogen Generation

One alternative for nitrogen supply is what is called on-site generation of nitrogen. There are primarily three on-site generation methods: 1) Cryogenic on-site generator, 2) membrane or 3) a PSA (Pressure Swing Adsorption) unit. These supply methods are explained in reference [2].

Especially membrane generators may be an advantageous alternative compared to high purity liquid nitrogen. Membrane nitrogen typically has a concentration level of the order of 0.5-2-vol% of the impurity oxygen. The cost for nitrogen is lowered with an increased concentration level of the impurity oxygen. A carburizing atmosphere typically has 60 vol% of the reducing species CO and H₂. A consequence of these high concentrations is that the oxygen in the membrane nitrogen stream is reduced, for instance in the reaction

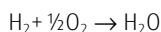


Figure 29: Examples of methanol injection lances

thereby eliminating the risk of oxidation. Studies have shown that an oxygen concentration level of the order of 0.5 -1.0 vol% in the membrane nitrogen stream does not increase the risk of internal oxidation [20]. However, as the nitrogen should be available for purging in safety situations the preferred maximum oxygen concentration level is 0.5vol%.

E. Atmosphere Control

Atmosphere control can be automatic, semiautomatic or manual. In 100% automatic control the flows of different media are automatically adjusted to ensure that the set points for the atmosphere carbon potential and composition are maintained. This is achieved by connecting gas sampling, gas analysis and flow control to the control cabinet that contains the required software algorithms, analyzers and controllers as shown for the example of a nitrogen/methanol system for a pusher furnace in Figure 30. (This system has the option of injecting water at the end of the furnace in order to lower the carbon potential and was made for development with results described in reference [21]).

As a safety precaution, all media except nitrogen should have safety shut-off devices. The most common method is to allow all additions only to be made above a given temperature. The additions should also be stopped at a given minimum flow or nitrogen pressure.

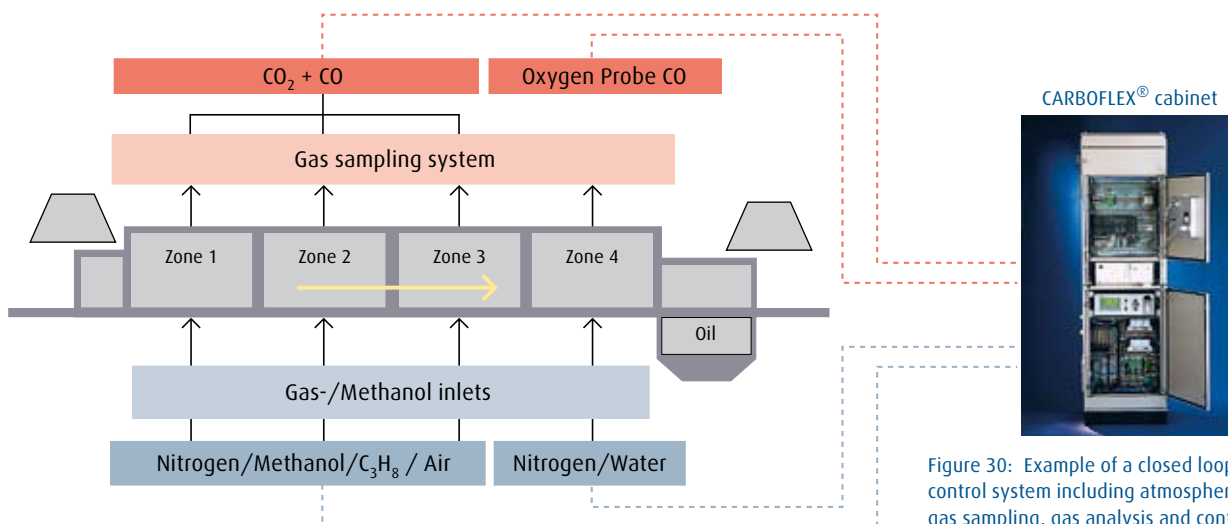


Figure 30: Example of a closed loop atmosphere control system including atmosphere flow control, gas sampling, gas analysis and control cabinet.

VII. Results

When the results achieved with nitrogen-based systems are evaluated, four beneficial factors in particular stand out:

- Productivity
- Reproducibility
- Safety
- Economy

A. Productivity and Reproducibility

The nitrogen gas technique often paves the way to higher production in existing plants. The simplicity and reliability of the gas supply system reduces production disruptions. Fast atmosphere conditioning reduces start up time. This feature may be enforced by the use of a low nitrogen flow during non-production time such as during weekends. This flexibility – in that each medium is controlled separately – permits variations during the course of the process, especially during carburizing, so that a shorter process time is achieved. As shown for instance in Figures 18 and 26, there are ways to drastically reduce carburizing times by using boost processes or the CARBOQUICK® technique.

The availability of nitrogen makes it possible to prevent the charge from being ruined as a result of power failures and the like.

A nitrogen based atmosphere system permits a uniform composition of the atmosphere in a furnace. Uniformity in turn means fewer rejections and makes it possible to work with closer tolerances on surface carbon content, hardness and case depth. A closed loop atmosphere control system helps to ensure close tolerances in the resulting case depths and surface carbon concentrations.

B. Safety

As methanol is supplied in a separate line from the storage to the furnace, there is no transport of combustible and toxic gas, as is the case, for instance, with endogas. Only when methanol is injected into the furnace are carbon monoxide and hydrogen formed. Compared with endogas supply the risk of leakages that may form poisonous or explosive gas mixtures is therefore eliminated.

The availability of the safe and inert nitrogen gas makes it possible to ensure safety purging in connection with rapid temperature drops, oil fires etc. Generally, the inert properties of the nitrogen should be used for protection wherever possible.

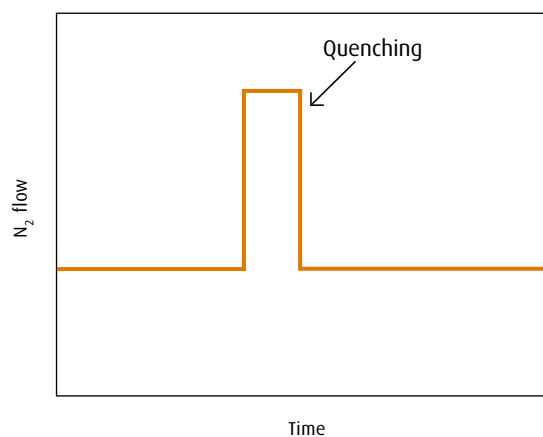


Figure 31: Temporary increase of nitrogen flow at the moment of quenching to counteract negative pressure which could draw air into the furnace.

C. Economy

All of the factors mentioned above contribute towards good overall economy. In evaluating the influence of the gas system on the economy of the process, two factors in particular can be pointed out:

- For nitrogen-based gas systems, the fixed cost is a small percentage of the total cost. Due to the low investment required, low maintenance costs, low material costs and low electricity costs etc., the quantity of gas consumed is the main cost. This in turn means that it pays to adjust consumption to the actual need. It has been shown to be possible to reduce the gas flow by up to 30 %. Moreover, less gas is consumed at the start, and very small flows can be used when the furnace is empty. In this way, the total gas saving can be even higher, in some cases up to 50 %.
- With nitrogen-based systems, the productivity of the process can often be enhanced in a number of ways. Firstly, its higher operational reliability permits high capacity utilization. Secondly, the quality of the gas ensures uniform and high yields. Thirdly, the composition of the gas can be controlled to minimize the process time. Lastly, both labor and furnace production time can be saved due to the fact that the start-up time after weekend interruptions and production stoppages is reduced.

The size of the savings that stand to be made varies between different furnaces and processes.

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IX Appendices

A. Appendix 1: Dew point – carbon potential tables for nitrogen/methanol atmospheres

Table 7a: Dew point (°C) for different carbon potentials in an atmosphere consisting of 100 % cracked methanol and 0 % nitrogen.

Table 7b: Dew point (°C) for different carbon potentials in an atmosphere consisting of 60 % cracked methanol and 40 % nitrogen.

Table 7c: Dew point (°C) for different carbon potentials in an atmosphere consisting of 20 % cracked methanol and 80 % nitrogen.

B. Appendix 2: CO₂ – carbon potential tables for nitrogen/methanol atmospheres

Table 8a: CO₂ content (vol-%) for different carbon potentials in an atmosphere consisting of 100 % cracked methanol and 0 % nitrogen.

Table 8b: CO₂ content (vol-%) for different carbon potentials in an atmosphere consisting of 60 % cracked methanol and 40 % nitrogen.

Table 8c: CO₂ content (vol-%) for different carbon potentials in an atmosphere consisting of 20 % cracked methanol and 80 % nitrogen.

C. Appendix 3: Oxygen probe mV - carbon potential tables for nitrogen/methanol atmospheres

Table 9a: Output signal from an oxygen probe (mV) for different carbon potentials in an atmosphere consisting of 100 % cracked methanol and 0 % nitrogen.

Table 9b: Output signal from an oxygen probe (mV) for different carbon potentials in an atmosphere consisting of 60 % cracked methanol and 40 % nitrogen.

Table 9c: Output signal from an oxygen probe (mV) for different carbon potentials in an atmosphere consisting of 20 % cracked methanol and 80 % nitrogen.

Dew point – carbon potential tables for nitrogen/methanol atmospheres

Table 7a

Appendix 1

Dew point (°C) for different carbon potentials in an atmosphere consisting of 100% cracked methanol and 0% nitrogen.

Furnace temperature, °C (°F)		820		830		840		850		860		870		880		890		900		910		920		930		940		950		960		970		980		990		1000	
C-pot., wt-% C		1508		1526		1544		1562		1580		1598		1616		1634		1652		1670		1688		1706		1724		1742		1760		1778		1796		1814		1832	
0.20	45.2	44.1	42.9	41.8	40.6	39.5	38.3	37.2	36.1	34.9	33.8	32.6	31.5	30.4	29.3	28.2	27.2	26.1	25.1																				
0.25	41.9	40.7	39.6	38.4	37.2	36.0	34.8	33.6	32.5	31.3	30.1	29.0	27.9	26.8	25.7	24.6	23.5	22.4	21.4																				
0.30	39.1	37.9	36.7	35.4	34.2	33.0	31.8	30.6	29.4	28.3	27.1	26.0	24.8	23.7	22.6	21.5	20.5	19.4	18.4																				
0.35	36.6	35.4	34.1	32.9	31.7	30.4	29.2	28.0	26.8	25.6	24.5	23.3	22.2	21.1	20.0	18.9	17.9	16.8	15.8																				
0.40	34.4	33.1	31.9	30.6	29.4	28.1	26.9	25.7	24.5	23.3	22.2	21.0	19.9	18.8	17.7	16.7	15.6	14.6	13.6																				
0.45	32.3	31.1	29.8	28.5	27.3	26.1	24.8	23.6	22.4	21.3	20.1	19.0	17.9	16.8	15.7	14.6	13.6	12.6	11.6																				
0.50	30.5	29.2	27.9	26.7	25.4	24.2	23.0	21.8	20.6	19.4	18.3	17.1	16.0	14.9	13.8	12.8	11.8	10.7	9.6																				
0.55	28.7	27.5	26.2	24.9	23.7	22.4	21.2	20.0	18.8	17.7	16.5	15.4	14.3	13.2	12.2	11.1	10.1	9.1	8.1																				
0.60	27.1	25.8	24.6	23.3	22.1	20.8	19.6	18.4	17.2	16.1	15.0	13.8	12.7	11.7	10.6	9.6	8.6	7.6	6.6																				
0.65	25.6	24.3	23.0	21.8	20.5	19.3	18.1	16.9	15.8	14.6	13.5	12.4	11.3	10.2	9.2	8.2	7.1	6.2	5.2																				
0.70	24.2	22.9	21.6	20.4	19.1	17.9	16.7	15.5	14.4	13.2	12.1	11.0	9.9	8.9	7.8	6.8	5.8	4.8	3.9																				
0.75	22.8	21.5	20.3	19.0	17.8	16.6	15.4	14.2	13.1	11.9	10.8	9.7	8.6	7.6	6.6	5.6	4.6	3.6	2.7																				
0.80	21.5	20.2	19.0	17.7	16.5	15.3	14.1	13.0	11.8	10.7	9.6	8.5	7.4	6.4	5.4	4.4	3.4	2.4	1.5																				
0.85	20.3	19.0	17.8	16.5	15.3	14.1	12.9	11.8	10.6	9.5	8.4	7.3	6.3	5.3	4.2	3.2	2.2	1.3	0.4																				
0.90	19.1	17.8	16.6	15.4	14.1	13.0	11.8	10.6	9.5	8.4	7.3	6.2	5.2	4.2	3.2	2.2	1.2	0.3	-0.4																				
0.95	-	-	15.5	14.2	13.0	11.9	10.7	9.6	8.4	7.3	6.3	5.2	4.2	3.2	2.1	1.2	0.2	-0.5	-1.3																				
1.00	-	-	-	13.2	12.0	10.8	9.6	8.5	7.4	6.3	5.2	4.2	3.2	2.2	1.2	0.2	-0.5	-1.3	-2.1																				
1.05	-	-	-	-	-	9.8	8.6	7.5	6.4	5.3	4.3	3.2	2.2	1.2	0.2	-0.5	-1.3	-2.1	-2.9																				
1.10	-	-	-	-	-	-	7.7	6.5	5.5	4.4	3.3	2.3	1.3	0.3	-0.4	-1.2	-2.0	-2.8	-3.6																				
1.15	-	-	-	-	-	-	-	-	4.5	3.5	2.4	1.4	0.4	-0.4	-1.1	-1.9	-2.7	-3.5	-4.4																				
1.20	-	-	-	-	-	-	-	-	-	2.6	1.5	0.5	-0.2	-1.1	-1.8	-2.6	-3.4	-4.2	-5.1																				
1.25	-	-	-	-	-	-	-	-	-	-	-	-0.1	-1.0	-1.8	-2.5	-3.3	-4.1	-5.0	-5.8																				
1.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																				
1.35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																				
1.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																				
1.45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																				
1.50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																				

Dew point (°C) for different carbon potentials in an atmosphere consisting of 60% cracked methanol and 40% nitrogen.

[illegible]

Appendix 1

Dew point (°C) for different carbon potentials in an atmosphere consisting of 20% cracked methanol and 80% nitrogen.

C-pot., wt-% C	Furnace temperature, °C (°F)																		
	820 1508	830 1526	840 1544	850 1562	860 1580	870 1598	880 1616	890 1634	900 1652	910 1670	920 1688	930 1706	940 1724	950 1742	960 1760	970 1778	980 1796	990 1814	1000 °C 1832 °F
0.20	-1.3	-2.3	-3.3	-4.3	-5.2	-6.1	-7.1	-8.0	-8.9	-9.7	-10.6	-11.4	-12.2	-13.0	-13.8	-14.6	-15.4	-16.1	-16.8
0.25	-4.0	-5.0	-6.0	-6.9	-7.9	-8.8	-9.7	-10.6	-11.5	-12.3	-13.2	-14.0	-14.8	-15.6	-16.4	-17.2	-17.9	-18.6	-19.3
0.30	-6.2	-7.2	-8.2	-9.1	-10.1	-11.0	-11.9	-12.8	-13.6	-14.5	-15.3	-16.1	-16.9	-17.7	-18.5	-19.2	-20.0	-20.7	-21.4
0.35	-8.1	-9.1	-10.1	-11.0	-11.9	-12.9	-13.8	-14.6	-15.5	-16.3	-17.1	-17.9	-18.7	-19.5	-20.3	-21.0	-21.7	-22.4	-23.1
0.40	-9.8	-10.8	-11.7	-12.7	-13.6	-14.5	-15.4	-16.2	-17.1	-17.9	-18.7	-19.5	-20.3	-21.1	-21.8	-22.5	-23.3	-24.0	-24.6
0.45	-11.3	-12.3	-13.2	-14.1	-15.1	-15.9	-16.8	-17.7	-18.5	-19.3	-20.1	-20.9	-21.7	-22.4	-23.2	-23.9	-24.6	-25.3	-26.0
0.50	-12.6	-13.6	-14.5	-15.5	-16.4	-17.3	-18.1	-19.0	-19.8	-20.6	-21.4	-22.2	-22.9	-23.7	-24.4	-25.1	-25.8	-26.5	-27.2
0.55	-13.9	-14.8	-15.8	-16.7	-17.6	-18.5	-19.3	-20.2	-21.0	-21.8	-22.6	-23.3	-24.1	-24.8	-25.6	-26.3	-27.0	-27.6	-28.3
0.60	-15.0	-16.0	-16.9	-17.8	-18.7	-19.6	-20.4	-21.2	-22.1	-22.9	-23.6	-24.4	-25.1	-25.8	-26.6	-27.3	-28.0	-28.6	-29.3
0.65	-16.1	-17.0	-18.0	-18.9	-19.7	-20.6	-21.4	-22.3	-23.1	-23.9	-24.6	-25.4	-26.1	-26.8	-27.6	-28.2	-28.9	-29.6	-30.2
0.70	-17.1	-18.0	-18.9	-19.8	-20.7	-21.6	-22.4	-23.2	-24.0	-24.8	-25.6	-26.3	-27.0	-27.8	-28.5	-29.1	-29.8	-30.5	-31.1
0.75	-18.1	-19.0	-19.9	-20.8	-21.6	-22.5	-23.3	-24.1	-24.9	-25.7	-26.4	-27.2	-28.0	-28.6	-29.3	-30.0	-30.7	-31.3	-31.9
0.80	-18.9	-19.9	-20.7	-21.6	-22.5	-23.3	-24.1	-24.9	-25.7	-26.5	-27.2	-28.0	-28.7	-29.4	-30.1	-30.8	-31.4	-32.1	-32.7
0.85	-19.8	-20.7	-21.6	-22.4	-23.3	-24.1	-24.9	-25.7	-26.5	-27.3	-28.0	-28.8	-29.5	-30.2	-30.9	-31.5	-32.2	-32.9	-33.5
0.90	-20.6	-21.5	-22.4	-23.2	-24.1	-24.9	-25.7	-26.5	-27.3	-28.0	-28.8	-29.5	-30.2	-30.9	-31.6	-32.2	-32.9	-33.5	-34.2
0.95	-	-	-23.1	-24.0	-24.8	-25.6	-26.4	-27.2	-28.0	-28.7	-29.5	-30.2	-30.9	-31.6	-32.3	-32.9	-33.6	-34.2	-34.8
1.00	-	-	-	-24.7	-25.5	-26.3	-27.1	-27.9	-28.7	-29.4	-30.2	-30.9	-31.6	-32.2	-32.9	-33.6	-34.2	-34.8	-35.5
1.05	-	-	-	-	-	-27.0	-27.8	-28.6	-29.3	-30.1	-30.8	-31.5	-32.2	-32.9	-33.6	-34.2	-34.8	-35.5	-36.1
1.10	-	-	-	-	-	-	-28.5	-29.2	-30.0	-30.7	-31.4	-32.1	-32.8	-33.5	-34.2	-34.8	-35.4	-36.1	-36.7
1.15	-	-	-	-	-	-	-	-	-30.6	-31.3	-32.0	-32.7	-33.4	-34.1	-34.7	-35.4	-36.0	-36.6	-37.2
1.20	-	-	-	-	-	-	-	-	-	-31.9	-32.6	-33.3	-34.0	-34.7	-35.3	-36.0	-36.6	-37.2	-37.8
1.25	-	-	-	-	-	-	-	-	-	-	-	-33.9	-34.6	-35.2	-35.9	-36.5	-37.1	-37.7	-38.3
1.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-35.8	-36.4	-37.0	-37.6	-38.2	-38.8
1.35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-36.9	-37.5	-38.1	-38.7	-39.3
1.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-38.6	-39.2	-39.8	-40.3
1.45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 8b

Appendix 2

CO₂ content (vol-%) for different carbon potentials in an atmosphere consisting of 60% cracked methanol and 40% nitrogen.

C-pot., wt-% C	Furnace temperature, °C (°F)																			
	820	830	840	850	860	870	880	890	900	910	920	930	940	950	960	970	980	990	1000 °C	1832 °F
1508	1526	1544	1562	1580	1598	1616	1634	1652	1670	1688	1706	1724	1742	1760	1778	1796	1814	1832		
0.20	1.924	1.740	1.573	1.421	1.284	1.161	1.050	0.950	0.859	0.778	0.705	0.640	0.581	0.528	0.480	0.437	0.398	0.363	0.332	
0.25	1.577	1.421	1.260	1.153	1.039	0.936	0.844	0.762	0.688	0.622	0.563	0.510	0.462	0.420	0.381	0.347	0.316	0.288	0.263	
0.30	1.328	1.193	1.072	0.963	0.866	0.779	0.702	0.633	0.571	0.515	0.466	0.421	0.382	0.346	0.314	0.286	0.260	0.237	0.216	
0.35	1.140	1.022	0.917	0.823	0.739	0.664	0.597	0.538	0.484	0.437	0.395	0.357	0.323	0.293	0.266	0.242	0.220	0.200	0.183	
0.40	0.994	0.900	0.797	0.714	0.641	0.575	0.517	0.465	0.419	0.378	0.341	0.308	0.279	0.253	0.229	0.208	0.190	0.173	0.157	
0.45	0.877	0.794	0.701	0.628	0.563	0.505	0.454	0.408	0.367	0.331	0.299	0.270	0.244	0.221	0.201	0.182	0.166	0.151	0.138	
0.50	0.781	0.707	0.623	0.558	0.500	0.448	0.402	0.362	0.325	0.293	0.265	0.239	0.216	0.196	0.178	0.161	0.147	0.134	0.122	
0.55	0.701	0.627	0.559	0.500	0.448	0.401	0.360	0.324	0.291	0.262	0.237	0.214	0.193	0.175	0.159	0.144	0.131	0.119	0.109	
0.60	0.633	0.565	0.504	0.451	0.404	0.362	0.325	0.292	0.263	0.236	0.213	0.193	0.174	0.158	0.143	0.130	0.118	0.108	0.098	
0.65	0.575	0.512	0.458	0.409	0.366	0.328	0.294	0.265	0.238	0.214	0.193	0.175	0.158	0.143	0.130	0.118	0.107	0.098	0.089	
0.70	0.525	0.463	0.418	0.374	0.334	0.299	0.269	0.241	0.217	0.195	0.176	0.159	0.144	0.130	0.118	0.108	0.098	0.089	0.081	
0.75	0.481	0.420	0.383	0.342	0.306	0.274	0.246	0.221	0.199	0.179	0.162	0.146	0.132	0.120	0.108	0.099	0.090	0.082	0.074	
0.80	0.443	0.395	0.352	0.315	0.282	0.252	0.226	0.203	0.183	0.165	0.149	0.134	0.122	0.110	0.100	0.091	0.083	0.075	0.069	
0.85	0.409	0.364	0.325	0.291	0.260	0.233	0.209	0.188	0.169	0.152	0.137	0.124	0.112	0.102	0.092	0.084	0.076	0.069	0.063	
0.90	0.378	0.337	0.301	0.269	0.241	0.216	0.194	0.174	0.157	0.141	0.127	0.115	0.104	0.094	0.086	0.078	0.071	0.064	0.059	
0.95	-	-	0.280	0.250	0.224	0.200	0.180	0.162	0.145	0.131	0.118	0.107	0.097	0.088	0.080	0.072	0.066	0.060	0.055	
1.00	-	-	-	0.233	0.208	0.187	0.168	0.151	0.135	0.122	0.110	0.100	0.090	0.082	0.074	0.067	0.061	0.056	0.051	
1.05	-	-	-	-	-	0.174	0.156	0.141	0.126	0.114	0.103	0.093	0.084	0.076	0.069	0.063	0.057	0.052	0.048	
1.10	-	-	-	-	-	-	0.146	0.131	0.118	0.107	0.096	0.087	0.079	0.071	0.065	0.059	0.054	0.049	0.045	
1.15	-	-	-	-	-	-	-	-	0.111	0.100	0.090	0.082	0.074	0.067	0.061	0.055	0.050	0.046	0.042	
1.20	-	-	-	-	-	-	-	-	-	0.094	0.085	0.077	0.069	0.063	0.057	0.052	0.047	0.043	0.039	
1.25	-	-	-	-	-	-	-	-	-	-	-	0.072	0.065	0.059	0.054	0.049	0.045	0.041	0.037	
1.30	-	-	-	-	-	-	-	-	-	-	-	-	-	0.056	0.051	0.046	0.042	0.038	0.035	
1.35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.048	0.044	0.040	0.036	0.033	
1.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.038	0.034	0.031	
1.45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
1.50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	

Appendix 2

CO₂ content (vol.-%) for different carbon potentials in an atmosphere consisting of 20% cracked methanol and 80% nitrogen.

C-pot., wt-% C	Furnace temperature, °C (°F)																		
	820 1508	830 1526	840 1544	850 1562	860 1580	870 1598	880 1616	890 1634	900 1652	910 1670	920 1688	930 1706	940 1724	950 1742	960 1760	970 1778	980 1796	990 1814	1000 °C 1832 °F
0.20	0.252	0.225	0.200	0.178	0.159	0.143	0.128	0.114	0.103	0.092	0.083	0.075	0.068	0.061	0.056	0.050	0.046	0.042	0.038
0.25	0.201	0.179	0.159	0.142	0.126	0.113	0.101	0.090	0.081	0.073	0.066	0.059	0.053	0.048	0.044	0.040	0.036	0.033	0.030
0.30	0.166	0.147	0.131	0.116	0.104	0.093	0.083	0.074	0.067	0.060	0.054	0.049	0.044	0.040	0.036	0.033	0.030	0.027	0.024
0.35	0.140	0.124	0.111	0.098	0.088	0.078	0.070	0.063	0.056	0.050	0.045	0.041	0.037	0.033	0.030	0.027	0.025	0.023	0.021
0.40	0.121	0.107	0.095	0.085	0.075	0.067	0.060	0.054	0.048	0.043	0.039	0.035	0.032	0.029	0.026	0.024	0.021	0.019	0.018
0.45	0.106	0.094	0.083	0.074	0.066	0.059	0.053	0.047	0.042	0.038	0.034	0.031	0.028	0.025	0.023	0.021	0.019	0.017	0.015
0.50	0.093	0.083	0.073	0.065	0.058	0.052	0.046	0.042	0.037	0.033	0.030	0.027	0.025	0.022	0.020	0.018	0.017	0.015	0.014
0.55	0.083	0.074	0.066	0.058	0.052	0.046	0.041	0.037	0.033	0.030	0.027	0.024	0.022	0.020	0.018	0.016	0.015	0.013	0.012
0.60	0.075	0.066	0.059	0.052	0.047	0.042	0.037	0.033	0.030	0.027	0.024	0.022	0.020	0.018	0.016	0.015	0.013	0.012	0.011
0.65	0.068	0.060	0.053	0.047	0.042	0.038	0.034	0.030	0.027	0.024	0.022	0.020	0.018	0.016	0.015	0.013	0.012	0.011	0.010
0.70	0.062	0.055	0.049	0.043	0.038	0.034	0.031	0.028	0.025	0.022	0.020	0.018	0.016	0.015	0.013	0.012	0.011	0.010	0.009
0.75	0.056	0.050	0.044	0.040	0.035	0.031	0.028	0.025	0.023	0.020	0.018	0.016	0.015	0.013	0.012	0.011	0.010	0.009	0.008
0.80	0.052	0.046	0.041	0.036	0.032	0.029	0.026	0.023	0.021	0.019	0.017	0.015	0.014	0.012	0.011	0.010	0.009	0.008	0.008
0.85	0.048	0.042	0.038	0.033	0.030	0.027	0.024	0.021	0.019	0.017	0.016	0.014	0.013	0.011	0.010	0.009	0.009	0.008	0.007
0.90	0.044	0.039	0.035	0.031	0.028	0.025	0.022	0.020	0.018	0.016	0.014	0.013	0.012	0.011	0.010	0.009	0.008	0.007	0.007
0.95	-	-	0.032	0.029	0.026	0.023	0.020	0.018	0.016	0.015	0.013	0.012	0.011	0.010	0.009	0.008	0.007	0.006	0.006
1.00	-	-	-	0.027	0.024	0.021	0.018	0.016	0.014	0.013	0.012	0.010	0.009	0.008	0.007	0.007	0.006	0.006	0.005
1.05	-	-	-	-	-	-	-	-	0.013	0.011	0.010	0.009	0.008	0.008	0.007	0.007	0.006	0.005	0.005
1.10	-	-	-	-	-	-	-	-	-	0.011	0.010	0.009	0.008	0.008	0.007	0.006	0.006	0.005	0.005
1.15	-	-	-	-	-	-	-	-	-	-	0.010	0.009	0.008	0.007	0.006	0.006	0.005	0.005	0.004
1.20	-	-	-	-	-	-	-	-	-	-	-	0.009	0.008	0.007	0.006	0.006	0.005	0.005	0.004
1.25	-	-	-	-	-	-	-	-	-	-	-	0.008	0.007	0.007	0.006	0.005	0.005	0.005	0.004
1.30	-	-	-	-	-	-	-	-	-	-	-	-	0.008	0.007	0.006	0.005	0.005	0.004	0.004
1.35	-	-	-	-	-	-	-	-	-	-	-	-	-	0.007	0.006	0.005	0.005	0.004	0.004
1.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.005	0.005	0.004	0.004	0.004
1.45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.004	0.004	0.004
1.50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.004	0.003

Oxygen probe mV – carbon potential tables for nitrogen/methanol atmospheres

Table 9a

Appendix 3

Output signal from an oxygen probe (mV) for different carbon potentials in an atmosphere consisting of 100% cracked methanol and 0% nitrogen.

C-pot., wt-% C	Furnace temperature, °C (°F)																		
	820 1508	830 1526	840 1544	850 1562	860 1580	870 1598	880 1616	890 1634	900 1652	910 1670	920 1688	930 1706	940 1724	950 1742	960 1760	970 1778	980 1796	990 1814	1000 °C 1832 °F
0.20	1019.2	1020.2	1021.4	1022.5	1023.8	1025.1	1026.4	1027.8	1029.3	1030.7	1032.2	1033.6	1035.4	1037.0	1038.6	1040.2	1041.9	1043.6	1045.3
0.25	1029.0	1030.3	1031.6	1033.0	1034.4	1035.9	1037.5	1039.0	1040.6	1042.3	1043.9	1045.6	1047.4	1049.1	1050.9	1052.7	1054.5	1056.3	1058.1
0.30	1037.4	1038.9	1040.4	1041.9	1043.5	1045.1	1046.8	1048.5	1050.2	1052.0	1053.8	1055.6	1057.4	1059.3	1061.2	1063.1	1065.0	1066.9	1068.8
0.35	1044.8	1046.4	1048.0	1049.6	1051.4	1053.1	1054.9	1056.7	1058.5	1060.4	1062.3	1064.2	1066.2	1068.1	1070.1	1072.1	1074.1	1076.1	1078.1
0.40	1051.4	1053.1	1054.8	1056.6	1058.4	1060.2	1062.1	1064.0	1065.9	1067.9	1069.9	1071.9	1073.9	1075.9	1078.0	1080.0	1082.1	1084.2	1086.3
0.45	1057.4	1059.2	1061.0	1062.8	1064.7	1066.6	1068.6	1070.6	1072.6	1074.7	1076.8	1078.8	1080.9	1083.0	1085.1	1087.2	1089.3	1091.5	1093.6
0.50	1062.9	1064.8	1066.7	1068.6	1070.6	1072.6	1074.6	1076.7	1078.7	1080.8	1082.9	1085.1	1087.2	1089.4	1091.5	1093.7	1095.9	1098.1	1100.3
0.55	1068.0	1069.9	1071.9	1073.9	1076.0	1078.0	1080.1	1082.2	1084.4	1086.5	1088.7	1090.9	1093.1	1095.3	1097.5	1099.7	1102.0	1104.2	1106.5
0.60	1072.8	1074.8	1076.8	1078.9	1081.0	1083.1	1085.3	1087.4	1089.6	1091.8	1094.0	1096.3	1098.5	1100.8	1103.1	1105.3	1107.6	1109.9	1112.2
0.65	1077.3	1079.4	1081.5	1083.6	1085.7	1087.9	1090.1	1092.3	1094.5	1096.8	1099.1	1101.3	1103.6	1105.9	1108.2	1110.6	1112.9	1115.2	1117.5
0.70	1081.6	1083.7	1085.8	1088.0	1090.2	1092.4	1094.7	1096.9	1099.2	1101.5	1103.8	1106.1	1108.4	1110.8	1113.1	1115.5	1117.8	1120.2	1122.6
0.75	1085.7	1087.8	1090.0	1092.2	1094.4	1096.7	1099.0	1101.3	1103.6	1105.9	1108.3	1110.6	1113.0	1115.4	1117.7	1120.1	1122.5	1124.9	1127.3
0.80	1089.6	1091.7	1094.0	1096.2	1098.5	1100.8	1103.1	1105.4	1107.8	1110.2	1112.5	1114.9	1117.3	1119.7	1122.1	1124.6	1127.0	1129.4	1131.9
0.85	1093.3	1095.5	1097.8	1100.1	1102.4	1104.7	1107.0	1109.4	1111.8	1114.2	1116.6	1119.0	1121.5	1123.9	1126.3	1128.8	1131.3	1133.7	1136.2
0.90	1096.9	1099.1	1101.4	1103.7	1106.1	1108.4	1110.8	1113.2	1115.6	1118.1	1120.5	1123.0	1125.4	1127.9	1130.4	1132.8	1135.3	1137.8	1140.3
0.95	-	-	1104.9	1107.3	1109.7	1112.1	1114.5	1116.9	1119.3	1121.8	1124.3	1126.7	1129.2	1131.7	1134.2	1136.7	1139.2	1141.8	1144.3
1.00	-	-	-	1110.7	1113.1	1115.5	1118.0	1120.4	1122.9	1125.4	1127.9	1130.4	1132.9	1135.4	1137.9	1140.5	1143.0	1145.5	1148.1
1.05	-	-	-	-	-	1118.9	1121.4	1123.9	1126.4	1128.9	1131.4	1133.9	1136.4	1139.0	1141.5	1144.1	1146.6	1149.2	1151.8
1.10	-	-	-	-	-	-	1124.7	1127.2	1129.7	1132.2	1134.8	1137.3	1139.9	1142.4	1145.0	1147.6	1150.2	1152.7	1155.3
1.15	-	-	-	-	-	-	-	-	1132.9	1135.5	1138.0	1140.6	1143.2	1145.8	1148.4	1151.0	1153.6	1156.2	1158.8
1.20	-	-	-	-	-	-	-	-	-	1138.6	1141.2	1143.8	1146.4	1149.0	1151.6	1154.3	1156.9	1159.5	1162.1
1.25	-	-	-	-	-	-	-	-	-	-	1146.9	1149.6	1152.2	1154.8	1157.5	1160.1	1162.7	1165.4	1168.1
1.30	-	-	-	-	-	-	-	-	-	-	-	1146.9	1149.6	1152.2	1154.8	1157.5	1160.1	1162.7	1165.4
1.35	-	-	-	-	-	-	-	-	-	-	-	-	-	1155.3	1157.9	1160.6	1163.2	1165.9	1168.6
1.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1166.3	1169.0	1171.7
1.45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1169.3	1172.0	1174.7
1.50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1174.9	1178.5

Appendix 3

C-pot., | Furnace temperature, °C (°F)

		820	830	840	850	860	870	880	890	900	910	920	930	940	950	960	970	980	990	1000 °C
		1508	1526	1544	1562	1580	1598	1616	1634	1652	1670	1688	1706	1724	1742	1760	1778	1796	1814	1832 °F
0.20	1039.5	1041.1	1042.7	1044.3	1046.0	1047.7	1049.5	1051.3	1053.1	1054.9	1056.8	1058.7	1060.6	1062.6	1064.5	1066.5	1068.4	1070.4	1072.4	1072.4
0.25	1050.0	1051.7	1053.5	1055.3	1057.1	1059.0	1060.9	1062.9	1064.8	1066.8	1068.8	1070.9	1072.9	1075.0	1077.0	1079.1	1081.2	1083.3	1085.4	1085.4
0.30	1058.8	1060.7	1062.6	1064.5	1066.5	1068.5	1070.5	1072.6	1074.7	1076.8	1078.9	1081.0	1083.2	1085.3	1087.5	1089.7	1091.9	1094.1	1096.3	1096.3
0.35	1064.5	1068.5	1070.5	1072.5	1074.6	1076.7	1078.9	1081.0	1083.2	1085.4	1087.6	1089.8	1092.0	1094.3	1096.5	1098.8	1101.1	1103.3	1105.6	1105.6
0.40	1073.4	1075.4	1077.6	1079.7	1081.9	1084.1	1086.3	1088.5	1090.8	1093.1	1095.3	1097.6	1099.9	1102.2	1104.5	1106.8	1109.1	1111.4	1113.7	1113.9
0.45	1079.6	1081.7	1083.9	1086.1	1088.4	1090.6	1092.9	1095.2	1097.6	1099.9	1102.2	1104.6	1106.9	1109.3	1111.7	1114.1	1116.5	1118.9	1121.3	1121.3
0.50	1085.3	1087.5	1089.8	1092.1	1094.4	1096.7	1099.0	1101.4	1103.8	1106.1	1108.5	1110.9	1113.4	1115.8	1118.2	1120.7	1123.1	1125.6	1128.0	1128.0
0.55	1090.6	1092.9	1095.2	1097.5	1099.9	1102.2	1104.6	1107.1	1109.5	1111.9	1114.4	1116.8	1119.3	1121.8	1124.2	1126.7	1129.2	1131.7	1134.2	1134.2
0.60	1095.5	1097.8	1100.2	1102.6	1105.0	1107.4	1109.9	1112.3	1114.8	1117.3	1119.8	1122.3	1124.8	1127.3	1129.8	1132.3	1134.8	1137.4	1140.0	1140.0
0.65	1100.1	1102.5	1104.9	1107.4	1109.8	1112.3	1114.8	1117.3	1119.8	1122.3	1124.8	1127.4	1129.9	1132.5	1135.0	1137.6	1140.2	1142.8	1145.3	1145.3
0.70	1104.5	1107.0	1109.4	1111.9	1114.4	1116.9	1119.4	1121.9	1124.5	1127.0	1129.6	1132.2	1134.8	1137.4	1140.0	1142.6	1145.2	1147.8	1150.4	1150.4
0.75	1108.7	1111.2	1113.6	1116.2	1118.7	1121.2	1123.8	1126.4	1128.9	1131.5	1134.1	1136.7	1139.4	1142.0	1144.6	1147.2	1149.9	1152.5	1155.2	1155.2
0.80	1112.7	1115.2	1117.7	1120.2	1122.8	1125.4	1128.0	1130.6	1133.2	1135.8	1138.4	1141.1	1143.7	1146.4	1149.0	1151.7	1154.4	1157.0	1159.7	1159.7
0.85	1116.5	1119.0	1121.5	1124.1	1126.7	1129.3	1131.9	1134.6	1137.2	1139.9	1142.5	1145.2	1147.9	1150.6	1153.2	1155.9	1158.6	1161.3	1164.0	1164.0
0.90	1120.1	1122.7	1125.3	1127.9	1130.5	1133.1	1135.8	1138.4	1141.1	1143.8	1146.5	1149.2	1151.9	1154.6	1157.3	1160.0	1162.7	1165.4	1168.2	1168.2
0.95	-	-	1128.8	1131.5	1134.1	1136.8	1139.4	1142.1	1144.8	1147.5	1150.2	1152.9	1155.7	1158.4	1161.2	1163.9	1166.7	1169.4	1172.2	1172.2
1.00	-	-	-	1134.9	1137.6	1140.3	1143.0	1145.7	1148.4	1151.1	1153.9	1156.6	1159.4	1162.1	1164.9	1167.7	1170.4	1173.2	1176.0	1176.0
1.05	-	-	-	-	-	1143.7	1146.4	1149.1	1151.9	1154.6	1157.4	1160.2	1162.9	1165.7	1168.5	1171.3	1174.1	1176.9	1179.7	1179.7
1.10	-	-	-	-	-	-	1149.7	1152.5	1155.2	1158.0	1160.8	1163.6	1166.4	1169.2	1172.0	1174.8	1177.6	1180.4	1183.2	1183.2
1.15	-	-	-	-	-	-	-	-	1164.5	1167.3	1170.1	1172.9	1175.7	1178.5	1181.3	1184.1	1186.9	1189.7	1192.5	1192.5
1.20	-	-	-	-	-	-	-	-	-	1168.5	1171.3	1174.1	1176.9	1179.7	1182.5	1185.3	1188.1	1190.9	1193.7	1193.7
1.25	-	-	-	-	-	-	-	-	-	-	1172.5	1175.3	1178.1	1180.9	1183.7	1186.5	1189.3	1192.1	1194.9	1194.9
1.30	-	-	-	-	-	-	-	-	-	-	1176.5	1179.3	1182.1	1184.9	1187.7	1190.5	1193.3	1196.1	1198.9	1198.9
1.35	-	-	-	-	-	-	-	-	-	-	1180.5	1183.3	1186.1	1188.9	1191.7	1194.5	1197.3	1200.1	1202.9	1202.9
1.40	-	-	-	-	-	-	-	-	-	-	1184.5	1187.3	1190.1	1192.9	1195.7	1198.5	1201.3	1204.1	1206.9	1206.9
1.45	-	-	-	-	-	-	-	-	-	-	1188.5	1191.3	1194.1	1196.9	1199.7	1202.5	1205.3	1208.1	1210.9	1210.9
1.50	-	-	-	-	-	-	-	-	-	-	1192.5	1195.3	1198.1	1200.9	1203.7	1206.5	1209.3	1212.1	1214.9	1214.9

Appendix 3

Output signal from an oxygen probe (mV) for different carbon potentials in an atmosphere consisting of 20% cracked methanol and 80% nitrogen.

C-pot., wt-% C	Furnace temperature, °C (°F)																			
	820 1508	830 1526	840 1544	850 1562	860 1580	870 1598	880 1616	890 1634	900 1652	910 1670	920 1688	930 1706	940 1724	950 1742	960 1760	970 1778	980 1796	990 1814	1000 °C 1832 °F	
0.20	1087.4	1089.7	1092.1	1094.5	1096.9	1099.4	1101.8	1104.3	1106.8	1109.2	1111.7	1114.2	1116.7	1119.3	1121.8	1124.3	1126.8	1129.4	1131.9	
0.25	1098.5	1101.0	1103.5	1106.0	1108.6	1111.1	1113.7	1116.3	1118.9	1121.5	1124.1	1126.7	1129.3	1131.9	1134.5	1137.2	1139.8	1142.4	1145.1	
0.30	1107.8	1110.4	1113.0	1115.6	1118.3	1120.9	1123.6	1126.3	1128.9	1131.6	1134.3	1137.0	1139.7	1142.4	1145.1	1147.9	1150.6	1153.3	1156.0	
0.35	1115.9	1118.5	1121.2	1123.9	1126.7	1129.4	1132.1	1134.9	1137.6	1140.4	1143.2	1145.9	1148.7	1151.5	1154.3	1157.1	1159.9	1162.6	1165.4	
0.40	1123.0	1125.7	1128.5	1131.3	1134.1	1136.9	1139.7	1142.5	1145.3	1148.2	1151.0	1153.8	1156.7	1159.5	1162.3	1165.2	1168.0	1170.9	1173.7	
0.45	1129.4	1132.2	1135.1	1137.9	1140.8	1143.6	1146.5	1149.4	1152.2	1155.1	1158.0	1160.9	1163.8	1166.7	1169.6	1172.5	1175.4	1178.3	1181.2	
0.50	1135.2	1138.2	1141.0	1143.9	1146.8	1149.8	1152.7	1155.6	1158.5	1161.4	1164.4	1167.3	1170.3	1173.2	1176.2	1179.1	1182.1	1185.0	1188.0	
0.55	1140.7	1143.6	1146.6	1149.5	1152.4	1155.4	1158.4	1161.3	1164.3	1167.3	1170.3	1173.2	1176.2	1179.2	1182.2	1185.2	1188.2	1191.2	1194.2	
0.60	1145.8	1148.7	1151.7	1154.7	1157.7	1160.7	1163.7	1166.7	1169.7	1172.7	1175.7	1178.7	1181.8	1184.8	1187.8	1190.8	1193.9	1196.9	1200.0	
0.65	1150.5	1153.5	1156.5	1159.5	1162.5	1165.6	1168.6	1171.7	1174.7	1177.8	1180.8	1183.9	1186.9	1190.0	1193.1	1196.1	1199.2	1202.3	1205.3	
0.70	1154.9	1158.0	1161.0	1164.1	1167.1	1170.2	1173.3	1176.4	1179.4	1182.5	1185.6	1188.7	1191.8	1194.9	1198.0	1201.1	1204.2	1207.3	1210.4	
0.75	1159.2	1162.2	1165.3	1168.4	1171.5	1174.6	1177.7	1180.8	1183.9	1187.0	1190.2	1193.3	1196.4	1199.5	1202.7	1205.8	1208.9	1212.1	1215.2	
0.80	1163.2	1166.3	1169.4	1172.5	1175.6	1178.8	1181.9	1185.0	1188.2	1191.3	1194.5	1197.6	1200.8	1203.9	1207.1	1210.3	1213.4	1216.6	1219.8	
0.85	1167.0	1170.2	1173.3	1176.4	1179.6	1182.7	1185.9	1189.1	1192.2	1195.4	1198.6	1201.8	1205.0	1208.1	1211.3	1214.5	1217.7	1220.9	1224.1	
0.90	1170.7	1173.9	1177.0	1180.2	1183.4	1186.5	1189.7	1192.9	1196.1	1199.3	1202.5	1205.7	1208.9	1212.2	1215.4	1218.6	1221.8	1225.0	1228.2	
0.95	-	-	1180.6	1183.8	1187.0	1190.2	1193.4	1196.6	1199.9	1203.1	1206.3	1209.5	1212.8	1216.0	1219.3	1222.5	1225.7	1229.0	1232.2	
1.00	-	-	1187.3	1190.5	1193.7	1196.9	1200.2	1203.5	1206.7	1210.0	1213.2	1216.5	1219.7	1223.0	1226.3	1229.6	1232.9	1236.1	1239.4	
1.05	-	-	-	-	-	1197.2	1200.4	1203.7	1206.9	1210.2	1213.5	1216.8	1220.0	1223.3	1226.6	1229.9	1233.2	1236.5	1239.8	
1.10	-	-	-	-	-	-	1203.7	1207.0	1210.3	1213.6	1216.9	1220.2	1223.5	1226.8	1230.1	1233.4	1236.7	1240.0	1243.3	
1.15	-	-	-	-	-	-	-	-	1213.6	1216.9	1220.2	1223.5	1226.8	1230.1	1233.5	1236.8	1240.1	1243.5	1246.8	
1.20	-	-	-	-	-	-	-	-	1220.1	1223.4	1226.7	1230.1	1233.4	1236.7	1240.1	1243.4	1246.8	1250.1	1253.4	
1.25	-	-	-	-	-	-	-	-	-	1229.9	1233.2	1236.6	1239.9	1243.3	1246.7	1250.0	1253.4	1256.7	1260.0	
1.30	-	-	-	-	-	-	-	-	-	-	1239.7	1243.1	1246.5	1249.9	1253.3	1256.7	1260.0	1263.4	1266.7	
1.35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1246.1	1249.5	1252.9	1256.3	1259.7	
1.40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1255.9	1259.3	1262.7	
1.45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1262.2	1265.6	1269.0	
1.50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	

D. Appendix 4:

Selection of European and American Safety Standards

The European Committee for Standardization, CEN, issues its standards in English, French and German. The CEN members translate the standards into their own languages. In addition to the European Standards, EN, there are national standards and safety regulations that have to be taken into account. The CEN homepage is at www.cenorm.be, from where links are given to national standards authorities.

In the USA the National Fire Protection Association (NFPA) maintains the main safety standard for heat treatment. In addition standards

and regulations are issued by the U.S. Occupational Safety and Health Administration (OSHA), and by insurance underwriters. The Compressed Gas Association (CGA) maintains standards for gases. National Electrical Codes and local requirements of states and communities will also apply. NFPA standards can be ordered on-line at www.nfpa.org

The standards given below are a selection of existing standards; for a full listing of standards the reader is advised to obtain the information from the standardization authorities

Selected European safety standards related to carburizing and carbonitriding

EN-746-1, 1997:	Industrial thermoprocessing equipment - Part 1: Common safety requirements for industrial thermoprocessing equipment.
EN-746-2, 1997:	Industrial thermoprocessing equipment - Part 2: Safety requirements for combustion and fuel handling systems.
EN-746-3, 1997:	Industrial thermoprocessing equipment - Part 3: Safety requirements for the generation and use of atmosphere gases.
EIGA: IGC Doc 17/85	Liquid nitrogen and liquid argon storage installations at user's premises

Selected American safety standards related to carburizing and carbonitriding

NFPA 86	Standard for Ovens and Furnaces, 2003 Edition
CGA P-18	Standard for Bulk Inert Gas Systems at Consumer Sites
CGA G-2.1, 1999	Safety Requirements for the Storage and Handling of Anhydrous Ammonia

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