

Introduction to Carburizing and Carbonitriding

Basic Carburizing Reactions

There are certain chemical reactions that are common to all carburizing methods. Carburization is a complex process where multiple reactions occur simultaneously. These reactions control the delivery (carburization) or removal (decarburization) of carbon from the surface and the oxidation or reduction of steel. The success or failure of the process depends on ensuring that the reactions are driven in the intended direction until the desired surface equilibrium and case depth are reached. Reactions and mass transfer take place in four distinct zones: the medium, the boundary layer, the surface, and within the steel. This is represented graphically in [Fig. 8](#).

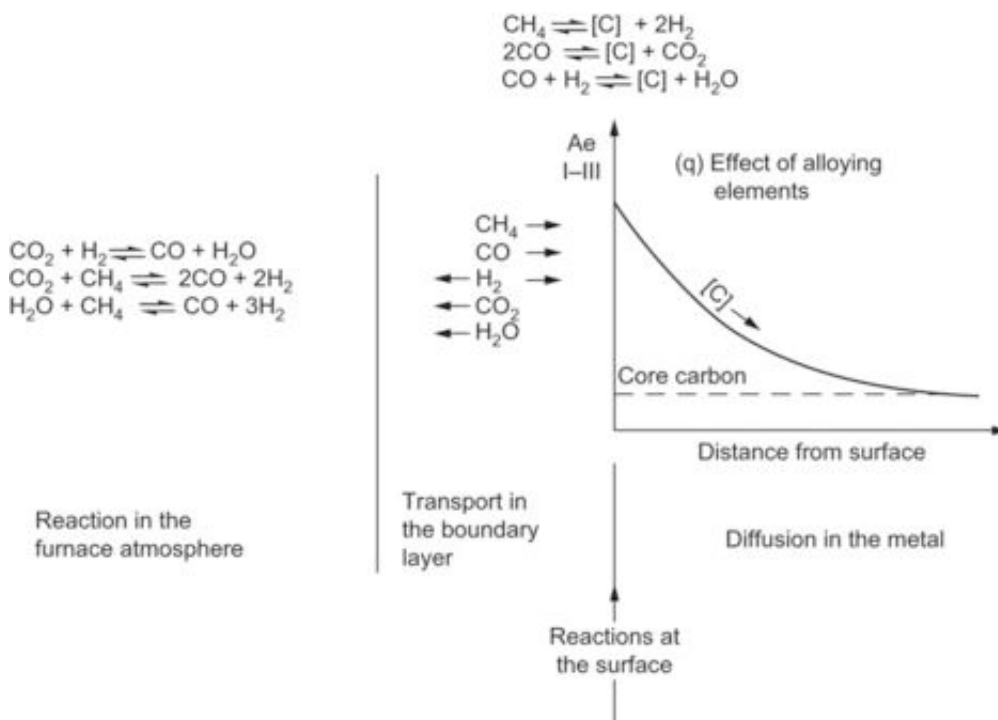
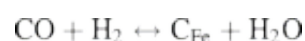
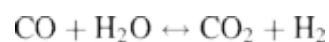
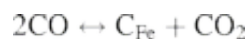


Fig. 8 Schematic representation of the various steps in the gas carburizing process. This diagram is specific for gas carburizing. Source: [Ref 1](#)

When considering generic carburizing, the following reactions are involved:



These reactions control the balance of carbon monoxide, carbon dioxide, and water vapor. The first equation is of particular utility in controlling the carburization process. The second equation, known as the water-gas reaction and in combination with the first equation, describes the relationship between carbon potential and water content at the boundary layer/iron interface.

Diffusion and the Effects of Time and Temperature. Because carburization is a diffusion-dependent

process, it is worthwhile to look at the basic concepts that describe the behavior of carbon diffusion in steel. Quantitative work in diffusion became possible in 1855 when Adolf Fick introduced of a formula to describe the “flux” of gases from a region of high concentration to one of low concentration. In a single dimension, this equation, which became known as Ficks' First Law, is written as:

$$J = -D \left(\frac{dc}{dx} \right)$$

where J is the diffusion flux or rate of diffusion per unit area, D is the diffusion coefficient of carbon in steel, and (dc/dx) is the concentration gradient (carbon with respect to distance). This equation assumes that the rate of transfer is proportional to the concentration gradient as measured perpendicular to the surface in question.

Basic diffusion takes place wherever there is a concentration gradient. In the case of carburization, the concentration gradient of concern is that of carbon. In carburization, the required gradient is created through the use of a low-carbon steel and a high-carbon medium. By placing the two in intimate contact at a suitable temperature, the conditions necessary to allow transfer of carbon from the medium (liquid, solid, or gas) into the workpiece are created. The speed of carbon diffusion in steel is greatly influenced both by temperature and the magnitude of the concentration gradient.

Given sufficient time, carbon will continue to transfer from the medium into the steel until equilibrium is achieved and the concentration is equal throughout the steel and the medium. Through carburization is not commonly practiced for commercial components, but this technique does have application in shim stock analysis, which is discussed later.

Increasing the rate of diffusion by maximizing the carbon gradient is exploited in the “boost-diffuse” technique, where a higher carbon potential is used early in the process (boost phase) and reduced to a lower carbon potential in the latter half of the process (diffuse phase). Boost-diffuse has been shown to reduce the overall time required to achieve a particular case depth when compared to single-step carburization, where the carbon potential is held constant throughout the process.

To predict the effects of carburization, one must first determine the value for the diffusivity of carbon in austenite. Numerous formulas for this value have been proposed (Ref 3). The formula for a particular process and material is used from best fit with the empirical experience. There are two main approaches to calculating diffusivity of carbon in austenite. One approach is to consider only the effect of temperature; the other is to consider the combined influences of temperature and carbon content. First, a temperature-dependent diffusivity (D_T) is considered:

$$D_T = 0.162 \exp \left(\frac{-137,800}{RT} \right) \quad (\text{Eq 1})$$

where D_T is the diffusivity of carbon in austenite (cm^2/s), R is the ideal gas constant ($8.31 \text{ J/mol} \cdot \text{K}$), and T is the absolute temperature (Kelvin).

Values for Eq 1 are plotted in Fig. 9. It is evident from Fig. 9 that the diffusivity of carbon in austenite increases with temperature. It is this relationship that is exploited during the carburizing process and why it is beneficial to use the highest possible carburizing temperature in production.

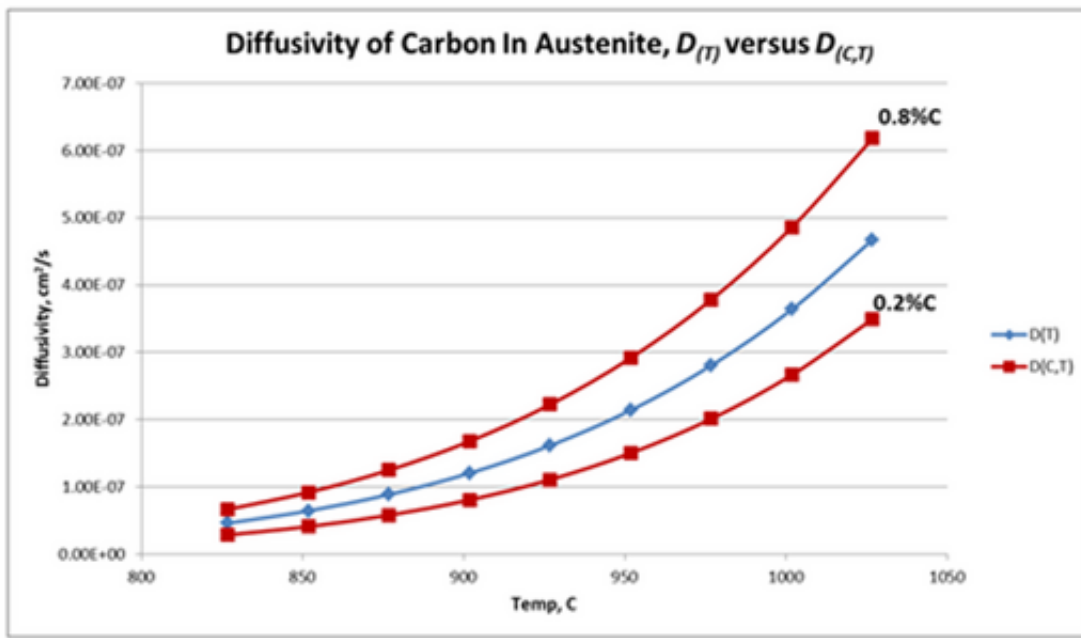


Fig. 9 Comparison of $D(T)$ and $D(C,T)$ at 0.2 and 0.8 wt% C. Because $D(T)$ is independent of carbon content, it is the same for both 0.2 and 0.8 %.

D_T is useful for estimations, but it is understood that the diffusivity of carbon in austenite is also highly affected by the carbon concentration of the steel. This makes using a temperature- and carbon-content-dependent diffusivity, $D_{(C,T)}$, a more realistic approach.

Like D_T , there are many $D_{(C,T)}$ formulas available to choose from. A commonly used formula for $D_{(C,T)}$ is:

$$D_{(C,T)} = 0.47 * \exp\left(-1.6 * C - \frac{37,000 - 6,600C}{RT}\right) \quad (\text{Eq 2})$$

where $D_{(C,T)}$ is the carbon- and temperature-dependent diffusivity of carbon in austenite (cm^2/s), C is the carbon content (weight percent), R is the ideal gas constant ($1.99 \text{ cal/mol} \cdot \text{K}$), and T is the absolute temperature (Kelvin).

Because the values of Eq 2 are a function of both temperature and carbon content, a comparison between D_T and $D_{(C,T)}$ at two different carbon levels (0.2 and 0.8%) is shown graphically in Fig. 9. D_T is greater than $D_{(C,T)}$ at lower carbon concentrations, but that as the carbon content increases, this relationship is reversed and the $D_{(C,T)}$ diffusivity of carbon in austenite is higher. It is this behavior that is exploited during boost-diffuse carburization.

Once a method of calculating diffusivity has been chosen, a useful formula for estimating the carbon profile resulting from the carburization process can be derived from Fick's Second Law and appears as:

$$C_{(x,t)} = C_s \left[1 - \left(1 - \frac{C_i}{C_s} \right) \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right]$$

where $C_{(x,t)}$ is the carbon content in weight percent at a depth x and time, t ; C_s is the carbon content in weight percent at the surface; C_i is the carbon content in weight percent of the base material; x is the depth (centimeters); t is the time (seconds); D is the diffusivity of carbon in austenite (cm^2/s); and erf is the error function of the argument.

This formula can be used to predict the effects of several key process variables, including temperature, time, and surface carbon level, and is valid for what is known as single-stage carburization. Single-stage carburization takes place at a constant temperature and surface carbon content. Some production processes use a technique known as boost-diffuse

carburization. This is done to take advantage of the increased diffusivity that occurs at higher carbon levels during the early stages, with the goal of reducing overall process time.

Predicted carbon profiles using $D_{(C,T)}$ at various processing times are plotted in Fig. 10. Plots such as this are easily accomplished using common spreadsheet applications. The practicality of such an estimate can be seen in Fig. 11, where 8620-grade steel was carburized in a single-stage process at a temperature of 963 °C (1765 °F) and a surface carbon potential of 1.30%. Neither prediction matches the experimental data exactly, but the profile calculated using $D_{(C,T)}$ is a better fit for the actual carbon profile than is the profile calculated using D_T , especially at greater values of x , which are the most important for determining case depth.

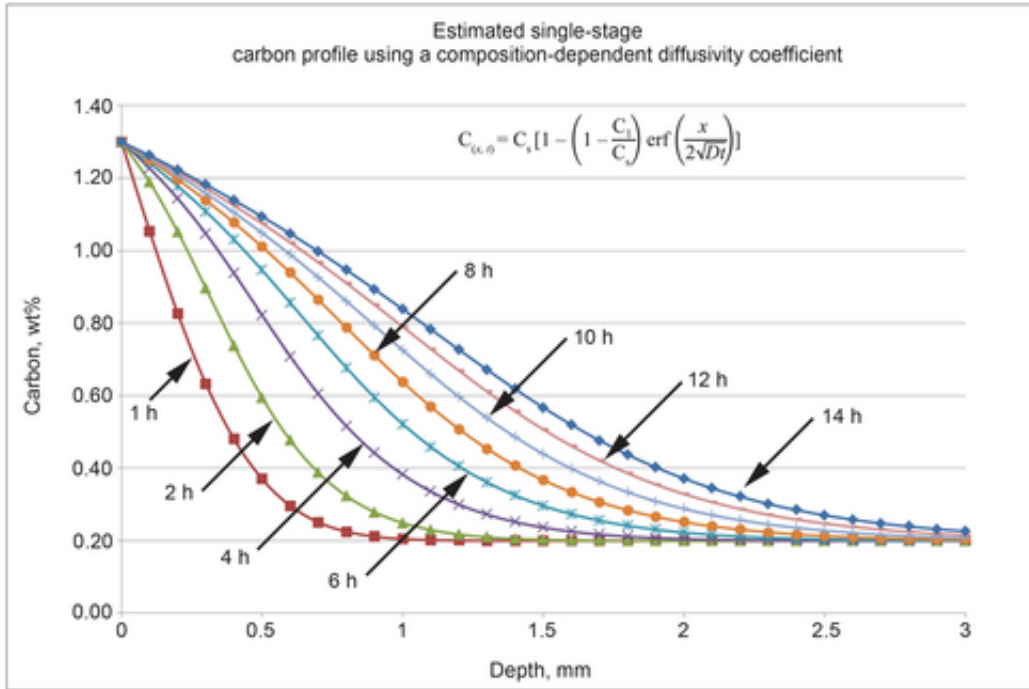


Fig. 10 Estimated single-stage carbon profiles at various carburizing times using a composition-dependent diffusivity coefficient, $D_{(C,T)}$

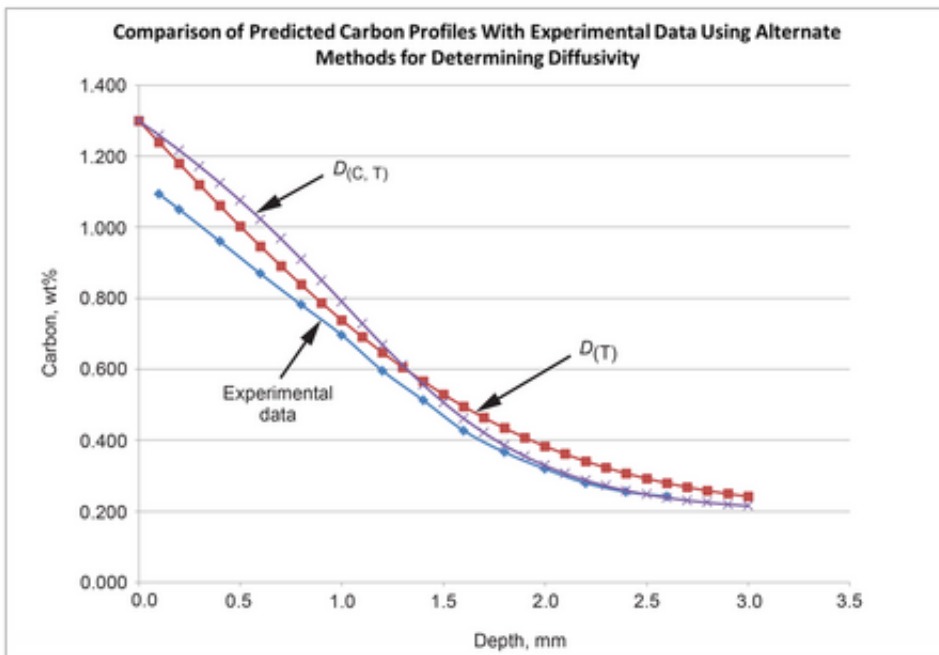
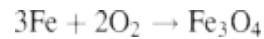
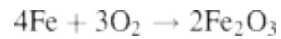
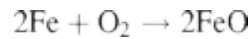


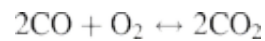
Fig. 11 Comparison of actual carbon profile with profiles predicted with experimental data using alternate methods for determining diffusivity using $D_{(T)}$ and $D_{(C,T)}$

Many controls companies now offer instrumentation and computer simulation software that use proprietary diffusion equations based on variations of the concepts presented here.

Oxidation. The reactions that occur at the surface of steel during carburization are complex and numerous. In addition to the carbon monoxide and carbon dioxide reactions described previously, many carburizing processes also must contend with oxidation. Oxidation can be described by the following reactions:

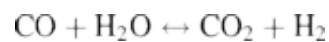


The oxygen for these reactions is provided by the CO/CO₂ reaction:



This reaction is important in describing the formation of intergranular oxidation and also in helping control carburizing processes through the use of zirconia oxygen probes. The principle of operation for zirconia oxygen probes is described in the next section.

Atmosphere Measurement and Control. For a carburizing process to deliver the desired results, the heat treater must be able to produce the required carbon potential in the carburizing medium. Fortunately, the numerous simultaneously occurring reactions can be exploited for this purpose. One reaction in particular has been found to be of primary importance in the control of gas carburizing atmospheres. It is known as the water-gas reaction:



This reaction can be used to show that there is a relationship between the carbon potential of an atmosphere and its water content. The relationship between water and carbon dioxide has proven to be particularly useful for this purpose. This relationship is displayed graphically for manufactured endothermic gas carburizing atmosphere produced from propane and natural gas (methane) in [Fig. 12](#) and [13](#).

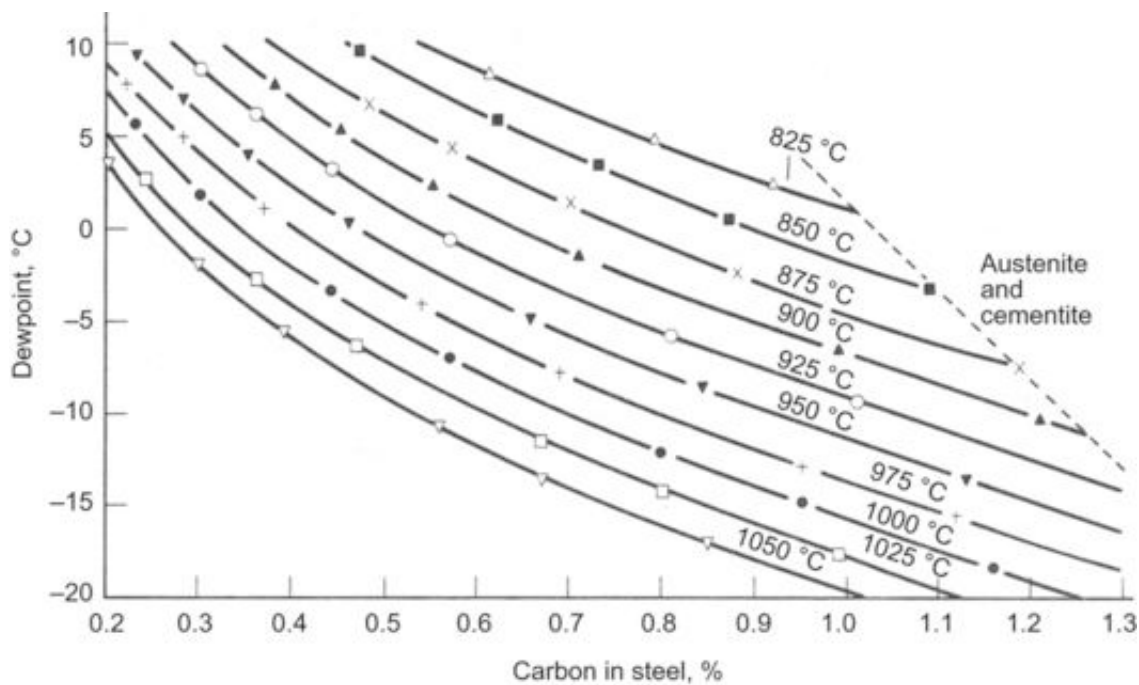


Fig. 12 Theoretical dewpoint versus carbon potential in propane endo. Source: [Ref 1](#)

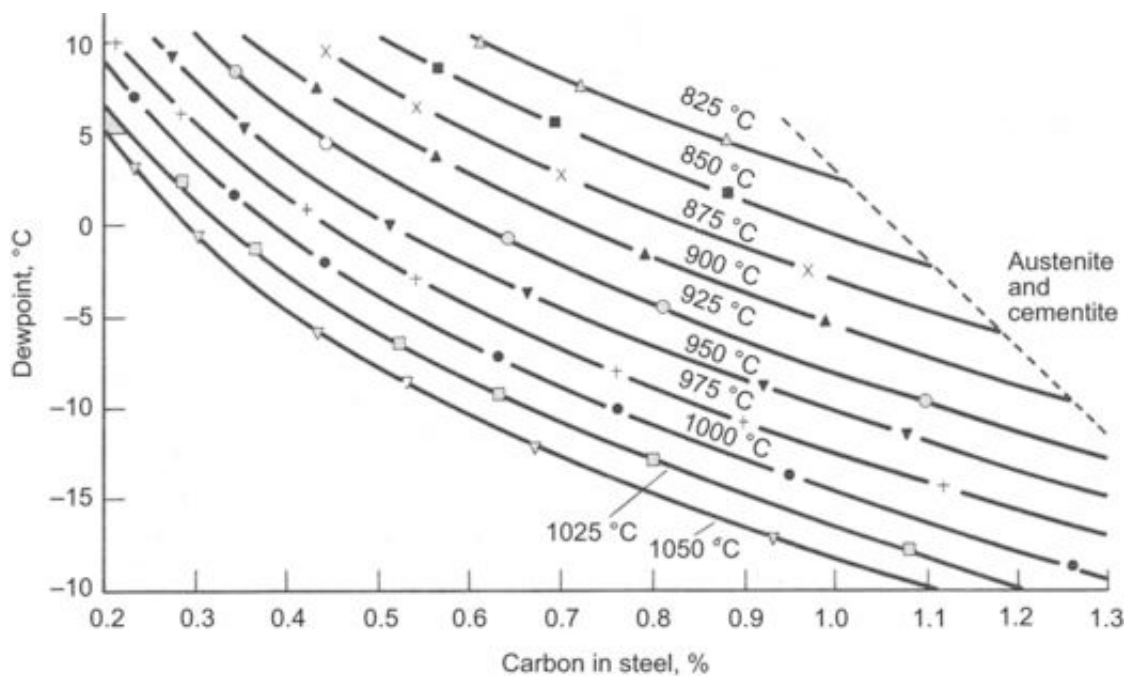


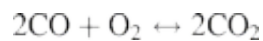
Fig. 13 Theoretical dewpoint versus carbon potential in natural gas endo. Source: [Ref 1](#)

This relationship has been used for many years as the principal method to measure carbon potential. For many years, instruments that measured the dewpoint of carburizing atmospheres by means of adiabatic expansion were the primary means of determining the quality of carburizing atmospheres.

Dewpoint measurement was a tremendous advancement in the technology of carburizing, but it was limited by the fact that adiabatic expansion instruments cannot be used for continuous monitoring.

In the 1980s, the zirconia oxygen probe began to supplant dewpoint measurement as the primary measurement method for carburizing atmospheres. An advantage of the zirconia oxygen probe over dewpoint measurement is that zirconia probes are well suited to continuous monitoring of the carburizing atmosphere and are continually calibrated by the oxygen in the air outside the furnace. This has opened the door for tremendous advances in instrumentation to control carburizing processes.

Oxygen probes work on the assumption that the following reaction is in equilibrium:



From this equation, it can be seen that there is a relationship between the oxygen content of the atmosphere and the CO:CO₂ ratio.

Certain materials have been found to exhibit measurable changes in electrical conductivity due almost exclusively to the transfer of oxygen ions through the material matrix. One such material, zirconia, when stabilized by small additions of other oxides such as Y₂O₃, has been found to be particularly useful in this regard. The added oxides serve to create oxygen vacancies in the zirconia matrix, which greatly facilitate the mobility of oxygen ions through the substrate. Placing platinum electrodes on either side of the zirconia substrate permits the measurement of conductivity across the material ([Fig. 14](#)).

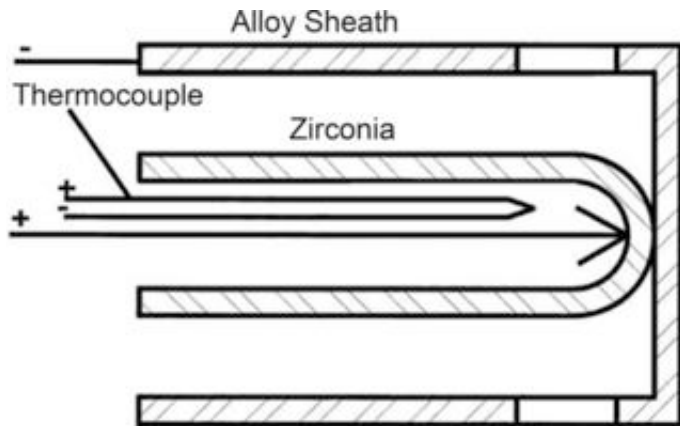


Fig. 14 Schematic of a zirconia oxygen probe. Source: [Ref 4](#)

This property is extremely useful because it is relatively simple to precisely measure the change in conductivity of the zirconia material. The following relationship describes the change of zirconia probe potential with oxygen content:

$$v(\text{millivolts}) = 0.0496T \log_{10} \frac{P_0}{P_1}$$

where T is the absolute temperature (Kelvin), P_0 is the oxygen partial pressure at the inner electrode (reference), and P_1 is the oxygen partial pressure at the outer electrode (atmosphere).

The oxygen content of the carburizing atmosphere can be easily determined by measuring the voltage of the sensor and knowing the oxygen content of a reference gas (typically room air). The oxygen content of the reference air is used to calculate the dewpoint of the atmosphere by using the relationship between oxygen and water content. The specific formulas used to produce these values are typically proprietary to each manufacturer. To allow for small “fine-tuning” adjustments, these algorithms typically include an adjustment factor that is intended to be used by the heat treater to improve measurement accuracy by bringing the probe output into line with actual furnace conditions. A typical oxygen probe installation is represented in [Fig. 15](#).

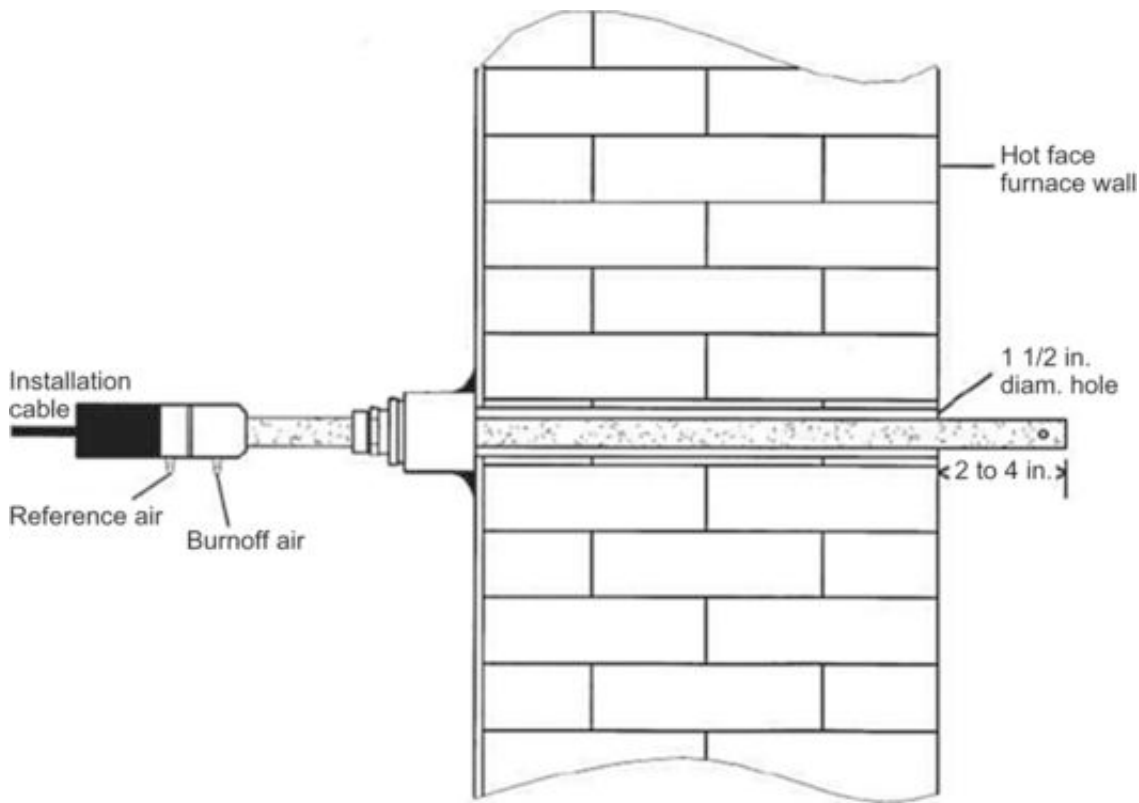


Fig. 15 Typical oxygen probe installation in a carburizing furnace. Source: [Ref 4](#)

How can a heat treater know the actual atmosphere conditions inside the furnace? A simple technique known as the shim stock test is often used for this purpose (see the article “Evaluation of Carbon Control in Carburized Parts” in this Volume). The shim stock test involves inserting a thin foil of low-carbon steel into the furnace atmosphere through a special port in the furnace wall ([Fig. 16](#)). The shim itself is usually made of AISI grade 1010 steel at a thickness of between 0.025 and 0.075 mm (0.001 and 0.003 in). A special fixture is typically fabricated to hold the specimen. Due to its thin cross section, the shim rapidly reaches the carburizing temperature and assumes equilibrium with the carbon potential of the furnace atmosphere. The actual time required will depend on the furnace temperature, carbon potential, and shim thickness, but it is typically less than 1 h.

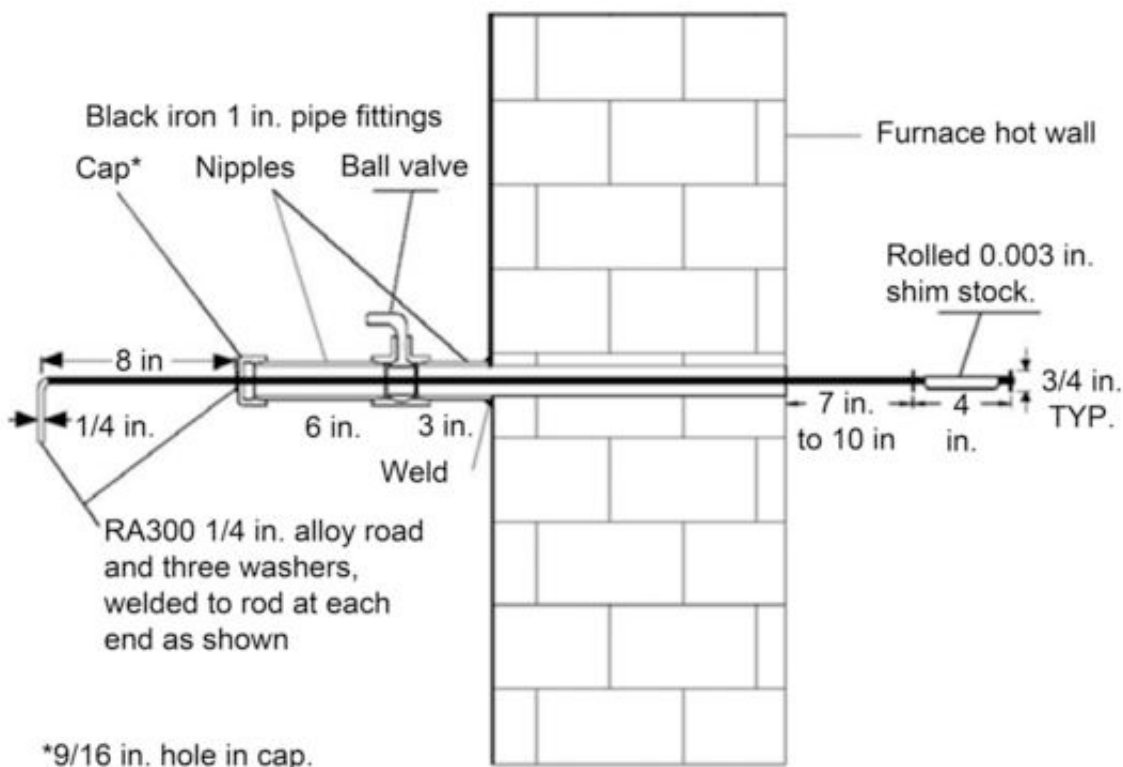


Fig. 16 Schematic of the hardware required to perform a shim stock test in an atmosphere

furnace. Source: [Ref 5](#)

Historically, the carbon content of the shim was determined by precisely weighing the shim before and after carburization and calculating the carbon pickup by the weight difference. However, with today's (2013) prevalence of combustion-type carbon analyzers, it is simpler to analyze the strip to determine the actual carbon content.

If the shim test is performed properly, the result will provide the heat treater with the carbon potential in the furnace atmosphere at the time of the test. This information can be used to select the appropriate adjustment factor to adjust the oxygen probe so that it reads the actual carbon potential of the furnace.

There are some precautions to consider when performing shim stock analysis:

- The shim should be cleaned both before and after exposure with a solvent such as alcohol to remove any residues or contamination.
- The shim test result will only be meaningful if the furnace atmosphere is stable.
- Oxidation of the test strip must be prevented because it will affect the results. It is good practice to withdraw the strip into the sample port and allow it to cool before unsealing the port and exposing the shim to air.
- The shim will only represent the particular zone or location in which it is tested. For best results, the shim port should be close to the oxygen probe. Fortunately, it is common practice for most furnace manufacturers to include a port in close proximity to the probe.
- Depending on the carbon content of the furnace, a properly prepared shim should appear either bright and clean or matte gray. Discoloration (blue or brown) indicates that the shim has oxidized. Interaction of oxygen with a hot shim will lead to decarburization of the shim and skewed carbon values.

References cited in this section

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