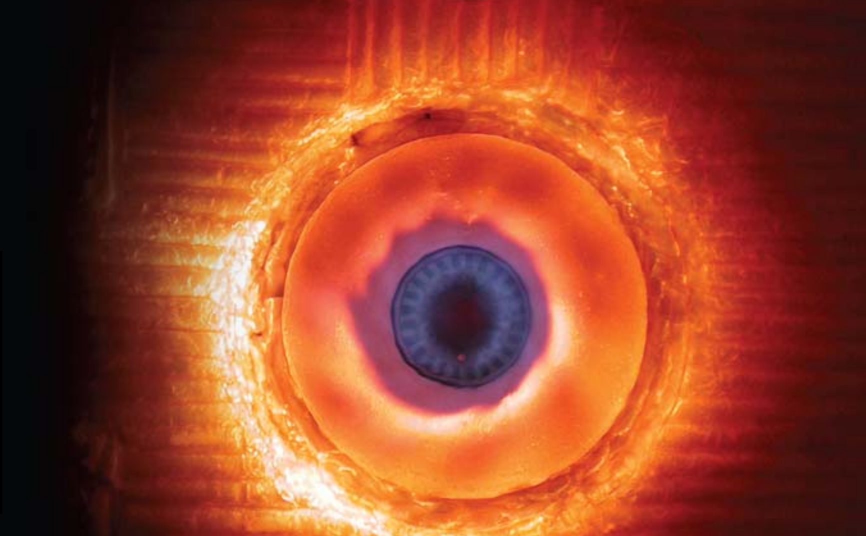
Considerations in Heat Treatment

Part One: Furnace Atmospheres

Daniel H. Herring – The HERRING GROUP, Inc., Elmhurst, Ill.



Kromschröder BIC Burner - Courtesy of Hauck Manufacturing Company

A key heat-treat consideration is the creation of an atmosphere within the furnace that is neutral to the parts being processed. This can be done a number of ways and depends on the temperature of the process and the carbon content of the parts.

A critical consideration in heat treatment is the type, consistency and control of the furnace atmosphere. The purpose of a furnace atmosphere varies with the desired end result of the heat-treating process. The atmospheres used in the heat-treat industry have one of two common purposes:

- To protect the components being processed from harmful chemical reactions that could occur on their surfaces (such as oxidation or carburization) – that is, to be passive (chemically inert) to the metal surface.
- To allow the surface of the parts to be changed (by adding carbon, nitrogen or both) – that is, to be reactive (chemically active) to the metal surface.

Types of Furnace Atmospheres

Many types of furnace atmospheres are available for use in heat treating (Table 1). In most instances, hardening and case hardening operations use endothermic gas or nitrogen/methanol systems. Most tempering operations are performed in air atmosphere as long as the presence of a tightly adherent oxide surface ("skin") will not affect the part's performance. Otherwise, an inert gas (vacuum) is selected.

Endothermic Gas Atmospheres

Endothermic gas generators are common equipment in the heat-treat shop. The main components of an endothermic generator (Fig. 1) consist of:

- Heated reaction retort with catalyst
- Air-gas proportioning control components
- Pump to pass the air-gas mixture through the retort
- Cooler to "freeze" the reaction and prevent soot formation

Endothermic gas – also called endo or Rx™ gas – is produced when a mixture of air and fuel is introduced into an externally heated retort at such a low air-to-gas ratio that it will normally not burn. The retort contains an active catalyst, which is needed for cracking the mixture. Leaving the retort, the gas is cooled rapidly to avoid carbon reformation (in the form of soot) before it is sent into the furnace.

Table 1. Common types of furnace atmospheres

Type	Symbol	Remarks
Air		Typically used in tempering operations
Argon	Ar	An inert gas
Carbon Dioxide	CO_2	A common constituent in generated atmospheres
Carbon Monoxide	CO	A common constituent in generated atmospheres
Custom Blends		Examples include alcohols and combinations of nitrogen and hydrocarbon gases
Generated atmospheres		Endothermic, exothermic, dissociated ammonia
Helium	He	An inert gas
Hydrocarbon Gases		Typically used as additions or enriching gases to furnace atmospheres. Common types include methane (CH_4), propane (C_3H_8) and butane (C_4H_{10}).
Hydrogen	H_2	A constituent of many furnace atmospheres used to aid in heat transfer and react with oxygen present.
Nitrogen	N_2	A blanketing gas that is not truly inert
Oxygen	O_2	Oxidizing to a hot steel surface
Products of combustion		Produced from a mixture of a hydrocarbon fuel gas and air, the atmosphere typically consists of high amounts of carbon dioxide and water vapor.
Steam	H_2O	Water vapor is most often used to impart a protective oxide layer.
Sulfur Dioxide	SO_2	Used in the heat treatment of magnesium alloys.
Synthetic atmospheres		Nitrogen and methanol (methyl alcohol)
Vacuum		The absence of an atmosphere

The endothermic-gas composition (Tables 2 & 3), by volume, varies depending on the type of hydrocarbon-gas feed stock.

Endothermic gas is used for neutral hardening and as a carrier gas for gas carburizing and carbonitriding. It is generally produced so that its composition is chemically inert to the surface of the steel and can be made chemically active by the addition of enrichment (hydrocarbon) gas, which is usually done at the furnace.

Nitrogen/Methanol or Nitrogen/Hydrogen Atmospheres

An endothermic equivalent gas atmosphere can be obtained by cracking liquid methanol (methyl alcohol) and combining it with nitrogen (Eq. 1), using a blend of 40% nitrogen and 60% methanol (dissociated).

$$CH_3OH + N_2 \rightarrow CO + H_2 + N_2 \quad (1)$$

This chemical reaction typically takes place inside the furnace as the liquid methanol and gaseous nitrogen are metered in through a special injector called a sparger, which atomizes the liquid and sprays it into the chamber, usually onto a hot target such as the furnace fan. The equivalent of 4 KW of heat is required per gallon to crack the methanol. One gallon per hour (3,785 ml/hour) of methanol liquid produces 241 cfh (6.8 m^3/hour) of dissociated methanol.

For some neutral-hardening applications, a gas is produced with a lower carbon monoxide value than an endothermic equivalent atmosphere (Table 3).

The most common problems with nitrogen/methanol systems have to do with the failure to properly atomize. Large droplets do not properly decompose, resulting in difficulties in furnace control. Also, methanol is corrosive to nickel alloys used for the internal furnace components (e.g., fans, radiant tubes, belts, etc.).

Other types of blended atmospheres (Table 4) produced with nitrogen and/or hydrogen are less common but have been used in some applications. The resultant atmosphere may not contain carbon dioxide (CO_2) or carbon monoxide (CO).

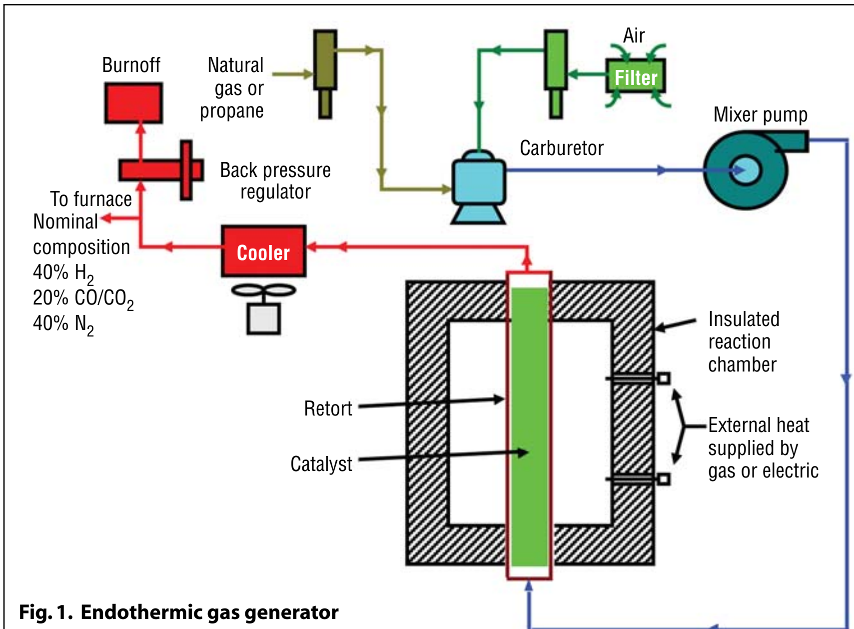


Fig. 1. Endothermic gas generator schematic piping arrangement

Table 2. Compositional ranges for endothermic gas

Gas constituent	Percentage (based on natural gas)	Percentage (based on propane)
N_2	40.9 %	40.9%
CO	19.6 %	23.3%
CO_2	0.4 %	0.1%
H_2	38.9 %	35.5%
CH_4	0.2 %	0.2%
Dew point	+20/+50°F	-10/-15°F
(Air/Gas) Ratio	2.6:1	7.8:1

Table 3. Nitrogen/methanol atmosphere field data[1]

Flow data[2]	% N_2	% H_2	% CO_2	% CO	% CH_4	Dew Point, °F (°C)
Nitrogen/methanol with natural gas and/or air enrichment	37-46	38-42	0.4–1.1	11.8–14.1	6-11	+30 to +65 (0 to +17)

Notes: A 2,000 lb/hour (900 kg/hour), 48-inch-wide (1.2-m) electrically heated mesh-belt conveyor furnace operating at carbon potential settings between 0.20-0.45%C. Approximate gas flows: 600-800 cfh (17-23 m^3/hour) nitrogen, 190 cfh methanol (3 l/hour), 200-300 cfh natural gas (6-9 m^3/hour), 40-50 cfh (1.0-1.5 m^3/hour) air.

Table 4. Comparison of synthetic furnace atmospheres

Atmosphere	Type	%H_2	%N_2	%CO	Dew Point, °F (°C)
Hydrogen	Pure	100	0	0	-95 to -120 (-70 to -85)
Dissociated Ammonia (DA)	Generated	75	25	0	- 40 to -50 (-40 to -75)
Nitrogen-DA	Blended	90	10	0	> -50
Endothermic	Generated	40	40	20	+40 to -10 (3 to -23)
Nitrogen-Endo	Blended	12	82	6	< 0
Nitrogen-Hydrogen	Blended	3–75	97–25	0	-60 (-51)

Gas Reactions

The gas reactions involved can be classified into four general categories:

- Oxidation reactions
- Reduction reactions
- Carburizing reactions
- Decarburizing reactions

Reactions Involving Oxygen

In the presence of oxygen, steel will oxidize. This tendency increases in severity as the temperature is raised. In addition, oxygen will decarburize steel. If steel is to be kept bright during heat treatment and free of decarburization, free oxygen (O_2) in the furnace atmosphere must be eliminated.

Reactions Involving Water Vapor

The water-gas reaction (Eq. 2) is the most important furnace-atmosphere chemical reaction. This equation involves the major constituents of the gas atmosphere as it controls the reactants formed on each side of the equation. The equal sign indicates chemical equilibrium – that is, the reaction can go either way, to form CO and water vapor (H_2O) or to form CO_2 and hydrogen (H_2) depending on the relative percentages of each in the furnace atmosphere.

(2) $CO_2 + H_2 = CO + H_2O$
(Water-Gas Reaction)

Water vapor and CO_2 both appear in this equation, and we can use this fact to control the carbon potential of a furnace atmosphere. In simplest terms, dew-point analyzers look at the H_2O/H_2 ratio in the water-gas reaction. Infrared analyzers and oxygen-probe devices look at the CO/CO_2 ratio in the water-gas reaction.

Water vapor is a strongly decarburizing gas. Any constituent such as CO_2 will have a tendency to form water vapor, therefore, CO_2 must also be closely controlled. In addition, to prevent decarburization by water vapor, the CO and H_2 must be present in amounts to satisfy the equilibrium condition at each temperature.

Water vapor and CO_2 oxidize and decarburize steel. Hydrogen is formed when water vapor oxidizes iron. Therefore, to prevent oxidation and to keep iron bright, a definite excess of H_2 over H_2O vapor is required for each temperature.

Reactions Involving Carbon Dioxide

CO_2 is one of the reaction products when a hydrocarbon fuel is burned in air. CO_2 oxidizes iron at elevated temperatures. To prevent oxidation, it is necessary to have an excess of CO. Therefore, to prevent oxidation, CO is a desirable constituent. CO_2 is not only oxidizing to steel but it is extremely decarburizing. To prevent decarburization, CO_2 must be controlled very closely. The actual amount depends upon the CO content, temperature and the carbon content of the steel.

Reactions Involving Carbon Monoxide

CO is a strong carburizing agent. The reversible reaction of CO to form carbon (C) and CO_2 is of particular interest in a furnace atmosphere. CO has a high carbon potential and becomes increasingly more stable at elevated temperatures. It is only at lower temperatures (900-1350°F) that CO will supply carbon (Eq. 3) in the form of soot in the so-called carbon-reversal reaction. Soot causes most of the maintenance-related issues with gas generators and heat-treating furnaces.

(3) $2CO = C + CO_2$

Reactions Involving Nitrogen

Below about 1850°F, molecular nitrogen (N_2) will not react with the surface of steel or stainless steel. However, atomic nitrogen (N), which does not normally occur in a furnace atmosphere unless it is purposely introduced by the addition of ammonia (NH_3), will react by being absorbed into the steel surface.

Reactions Involving Hydrocarbons

Methane and other hydrocarbons (propane and/or butane) are carburizing agents. At elevated furnace temperatures, methane (CH_4) breaks down into carbon (C) and H_2. The higher the furnace temperature, the greater the tendency for CH_4 to break down. Because of this tendency, CH_4 and other hydrocarbon gases are introduced into the furnace to help change the atmosphere from neutral to one with a high carbon potential (the driving force of carbon into the surface of the steel).

Table 5. Volume changes required for safe purging of furnaces

Number of volume changes	Percentage (%) of air remaining
0.1	90.48
0.2	81.87
0.3	74.08
0.5	60.65
1.0	36.79
2.0	13.53
3.0	4.98
4.0	1.83
5.0	0.67

Atmosphere Volume Requirements

During operation, the volume of protective atmosphere required for safe use in a particular heat-treating furnace and the ability to properly control that atmosphere depends to a great extent on the:

- Type and size of furnace
- Presence or absence of doors and/or curtains
- Environment (especially drafts)
- Size, loading, orientation and nature of the work being processed
- Metallurgical process involved

In all cases, the manufacturer's recommendations should be followed for gas introduction, purging and removal since the original equipment manufacturer has taken these factors into account during the design of the equipment.

National Fire Protection Association (NFPA) Standard 86, "Standard for Industrial Furnaces Using a Special Processing Atmosphere," applies to all furnaces, and the procedures listed within this standard must be followed.

A "rule of thumb" to remember is that to purge air out of a furnace prior to introduction of a combustible furnace atmosphere requires a minimum of five volume changes of the chamber (Table 5). This is to ensure that the oxygen content of the chamber is below 1% prior to the introduction of the atmosphere.

Important Cautions

In order to interpret furnace-atmosphere data correctly it is important to understand the whole picture, including knowing how the data was collected as well as understanding the exact furnace operating conditions at the time the data was collected (e.g., zone temperatures and gas flows, furnace pressure, exhauster settings, fan rotation and speed, etc.). Part two of this article will discuss atmosphere-control techniques. **IH**

References:

1. Herring, D. H., *Understanding Furnace Atmospheres, Atmosphere Operation and Atmosphere Safety*, Heat Treating Hints, Vol. 1 No. 7.
2. Mr. Thomas Philips, Air Products & Chemicals (www.airproducts.com), private correspondence.

For more information: Contact the author at The HERRING GROUP, Inc., P.O. Box 884, Elmhurst, IL 60126; tel: 630.834.3017; fax: 630.834.3117; e-mail: dherring@heat-treat-doctor.com; web: www.heat-treat-doctor.com

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