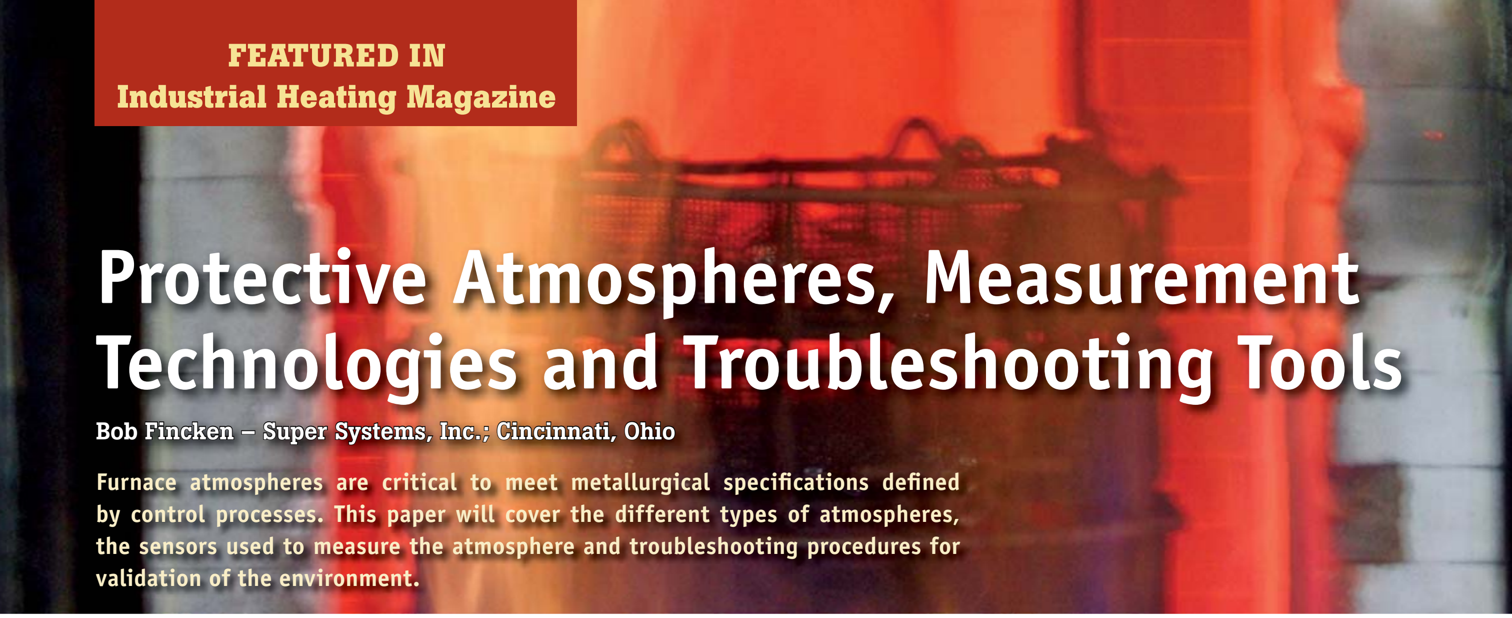

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Protective Atmospheres, Measurement Technologies and Troubleshooting Tools

Bob Fincken – Super Systems, Inc.; Cincinnati, Ohio

Furnace atmospheres are critical to meet metallurgical specifications defined by control processes. This paper will cover the different types of atmospheres, the sensors used to measure the atmosphere and troubleshooting procedures for validation of the environment.

The makeup of a furnace's atmosphere in the heat-treating process varies based upon the application.

Endothermic Atmosphere

Typical endothermic-gas generators supply an atmosphere using air and hydrocarbon gas, which are mixed and passed over nickel-bearing catalyst at about 1900°F. Using methane (CH_4) mixed at an air-to-gas ratio of 2.77:1, a properly functioning generator will theoretically produce an endothermic gas consisting of 20% carbon monoxide (CO), 40% hydrogen (H_2) and 40% nitrogen (N_2). Using propane (C_3H_8) in lieu of CH_4 and an air-to-gas ratio of 7.16 to 1, the resulting endothermic-gas composition will be approximately 24% CO, 32% H_2 and 44% N_2. The gas is then cooled to maintain the integrity of the gas composition. Correct cooling of the gas is critical to avoid CO from reversing into carbon (soot) and CO_2. This is the base atmosphere used in the carburizing process. A few assumptions must be made when determining carbon potential in the furnace with a supply of endothermic gas. Measuring this atmosphere can be accomplished in a number of ways. The focus of this article is use of oxygen sensors, dew point and infrared measurement.

Fig. 1. Composition of exothermic gas

	Rich exogas	Medium-rich exogas	Lean exogas
CO	11%	8%	5%
CO_2	5%	7%	9%
CH_4	5%	5%	5%
H_2	14%	10%	5%
N_2	Balance	Balance	Balance

Nitrogen Methanol

When used in a furnace at the typical operating temperatures, the methanol immediately dissociates into CO and H_2. When 60% methanol is mixed with 40% nitrogen, an endothermic-equivalent atmosphere is formed in the furnace.

$$2\ CH_3OH \rightarrow 33\%\ CO + 66\%\ H_2$$

Endothermic-equivalent gas =
$$19.8\%\ CO + 39.6\%\ H_2 + 40.6\%\ N_2$$

Methanol (methyl alcohol) has a boiling point of 149°F (65°C). One gallon of MeOH = 237 CFH of H_2 and CO. To calculate the correct flow of methanol and nitrogen required, divide the total furnace flow required by 1.6, then multiply by 66% for your N_2 and 33% for your methanol.

For example, if you require 400 SCFH, the results would be the following:

N_2 = 400/1.6 = 250 * 0.66 = 165 SCFH
MeOH = 400/1.6 = 250 * 0.33 = 82.5 SCFH

Assumptions are made when determining carbon potential. Using sensors and the base atmosphere in the furnace under equilibrium conditions, these assumptions must be consistent, known and repeatable.

Exothermic Atmosphere

Exothermic gas is the by-product of combustion and is widely used in the annealing process. Hydrocarbon gases such as natural gas, propane or butane are burned in an exothermic gas generator with air to create a rich or lean mixture based on the air-to-gas ratio. Rich, medium and lean mixtures are described in Figure 1. The mixtures do contain high moisture content.

Measuring an Endothermic Atmosphere in a Generator

The most common measurement of this atmosphere is confirmed by using a dew-point measuring device or an oxygen sensor. Dew point is the temperature and pressure at which gas begins to condense into a liquid. The dew-point measurement is accomplished by taking a sample of the atmosphere after the cooling section of the generator.

Using an oxygen sensor to measure and control the dew point in an endothermic generator is done via a calculation in the dew-point control instrument. This calculation uses the oxygen millivolts generated by the sensor, the hydrogen factor of the controlling instrument and the temperature of the oxygen sensor. The temperature is required for the calculation, but the dew point of the gas is not temperature dependent. Oxygen sensors are often installed at 1900°F (1038°C), although they will provide the same reading when operating at 1500°F (816°C). The generator gas exiting the retort is sent through a heat exchanger to freeze the composition. As long as the sensor is accurately measuring the oxygen millivolts of the gas, the temperature of the sensor can be as low as 1100°F (593°C).

Changes in sensor location have occurred over the years. Initially, a sensor would be mounted on the top of a retort in an air-cooled fabricated fixture to measure

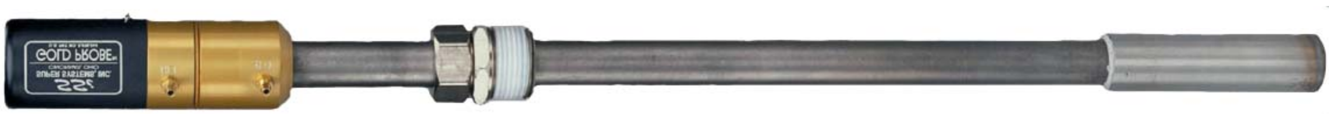

Fig. 2. Oxygen sensor with modified aluminized sheath with an integral reheat well

the oxygen. Then, a ceramic reheat well mounted through the sidewall of the generator was used. Now, a modified sheath with an integral reheat well makes the installation much easier. The sheath and the integral well are aluminized prior to assembly (Fig. 2). The nickel in the RA330 sheath material does not react with the endothermic gas. This is especially important between 900-1300°F, where the endothermic reaction will reverse over time if nickel is available. This type of design has the ability to run at lower temperatures, thus allowing many years of operation.

Lambda-style probes like those used in an automobile engine are used in generator applications, but they do not provide the long-term stability of the zirconia technology and must be re-oxidized to avoid drift.

Dew-point cells, like those used in portable units to verify the generator, can also be applied for continuous monitoring and control. A dew-point cell must provide good filtration and avoid water contamination for long-term stability.

Measuring an Endothermic Atmosphere in a Furnace

Dew point, shim stock and carbon sensors have traditionally been used to measure the endothermic atmosphere in a furnace. The carbon sensor is actually measuring the oxygen content in the furnace, which is why the terms oxygen and carbon probe are synonymous. An oxygen probe used in-situ for a furnace application has been the standard of the industry for years. Because of the durability, reaction time and continuous measurement, it is the most common form of control.

The oxygen probe will also react with the by-products of combustion if the furnace is gas fired and has a cracked radiant tube. The oxygen will dilute the atmosphere in the heat chamber when the furnace goes to high fire. As a result, the carbon controller will compensate by calling for more enriching gas to increase the carbon potential. This can often be identified on a chart or digital recorder with a saw-tooth look to the carbon trend (Fig. 3). Setting the control to low fire will eliminate the saw-tooth effect and prove the leaky tube as the issue. The next step is to determine which tube is the problem.

When using an oxygen sensor in a carburizing atmosphere, it may require air burnouts. The burnout frequency can be determined by the carburizing process in use.

A burnout consists of at least 10 CFH of air piped to the burn-off fitting on the head of the probe. Pumped room air or filtered combustion air are most commonly used. It is important not to use compressed air due to the contamination of water and oil often present, which can damage the oxygen probe. The carbon controller should control the frequency of the burnout and the duration. If this is not controlled by the carbon controller, excessive gas will be used while the burn-off is taking place to compensate for the flow of air to the probe. Burnout flow and duration recommendations vary by manufacturer based on sheath diameter and tip design. It is good practice never to exceed 90 seconds to avoid overheating the tip of the probe (Fig. 5).

A consistent way to verify a correct burnout is to monitor the oxygen millivolts of the carbon controller during the burnout phase. If a proper burnout is taking place, the oxygen millivolts will drop below 200. This can also vary based upon the circulation in the furnace and the probe placement. If you are not able to reduce the millivolts based on the air supply available, you can turn off the circulation fan. This will allow the concentration of air passing across the tip not to be diluted.

Fig. 3. Furnace chart displaying control with a cracked radiant tube

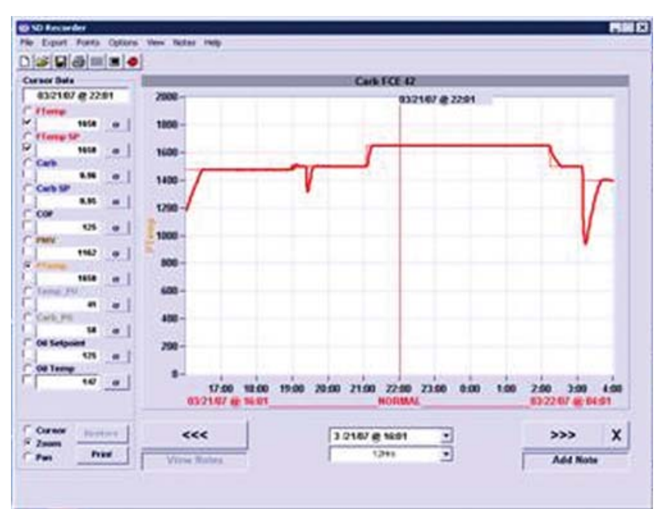

Fig. 4. Furnace chart displaying control with an intact radiant tube

Fig. 5. Recommended carbon-sensor burnout

Atmosphere type	Frequency of sensor burnout	Duration of sensor burnout	Flow of burnout air
Neutral	24 hours	90 seconds	Minimum 10 CFH
High carbon	8-12 hours	90 seconds	Minimum 10 CFH

Take great care not to leave the fan off for more than 120 seconds.

A possible side effect of extended burnout duration is the oxidation of the tip of the sensor. The problem can manifest itself with oxygen millivolts being elevated over time, which will require a lower CO factor setting for the same calculation of carbon. Consideration should be made for the duration of the burnout based upon the carbon level in the furnace.

A non-dispersive infrared (NDIR) three-gas analyzer can be used to measure the atmosphere in a furnace or generator. The consistency of the endothermic gas produced at the generator significantly affects all downstream processes. In order for the atmosphere to be controlled consistently and accurately in the furnace with an in-situ sensor, it assumes the content of the endothermic gas. You should always view values between 18.8 and 20.5 for CO. The CO_2 should be between 0.25 and 0.50 with a preferred value of 0.40 CO_2. The dew point in Fahrenheit can be calculated by multiplying the CO_2 by 100. If methane (CH_4) has a value of 0.50 or less, the generator is performing correctly. If the CH_4 is over 0.50, there may be a problem.

It is advisable to burnout the generator as quickly as the facility can take the generator off line. If after burn out the CH_4 climbs back above 0.5 within a week or two, then replace the catalyst. If the catalyst is depleted, uncracked CH_4 from 0.50-8.0 will be present. As a result, a low dew point (CH_4 uncracked is very dry) and an increase in the air ratio will occur. The end result will be a wet gas with soot and water coming out of the generator. The furnace will try to compensate by adding more gas. Based on NDIR gas readings with CH_4 exceeding 0.5%, a generator burnout is recommended.

To perform a generator burnout, stop the endothermic gas flow, reduce the temperature of the generator to 1600-1650°F and start flowing air up to 10% of the total endothermic flow. One should see a flame at the effluent. Once the available carbon is burned, the flame will go out. The lower temperature protects the retort in case of a carbon deposit. If there is a carbon deposit present and the temperature is not reduced, a localized area may increase dramatically in temperature and damage the retort.

Measuring a Nitrogen Methanol Atmosphere in a Furnace

If measuring at the furnace using NDIR, one should see 14.0-28.0% CO. An ideal CO measurement is 20%. In addition, the CO_2 (depending on carbon setpoint) will be from 0.10-0.80 CO_2. The CH_4 should be zero or as high as 8% depending on carbon setpoint. All testing should be done with a zero carbon setpoint and no CH_4 additions, if possible.

If the mixture is set incorrectly and a higher ratio of methanol to nitrogen is ob-

Industry Requirements for Carbon Control

Industry specifications and customer-specific guidelines dictate many of the processes that are put in place by heat treaters. CQI-9, SAE and AMS all call out steps that involve verification of accuracies related to control devices and sensors used in atmosphere control. CQI-9 even calls for management to review furnace data and alarm conditions every 24 hours with documentation that it has been reviewed.

When it comes to atmosphere, the heat-treat process and your control method will dictate the tools used for continuous measurement and secondary verification. CQI-9 specifically dictates that generator and furnace atmosphere shall be automatically controlled and documented except in furnaces that cannot support in-situ devices. Called-out methods for atmosphere control are oxygen probes or online infrared (IR) gas analysis. The heat treater is responsible for developing a control plan to define what are acceptable parameters regarding the tolerances for control. Many times, this is dictated by the customer or parts that are being heat treated. Heat treaters are required to have a backup method for verifying the atmosphere. These methods include shim stock, gas analysis, wire resistance, carbon bar, etc.

AMS 2759 is the general requirement defined by the SAE Aerospace group for the heat treatment of steel. The requirements of this document are a collaborative effort through a committee to ensure consistencies on heat-treating steps and end results that should be achieved. Within the AMS 2759 specification, additional documents are referenced. Specifically of interest is AMS 2759/1 and AMS 2759/2, which are the heat treatment of carbon and low-alloy steel. This specification does not specifically dictate how the atmosphere is to be controlled, but it does have requirements on tolerances that need to be achieved. AMS 2759/7 is the specification for Gas and Vacuum Carburizing and Heat Treatment of Carburizing-Grade Steel Parts. This specification does state that carbon potential shall be controlled and recorded by automatic equipment and that manual equipment may be used to verify the automatic equipment. The accuracy of the atmosphere control instruments is not specifically called out, but there must be a procedure in place to ensure the equipment is operating properly.

served, the readings may show a CO level below 20%. The CO_2 may be 0.60% or higher and the level of CH_4 between 2-4%. The CH_4 is actually uncracked methanol. Reduce the methanol flow and increase the N_2 until a 20% CO is observed and CH_4 and CO_2 readings are reduced. It is always good to figure out the gas mixtures with no CH_4 additions to start out.

Reasons for problems with nitrogen methanol might be flow mixture settings, plugging of the sparger, no sparger or nitrogen bubbles in the supply line. This may be due to pressurizing the methanol liquid with N_2 or a low methanol tank that requires a refill. Another problem may be a furnace that is not tight, allowing air to infiltrate.

If you are measuring an endothermic-generator-based atmosphere of a furnace, the trim gas can be turned off. This can be accomplished by setting a zero setpoint or by placing the atmosphere controller in manual mode and setting the output to zero. The gas measured should be the same as the generator. Always start at the generator to get a baseline. At the furnace, the CO should be slightly lower. If the generator was 20% CO, at the furnace 19.5% CO would be common. A CO_2 of 0.40 at the generator should result in a 0.40 to 0.45 CO_2 at the furnace. A CH_4 measurement at the furnace with no gas addition should be 0.50 or less.

After proving the generator's gas composition is accurate, enter a carbon setpoint and observe the three gases as they change. The CO will drop a little, the CO_2 will also go down and the CH_4 will go up. The higher the temperature, the more CH_4 will be converted into 20% CO, 40% H_2 and 40%N_2. All of this depends upon the temperature of the furnace and how much air infiltration of the furnace exists. Final readings should not be recorded until the carbon percentage and temperature are stable.

When measuring these various protective atmospheres, choosing the type of device needed may depend upon cost, longevity of operation and the amount of information required to properly run a process. The oxygen probe has proven itself to be a dependable, consistent device repeatable in operation. Dew-point measurement, while functionally the same over many years, has taken advantage of modern electronics to provide a more durable and easy-to-read display. NDIR has become the tool of choice for processes providing the most information available to help make a decision regarding changes to a process or the peace of mind that the process is within operating requirements. **IH**

For more information: Contact Bob Fincken, national sales manager, Super Systems, Inc., 7205 Edington Dr., Cincinnati, OH 45249; tel: 513-772-0060; fax: 513-772-9466; bfincken@supersystems.com; web: www.supersystems.com

Additional related information may be found by searching for these (and other) key words/terms via BNP Media SEARCH at www.industrialheating.com: oxygen sensor, dew point, infrared, NDIR, endothermic-equivalent atmosphere, exothermic atmosphere, CQI-9, AMS 2759