

Annealing of Wire Products: Atmospheres

by:

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The previous installment of this article series discussed annealing principles. Even with a relatively simple heat treatment, there are a number of factors that must be carefully considered and controlled. One of the most important is the furnace atmosphere that surrounds the parts as they heat and cool. This installment, part four of the series, discusses furnace atmospheres, atmosphere controls and common problems.

present as measured by use of an oxygen analyzer. The "rule of thumb" of five volume changes in an hour is often used to establish the required flowrate.¹

The purpose of a furnace atmosphere varies with the desired end result of the heat-treating process. In general, the atmospheres used in the heat-treating industry have one of two common purposes:

- To protect the material being processed from chemical reactions that could occur on their surfaces (e.g. oxidation), that is, to be passive (or chemically inert) to the metal surface.
- To allow the surface of the material being processed to change (e.g. adding carbon, or nitrogen, or both), that is, to be reactive (or chemically active) to the metal surface.

When annealing wire, rod and similar products, we most often want the atmosphere to protect the product in question rather than be reactive with it. Air atmospheres or those using products of combustion from direct-fired burners are not capable of preventing steel parts, for example, from oxidation or decarburization. It is for this reason that various protective atmospheres (generated, pure, or mixed) are used (Table 1). The type of gas or gas mixtures used depends on the metal being treated, the treatment temperature, part contamination limits and the surface requirements of the product being annealed. Atmosphere control is often an important consideration as well.

Purging is another critical first step in the annealing process and should take place when the workload is cold (prior to heating). Nitrogen or lean (non-combustible) Exothermic gas are common choices and purging is considered complete when less than 1% oxygen is

Table 1². Typical Atmosphere Types & Composition.

Atmosphere	Type	% H ₂	% N ₂	% CO	% CO ₂	Typical Dew Point °C (°F)
Endothermic	Generated	37.5 - 40	40	20	1 - 1.5	-1 to 10 (+30 to +50)
Exothermic (Rich)	Generated	12 - 14	71 - 76	8 - 10	4 - 6	+38 to -40 (+100 to -40)
Dissociated Ammonia	Generated	75	25	0	0	-40 to -75 (-40 to -50)
Hydrogen	Pure	100	0	0	0	-70 to -85 (-95 to -120)
Nitrogen-DA	Diluted	90	10	0	0	-45 (-50) or better
Nitrogen-Hydrocarbon	Blended	90 - 98	2 - 5	1 - 5	0.50	-60 (-80) or better
Nitrogen-H ₂	Mixed	3 - 5	95 - 97	0	0	-51 (-60)
Nitrogen-Methanol	Blended	35 - 40	38 - 45	20	1	-60 (-80) or better

Types of Annealing Atmospheres

Characteristics of the most common annealing furnace atmospheres can be summarized as follows:

Nitrogen & Nitrogen-Hydrocarbon Blends. Pure (100%) nitrogen atmospheres are seldom used in annealing as they are not air (oxygen) excluding. Leaks or other sources of air infiltration cannot be compensated for. However, nitrogen is often blended with small percentages of hydrocarbon gas (methane, propane, propylene) or combined with methanol (CH₃OH) to create a suitable atmosphere provided it is properly controlled (see below). The nitrogen-hydrocarbon flows are often dictated by a predetermined recipe (Figure 1).

Hydrogen & Hydrogen-Nitrogen Blends. Annealing under a controlled atmosphere of 100% hydrogen prevents oxidation and product discoloration. Hydrogen is a highly reducing gas, so hydrogen annealing promotes "surface cleaning" of oxidized parts by reducing the oxides present on the wire. It is commonly referred to as "bright annealing". Hydrogen may decarburize steel parts, so appropriate cautions must be taken. From an economic perspective, an atmosphere of 100% hydrogen is the most expensive. Lower cost nitrogen-hydrogen blends can also be used effectively.

Dissociated Ammonia. Dissociated ammonia is produced by the cracking (dissociation) of ammonia into a gas having a composition of 75% hydrogen, 25% nitrogen. It has many of the same benefits as hydrogen but can be supplied at lower cost.

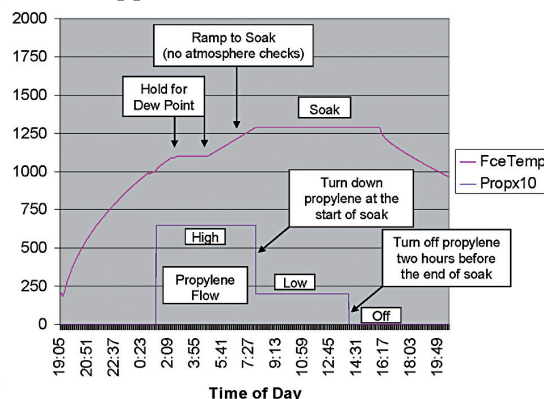


Fig. 1³ — Typical annealing cycle (nitrogen-hydrocarbon mixture).

Exothermic Gas. Rich exothermic gas is generated by partially combusting an air-gas mixture of (approximately) 6.5 parts of air to one part natural gas. Other hydrocarbon fuels can be used as well. Exothermic gas is the most widely used protective atmosphere for annealing, especially for annealing of low-carbon steel. However, it will decarburize medium-carbon and high-carbon steels because of the carbon dioxide and water vapor necessitating the use of coolers, reducing dew point from typically +38°C to 4.5°C (+100°F to +40°F), and in some cases refrigerant dryers further reducing dew point from typically +4.5°C to -40°C (+40°F to -40°F) when concerns about decarburization exist.

Purified rich exothermic gas, in which carbon dioxide (CO₂) levels are lowered to less than 0.1% CO₂ (typically 800 ppm or less), is used for short-cycle annealing and process annealing of medium and high-carbon steels of the straight-carbon and certain alloy types. However, for long-cycle annealing the high carbon monoxide (CO) content results in soot deposits on the work and other surface effects as a result of the relatively long soak times in which the work is in the critical low-temperature range of 700°C to 480°C (1300°F to 900°F) where these adverse gas reactions can occur. In short-cycle annealing, these effects are minimal, and in some instances, high CO gas is desirable because of its high carbon potential. Purified lean exothermic gas is sometimes used for long-cycle annealing of medium and high-carbon steels of the straight-carbon and alloy types.

Endothermic Gas. 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 2.5:1 to 3.5:1 air-to-gas ratios. 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. An Endothermic gas atmosphere requires carbon control for precise and repeatable carbon levels.

Vacuum. Vacuum is the absence of an atmosphere and represents the most ideal condition under which annealing can take place. Vacuum annealing, which can also be done in a partial pressure atmosphere of an inert (nitrogen or argon) or reactive gas (hydrogen) is sometimes referred to as “bright annealing” due to the surface finishes produced. However, it is also the most costly, time consuming and least conducive to mass production so for these reasons it is usually restricted to only certain materials (e.g., titanium, tantalum).

Control Schemes

The composition of the furnace atmosphere is constantly changing so we must use measurement and control devices (**Figure 2**) to ensure good metallurgical quality control. This is accomplished by making sure that several of the following control methods are monitoring and/or controlling the process:

- Dew point analysis.
- Infrared analyzer (single or multiple gas analyzers).
- Oxygen probes.

The trend today is to use multiple measurement tools to

get the most accurate snapshot of the atmosphere in real time. A typical process involves the following steps:

- Purge the retort with nitrogen until the oxygen level drops below 1%.
- Introduce the gas atmosphere (e.g., Endothermic) and cut back the flow of nitrogen when the temperature reaches approximately 900°F (480°C). Often blends (e.g., 50% Endo, 50% nitrogen) are used to produce a gas with 9% to 12% carbon monoxide (CO) so that the parts will not carburize or oxidize.
- Heat to annealing temp, soak and ramp down.

Oxygen Measurement. The measurement of oxygen is important to judge both the effectiveness of the purging cycle (<1% O₂) at the beginning of the run as well as the effectiveness of the atmosphere during cooling (ppm range). Oxygen analyzers and oxygen probes are used for this purpose. Many annealing applications use a specific millivolt range from the probe as the control parameter.

Gas Analysis Methods. A dew point analyzer is often used to measure the amount of water vapor present in the furnace atmosphere (**Table 2**). Dew point is defined as the temperature that water vapor starts to condense. Also, it is common practice to use infrared gas analysis to measure carbon dioxide (CO₂) levels in the furnace. Both methods are considered indirect measurement techniques since they involve extracting a gas sample.

Dew point, infrared (three-gas analyzers) and oxygen probes provide measurements commonly used to monitor the furnace atmosphere. The latter is an in-situ measurement device (it does not rely on a sample being drawn from the furnace). It is important to recognize that contaminants present on the wire or rod will tend to volatilize off during the initial heating phase. These contaminants must be removed by flushing (i.e., volume changeover) of the atmosphere and the atmosphere must be stable prior to the onset of further

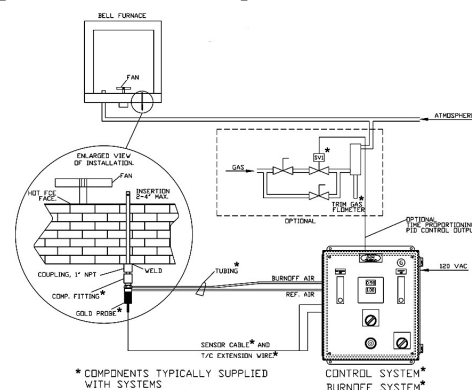


Fig. 2⁴ — Typical bell annealing furnace sampling system (schematic courtesy of Super Systems, Inc.).

Table 2³. Typical Dew Point Levels.

Dew Point, °F (°C)	Water Vapor (ppm)
+46 (+8)	10,590
+25 (-4)	4,320
0 (-18)	1,240
-40 (-40)	127
-90 (-68)	3.4

Note: 1% moisture = 127 ppm water vapor = +40°F dew point

Annealing of Wire Products ...continued

heating or soaking at temperature.

In another example, a properly controlled nitrogen/propylene atmosphere can be used to achieve repeatable results on subcritical annealing of ferrous wire and wire rod⁵. The balance of process parameters and cost include:

- Accurate and repeatable measurement/inference of decarburizing agents that occur at trace levels (O₂, H₂O, and CO₂).
- Integration of the temperature control with the atmosphere control.
- Control of the ramp from 1100°F (590°C) to the final soak temperature, typically 1300°F (705°C) in order to prevent decarburization.
- Avoidance of carbon deposition (soot) by shutting off the propylene during soak after all major reactions are complete.
- Lowering nitrogen flows to absolute minimum
- Using additional higher flows of propylene to speed up cycle time (leading to cost savings in fuel, electricity and nitrogen)
- Controlling depth of partial decarburization to meet specific wire manufacturing requirements.
- Reducing/eliminating the air burnoff segment to introduce less oxidation and speed-up the ramp time on subsequent cycles.

Annealing Equipment

Annealing can be performed in batch or continuous furnaces. The most common type of furnace used for annealing of steel coils is a bell type furnace (**Figure 3**, **Figure 4** and **Figure 5**). Car bottom, box and pit furnace styles are also used for batch loads.

Bell Annealing (**Figure 6**) heats batches of metal that are placed on a base assembly, enclosed by an inner cover, and covered by the heating bell (furnace). An overhead crane is used to load the base and move the heating bell that is suspended from a crane. The base assembly normally includes a fan (optional) to provide a source of convection heating to enhance the heat transfer to the charge. The inner cover seals in the desired atmosphere and protects the charge from the heating source. Direct fired, tangentially fired, radiant tube, and electric elements are common heating methods. After annealing, cooling is performed by removing the heating bell but leaving the inner cover in place to maintain the protective atmosphere. If a bright finish is desired, the metal must be cooled to near ambient temperature before opening the workload to air. A gas to water heat exchanger or forced-cooler system is often used to shorten the cooling times, especially at low temperatures. The forced-cooler replaces the heating bell at the end of the heating cycle and circulates air or sprays a fine water mist to accelerate the cooling of the outside of the inner cover.

Annealing Problems

Microstructural Issues. In heat-treating, changes happen to the internal structure (or microstructure) of the material and are not readily apparent to the naked eye.



Fig. 3⁶ — Typical workload (bell annealer).



Fig. 4⁶ — Retort being lowered into position.



Fig. 5⁶ — Heating bell being lowered in place.

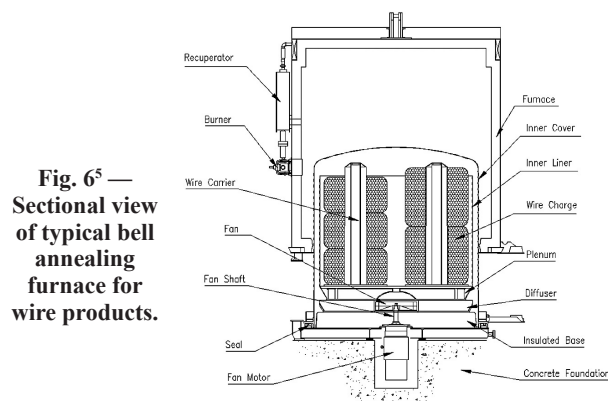


Fig. 6⁵ —
Sectional view
of typical bell
annealing
furnace for
wire products.

This is one of the reasons why process and equipment induced variables must be tightly controlled. For example, for many cold heading components, process anneals are used to try to obtain a spheroidized microstructure (as opposed to a more lamellar structure). If lamellar, in general, the more open (i.e. further apart) the lamellar structure, the softer and more easily worked. A typical low carbon steel microstructure (**Figure 7**) consists of ferrite (white areas) and pearlite (dark areas). Pearlite is a combination of ferrite and iron carbide (Fe_3C).

Properly distributed carbides are acceptable in most wire drawing operations. However, some process annealing cycles (**Figure 8**) produce agglomerated carbides (white globular regions) outlining the grain boundaries (i.e. necklacing) the result of which is that the wire will be more difficult to draw down to a smaller size without internal tears or breakage.

The presences of non-metallic inclusions, as well as the matrix microstructure are also important considerations. The carbon content and cleanliness of the steel influence the volume fractions of ferrite, pearlite and carbide – and what form the carbide is in (fine versus coarse) as well as the morphology of those particles – their size, shape and distribution. For example, fine wire drawers (e.g. tire wire, valve spring wire) are adamant about excluding non-deformable oxides, sulfides, carbides and nitrides for forming and fatigue reasons. Equally undesirable is carbon segregation especially along the centerline of the wire since it creates islands of martensite.

Decarburization. By definition, decarburization is a result of (usually unintentionally) removing carbon from the surface of steel when it is heated and held at temperature or when in contact with certain types of furnace atmosphere (**Figure 9**). The result is a change in mechanical properties at the surface, most notably lower surface hardness and loss of fatigue resistance. Decarburization can be total (100% ferrite or “free” ferrite) or partial and can vary in depth from a few ten thousandths to several thousandths of an inch but in most cases no more than 2% of the total thickness of the material. Carbon restoration can be used to reverse the effects of decarburization by driving carbon back into the surface of the rod or wire.

Soot. A carbon bearing furnace atmosphere can become out of control and cause sooting (carbon deposits) to occur on the wire surface (**Equation 1**). This Boudouard (or gas producer) reaction may occur in a CO rich furnace atmosphere in the critical range of 500°C (932°F) to 300°C (572°F). Of equal concern is carbon pickup that in some cases results in surface cracking.



Summing Up

The choice and control of the furnace atmosphere is critical to the success of the annealing process.

Furthermore, each step in the annealing process must be well understood in order to achieve the proper microstructure, grain size and mechanical properties in the annealed wire.

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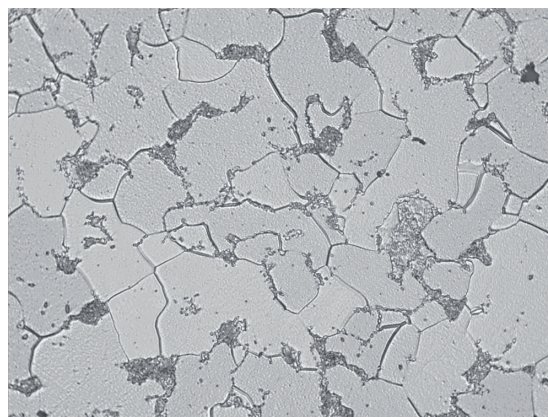


Fig. 7⁷ — Process annealed microstructure – low-carbon steel (photomicrograph courtesy of Aston Metallurgical Services Co., Inc.).



Fig. 8⁷ — Process annealed microstructure – low-carbon alloy steel (photomicrograph courtesy of Aston Metallurgical Services Co., Inc.).

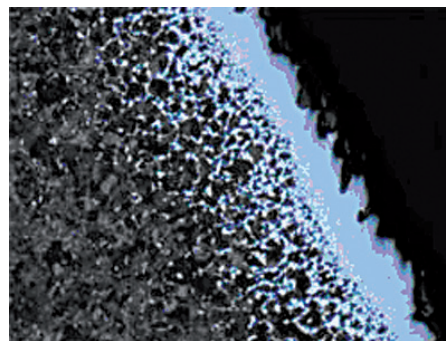


Fig. 9 — Decarburization surface microstructure.

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