Protective atmospheres for annealing and hardening steel

There are basically only two heat treatments carried out on semi-finished steel - heat and slow cool; and heat and quench. Finished components are often given a range of further thermochemical treatments, described in the automotive industry white paper. Ideally for both basic treatments the atmosphere within the furnace should not be oxidising, carburising or decarburising. These aims are not incompatible and many atmosphere systems will provide them with varying degrees of success. The most demanding processes are the ones that involve slow cooling or entail a need to prevent low temperature oxidation.

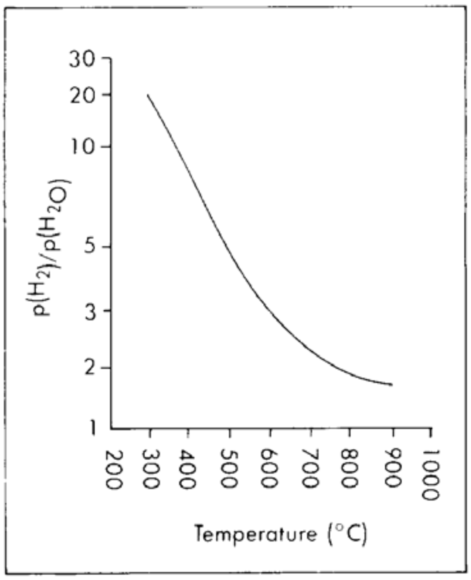
Eliminating oxidation is very simple in theory: All that is needed is to reduce the oxygen potential of the atmosphere below that required to oxidise iron. This should be achievable using very pure nitrogen but in practice even commercial high purity nitrogen contains enough free oxygen (up to 5vpm) to oxidise iron.

So, a positively reducing atmosphere is needed, and can be produced by reacting air with a hydrocarbon fuel gas either within the furnace or externally in an atmosphere generator. A slight excess of hydrocarbon will ensure that all the oxygen in the air is eliminated. Such reactions have proved difficult to control in the furnace with any degree of consistency [1]; nevertheless, the use of an internal or external exothermic generator with a hydrocarbon fuel gas has been the most popular method [2]. The products of combustion, (water and carbon dioxide) can be removed before the remaining gases, mainly nitrogen with up to 10% carbon monoxide and hydrogen, are fed into the furnace [3].

1. Nitrogen/hydrogen atmospheres

An alternative to a generated atmosphere is high purity nitrogen to which a small proportion of hydrogen has been added. Any leakage of oxygen into the furnace reacts with the hydrogen and, provided the leak rate is not too high, the H_2:H_2O ratio will be high enough to prevent oxidation.

Hydrogen reacts rapidly with oxygen to form water vapour at all normal heat treatment temperatures [4]. Under these circumstances, as all the oxygen has been consumed and no hydrocarbons are present, water is the only oxidant that needs to be considered.



The oxidation limit for iron

The hydrogen:water ratio is the most important factor that determines the oxidation/reduction potential of the atmosphere. The minimum hydrogen:water ratio required to suppress the oxidation of iron at

900°C is 1.6, but it rises increasingly rapidly with falling temperature, reaching 2.3 by 700°C and 20 by 300°C. So it is relatively easy to maintain reducing conditions in the hot zone of an annealing furnace with small hydrogen additions, but in the cooling zone the task becomes increasingly difficult.

In the hot zone of a typical annealing furnace with a nitrogen/3% hydrogen atmosphere, keeping the water content below 2% (18°C dewpoint) is sufficient to keep the steel bright but in the cooling zone of the same furnace the water content must be reduced below 0.03% (-32°C dewpoint) to avoid oxidation. In some critical applications where oxygen cannot be kept out to maintain the required levels, extra hydrogen may have to be added to the cooling zone to achieve the necessary product quality.

As nitrogen/hydrogen atmospheres contain no carbon-bearing compounds, they are intrinsically decarburising. The decarburising potential depends on the ratio of the hydrogen and water partial pressures:

$$C_{Fe}+H_2O \rightarrow CO+H_2 \qquad (1)$$

$$\text{Carbon potential} = \frac{K.p(H_2).p(CO)}{p(H_2O)} \qquad (2)$$

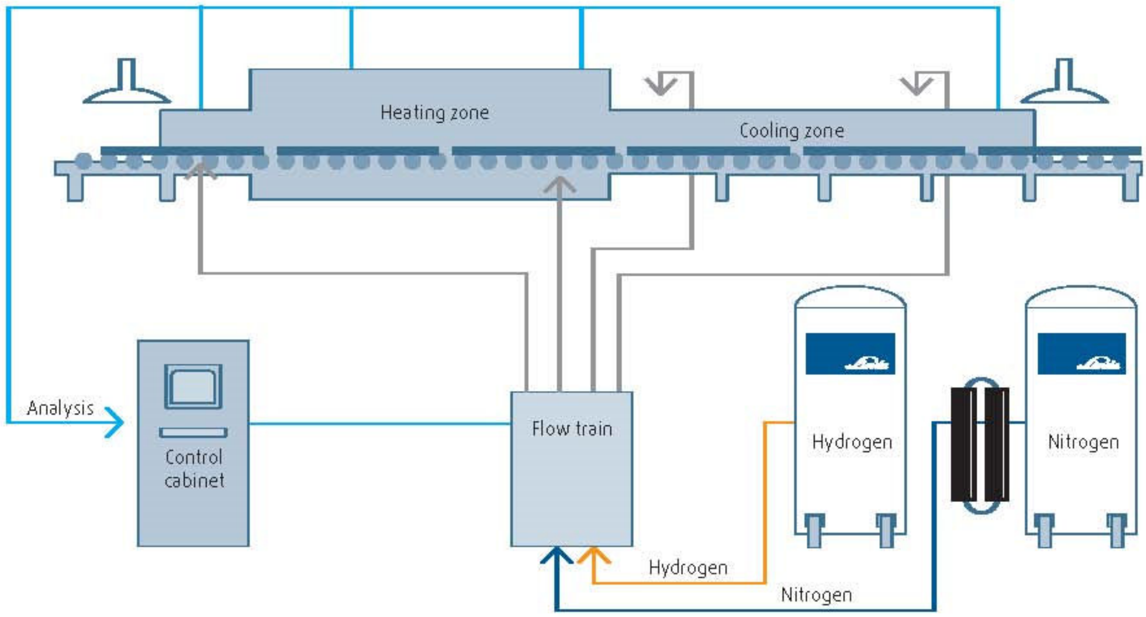
where K is the equilibrium constant.

However, if the hydrogen:water ratio is high and the hydrogen addition small, very little reaction will take place. The actual carbon loss will depend upon flowrate, surface area of the load treatment time and temperature. For a furnace processing 500 kg/hour of 0.8% carbon, 2 mm diameter steel wire in nitrogen/hydrogen with a dewpoint of -42°C, an atmosphere flowrate of 100 m^3/h would produce only 0.82 µm of total decarburisation per hour, even assuming all the water in the atmosphere was available for reaction.

For continuous furnaces, a HYDROFLEX® atmosphere control system affords optimal control of nitrogen/hydrogen atmospheres for steel annealing. HYDROFLEX® ensures the best atmospheres and monitors control of the atmosphere precisely to ensure high quality annealing with the following benefits:

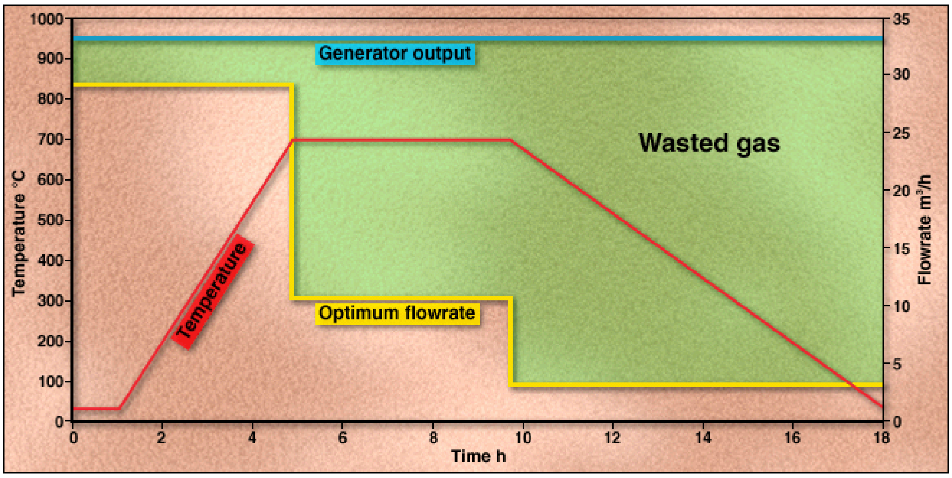
- Control of process parameters
- Lower costs for reworking and rejection
- No need for test charges
- Quick furnace start up
- Early warnings for maintenance
- Idle mode during downtime
- Automatic safety purging
- Process data storage
- Safe hydrogen usage

The process parameters that will deliver the required product properties are defined in a process recipe. Each recipe is customised according to material quality, dimensional requirements and other properties. Set points are defined in the HYDROFLEX® system in order to meet the recipe requirements for atmosphere control and process safety. The HYDROFLEX® system has independent gas supplies for hydrogen and nitrogen and several controllable gas inlets in the furnace. These allow the atmosphere composition to be adjusted to meet all possible requirements in the different zones of the furnace. The gas flows are controlled by means of the flow train. In the event of safety-related alarms or power failure, the hydrogen supply is automatically switched off and the furnace is purged with nitrogen.



A schematic of the HYDROFLEX® system

1.1. Bell furnace operations



The atmosphere flow requirements for a typical bell furnace cycle.

A major advantage that nitrogen-based atmosphere systems have over generator-based systems is the ability to instantaneously change flow rates. This is particularly important in bell furnace operations. At the start of the cycle and during heat-up a large flow is needed to purge the furnace and sweep out evaporated lubricants that would cause problems later in the cycle. When the charge has reached the process temperature, the flow can be reduced considerably, and during cooling all that is required is enough flow to maintain furnace pressure. This technique can save 70% of the overall atmosphere requirement for a bell furnace.

2. Nitrogen/hydrocarbon atmospheres

If an atmosphere is required which is reducing to iron, and is also not decarburising, then small quantities of hydrocarbon may be substituted for the hydrogen. The hydrocarbon may be methane, propane, or propylene depending upon availability, treatment temperature and furnace type. Methane, which has been found to be suitable for most applications, cracks slowly in the furnace to form graphitic carbon and hydrogen [5]:

$$CH_4 \Rightarrow C_g + 2H_2 \qquad (3)$$

CARBOFLEX™ nitrogen/hydrocarbon atmospheres are less reducing than nitrogen/hydrogen atmospheres, but they are sufficiently reducing to keep steel bright in furnaces with a low leak rate. Because the cracking reaction is slow, the hydrocarbon:hydrogen ratio is high and the atmosphere has a very high carbon potential.

$$\text{Carbon potential} = \frac{K\,p(CH_4)}{p(H_2)} \qquad (4)$$

The percentage of hydrocarbon needed depends on the furnace design, the product being treated and the process, but for most treatments 1-5% methane (or 0.1-1% propane/propylene) is sufficient. Very little carbon is therefore available. The amount is further reduced by the fact that when hydrocarbons crack on the metal surface, carbon tends to form as graphite, unlike the usual carburising/ decarburising reaction with carbon monoxide, where the carbon is adsorbed onto the surface. It is thermodynamically difficult to get graphite first to adsorb and then to diffuse into the steel. The combination of a very high carbon potential with a very low carbon availability renders the atmosphere effectively neutral to any type of steel.

In spherodise annealing of steel rod and wire in batch type furnaces, propane, propylene or mixtures of propadiene with methylacetylene can be added to nitrogen (about 1 to 3.5%, during the heating up step from 590°C to 720°C and about 0.3 to 0.8% at temperatures higher than 720°C and at soaking temperature).

A common heat treatment problem that can be solved by using nitrogen/hydrocarbon atmosphere systems is the variable surface carbon component, which normally occurs when machining is carried out after carburising. It generally requires the use of expensive stop-off compounds or copper plating if an active atmosphere such as endothermic gas is used during heat treatment. The nitrogen/hydrocarbon atmosphere is effectively neutral to all carbon levels, so the surface neither picks up nor loses carbon. Another useful application of this type of atmosphere is for hardening mixed loads of components with a range of carbon contents.

Nitrogen/hydrocarbon atmospheres have been widely adopted for the treatment of steels, particularly those where surface carbon control is required and no slow cooling is involved, for example hardening using an oil quench or austempering. However, the advantage of the system - its low reaction rate - can also be a disadvantage. It cannot be used where significant contamination by oxidants could occur, for example with a water or polymer quench, or in an excessively leaky furnace. Nor can it be used where rapid furnace conditioning is required between loads, as in a straight through type, sealed quench furnace that has direct access to the hot chamber for loading.

2.1. Decarburising control

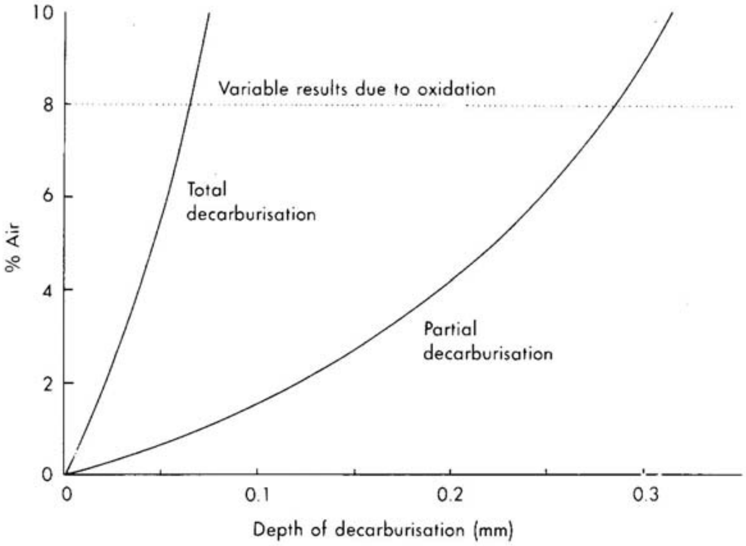
A typical application is the use of nitrogen with 4% natural gas for hardening at 850°C. As the leak rate increases, so does the decarburising potential:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (5)

$C_{Fe} + CO_2 \rightarrow 2CO$ (6)

$$\text{Carbon potential} = \frac{K\,p(CO)^2}{p(CO_2)} \quad (7)$$

The graph below shows the effect of this increasing decarburising potential on a low alloy steel exposed to the furnace atmosphere for 2 h at 850°C. The decarburisation curves indicate that the process is controlled by the surface reactions (5) and (1) rather than by diffusion, at least at low leak rates. When the oxygen potential decreases below the level required to oxidise iron, decarburisation can be reduced dramatically as the tenacious oxide layer formed acts as a diffusion barrier. The onset of oxidation is the limiting factor in many applications where the degree of decarburisation is not significant, but where the work must be oxide-free. At normal hardening or annealing temperatures, the methane mops up the oxygen, but below about 650°C reactions (3) and (5) do not occur to any significant degree during the time that the work stays in most types of furnace. The atmosphere therefore acts almost as nitrogen alone, and the small quantities of free oxygen are the only source of oxidation.



Effects of air leaks on decarburisation of SAE 8620 after 2 hours at 850°C in nitrogen/4% natural gas

A significant exception to this is in the operation of bell furnaces. These are normally 'capped' during cooling in annealing cycles, with only make-up gas being added. The residence time is therefore very long and reaction (3) is sufficient to maintain a reducing atmosphere down to room temperature. On the occasions where a nitrogen/hydrocarbon atmosphere is the most effective solution, but the furnace is not sufficiently tight to allow oxide-free cooling, a small quantity of hydrogen may be added to the cooling zone to produce the desired results.

Another significant drawback of this type of atmosphere is its propensity to form soot on cracking. The small volumes involved mean that there is no problem in many operations, but in electrically heated, open element furnaces soot can form on the elements over an extended period, eventually leading to shorting and element failure. The effect can be minimised by keeping the hydrocarbon addition small or by burning off any soot formed outside operating periods.

2.2. Soot Deposition

Soot can be deposited on annealed steel wire through incomplete removal of the residual drawing lubricant during heating up to the annealing soaking temperature, and by carbon monoxide and hydrocarbon contents in the annealing atmospheres (exothermic, endothermic and nitrogen based). Sooting can be reduced or eliminated in batch type furnaces by using a high atmosphere flow rate, to flush out the lubricants through the largely opened exhaust valves as soon as they volatise, and by heating up in stages or at a lower heating rate.

Soot deposition is difficult to avoid in the case of the nitrogen/hydrocarbon atmospheres with small additions of hydrocarbons (0.3 to 3.5%), used in annealing of structural steel rod and wire in conventional batch type furnaces. However, carbon deposition may be entirely prevented or reduced significantly by injecting air during the cooling stage of the annealing cycle, at a temperature between 620°C and 565°C, allowing soot to combust [6, 7].

3. Nitrogen/methanol atmosphere system

CARBOTHAN® nitrogen/methanol atmospheres provide many of the answers to the problems associated with nitrogen/hydrocarbon systems [8]. The atmosphere can be provided with a high proportion of active components so it is much less susceptible to leaks. Hydrocarbons and oxidant can be added to control the carbon potential and, at suitable active constituent levels, can therefore be used for carburising, decarburising or neutral hardening as desired and there is little tendency to deposit soot.

Methanol, when introduced into a furnace at above 750ºC, cracks to give carbon monoxide and hydrogen in the ratio 1:2.

$$CH_3OH \Rightarrow CO + 2H_2 \qquad (8)$$

When injecting methanol, particularly at low temperatures, care must be taken to ensure that it cracks rapidly to prevent lower temperature side reactions producing soot, carbon dioxide and water [9]. Nitrogen with 20 to 40% methanol, dissociated outside the furnace, in a methanol dissociator, could be used in low temperature (690°C - 810°C) annealing.

3.1 Non-cryogenic nitrogen

Because of the inherent ability of CARBOTHAN® nitrogen/methanol atmospheres to tolerate some oxygen, nitrogen produced by an ADSOSS-N nitrogen generation plant can be used instead of the more usual high purity nitrogen from a liquid source [11]. These plants generate nitrogen that still contains small amounts (0.01 to 3%) of residual oxygen. Nitrogen/methanol atmosphere systems have been shown to operate most economically with a residual oxygen content of 0.5% [11]. At this level there are no additional safety problems (the non-cryogenically generated gas can be used as purge gas) and few, if any, changes need to be made to control parameters or addition levels.

In most applications, non-cryogenically derived nitrogen for nitrogen/methanol atmosphere systems coupled with a liquid nitrogen supply as standby in the event of an emergency offer economic benefits compared with a system based on liquid nitrogen alone. Several examples of such systems are operating in the UK and elsewhere [12].

ADSOSS-N nitrogen generation plant

4. Endothermically generated atmospheres

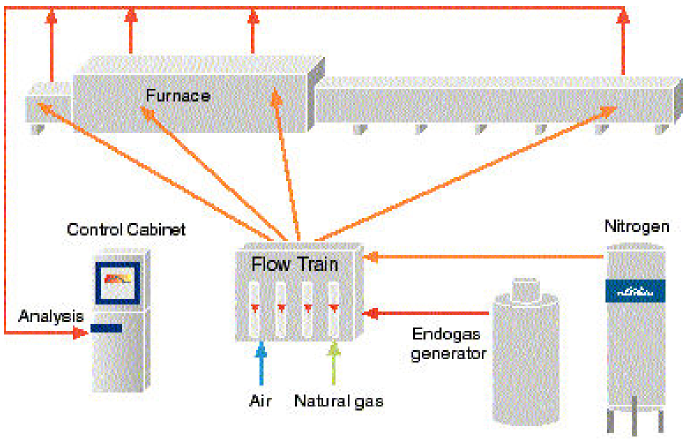
An endothermically generated gas (or endogas) can be used as an alternative to a CARBOTHAN® atmosphere, either from an external generator or, for large continuous furnaces, a CARBOCAT® gas generator can be used as the source. This type of atmosphere is usually diluted with nitrogen to reduce costs. The principle is that air and natural gas (or propane) are mixed and fed into a heated catalyst, where they react to form CO and H_2. In the patented CARBOCAT® in situ system endogas is produced directly inside the furnace chamber. The appropriate process recipe controls the gas flow and composition. Benefits associated with CARBOCAT® include:

- Elimination of the need for a cooling device for the gas
- Reduced energy consumption
- Reduced floor space requirements compared to an external endothermic gas generator

A CARBOCAT® installation

4.1. Control

A CARBOFLEX® control system can be used for carbon control. Process parameters to achieve the required product properties are defined in a process recipe. These recipes vary according to properties such as the steel quality and dimensional requirements. Setpoints are defined in the CARBOFLEX® control cabinet to meet the requirements for carbon control, surface appearance and process safety. A gas sample from a specific zone in the furnace is pumped to the control cabinet for analysis. Up to five different sampling positions are analysed in sequence. Gas flows and mixtures are adjusted in the flow train to maintain the setpoints in the different furnace zones (based on the recipe) and to minimise gas flows and so to reduce cost.



The CARBOFLEX® system

It can be diffucult to maintain a consistent atmosphere in large continuous furnaces without fans. If this is the case a CARBOJET® high speed gas injection system can be used to improve uniformity. CARBOJET™ is a technology patented by Linde Gas that allows better gas convection in heat treatment furnaces without fans. By injecting small amounts of nitrogen at high velocities (250-300 m/s) into several parts of a roller hearth furnace, CARBOJET™ creates a movement in the furnace gas to ensure homogeneous distribution of both gas and temperature. CARBOJET™ can be installed in every continuous furnace for neutral annealing, carburising and decarburising and can also be used in pit furnaces for wire annealing with nitrogen or natural gas/nitrogen mixtures.

- CARBOJET™ homogenises product quality in tube annealing and other heat treatment furnaces using endogas, exogas, or monogas.
- CARBOJET™ increases the utilization of carburising gases and reduces soot formation in heat treatment furnaces (such as roller hearth furnaces and walking beam furnaces). The high-speed injection of gases also optimises the functionality of analysing equipment by better gas mixing.
- CARBOJET™ increases the carbon transfer on material surfaces through forced convection of protective gases.
- CARBOJET™ allows a faster switch of atmospheres.
- CARBOJET™ allows the use of higher carbon potentials through premixing of gases.
- CARBOJET™ optimises the heat transfer in furnaces with convective heating.

The system consists of one or several CARBOJET™ lances with piping and flow train. The number of lances is adapted to the furnace size and the existing gas consumption. The lances can be controlled manually or through a CARBOFLEX® control unit. The specially designed lances are made of heat resistant material to ensure a long lifetime. Linde Gas provides tailor-made solutions by adapting its CARBOJET™ systems to individual customer needs.

5. Hydrogen atmospheres

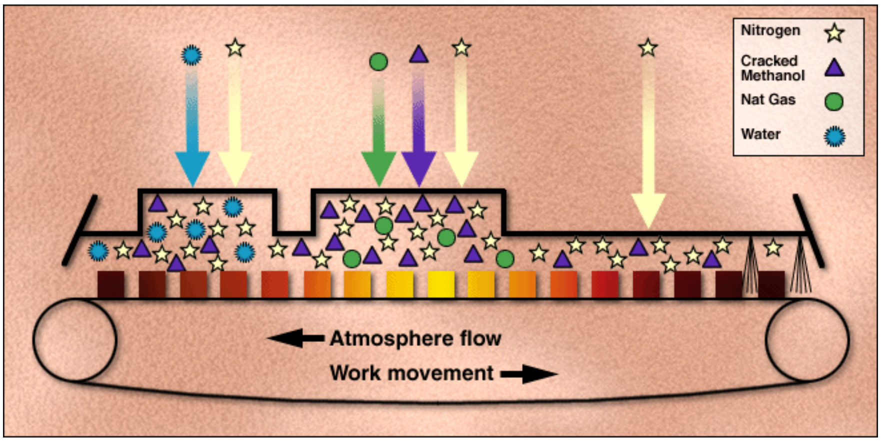
Hydrogen atmospheres are used more and more in advanced bell type furnaces for annealing structural and stainless steel strip. Heat transfer is more efficient in a hydrogen atmosphere. The use of high thermal conductivity hydrogen combined with intense recirculation of the furnace atmosphere reduces thermal gradients inside the strip coil, producing more consistent mechanical properties [6].

Hydrogen in the furnace atmosphere, hydrogenates the lubricant at approximately 400°C; this lowers the boiling point of the hydrocarbons and helps them to evaporate before they dissociate, reducing or eliminating soot deposition. The high-convection high flow atmosphere also helps to remove residual surface carbonaceous deposition trapped between turns of the tightly would strip coil [13].

6. Atmosphere zoning

There are two major disadvantages of the CARBOTHAN® nitrogen/methanol atmosphere system: in most cases the atmosphere is flammable; and the methanol is introduced into a zone of the furnace operating above 750ºC. Both of these disadvantages can be overcome by using hybrid techniques based on the patented [14] atmosphere zoning system [15-18].

For example, in a mesh belt furnace for the bright, decarburisation-free annealing of steel pipes, an atmosphere that was reducing to steel and with a neutral carbon potential was required in the furnace hot zone. Nitrogen/methanol was introduced into the zone in the ration of 70:30, with the amount of hydrocarbon controlled by an in situ oxygen probe.



A schematic of atmosphere zoning

The sections of pipe in this case were contaminated with lubricants, which would have stained the final product if they had remained on the components. Just enough nitrogen/water vapour mixture was therefore injected into the front end of the furnace to oxidise away the lubricants but without being oxidising to steel when mixed with the gases leaving the hot zone.

In the cooling zone all that was required was to keep the pipes bright, so in this area only nitrogen was used. Enough hydrogen was allowed to diffuse into the cooling zone to produce bright work but not sufficient to produce a flammable mixture at the exit end. As the atmosphere at the exit end was non-flammable, physical curtains could be used to reduce the amount of gas needed and to ensure that the atmosphere all flowed towards the entry end. This flow pattern ensured that the products of reaction from the drawing lubricant were ejected from the furnace and did not contaminate the hot zone.

7. Summary

Linde Gas nitrogen-based or hydrogen atmosphere technologies can provide solutions to many of the problems faced by heat treaters of semi-finished steel. Not only can quality be improved by the ability of nitrogen-based systems to be tailored to the exact requirements of a particular process but the flexibility of nitrogen-based systems can also be harnessed to improve both economics and safety.

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