Lecture 35: Atmosphere in Furnaces

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Key words: Heat treatment, furnaces, atmosphere, annealing, sintering, heating

Selection of atmosphere:

The surrounding in the thermal enclosure (furnace) is termed atmosphere. The atmosphere consists of gases and is usually air. However, in some heat treatment, thermo-mechanical processing, sintering etc special type of atmosphere is required to

- Prevent oxide formation, if the heating material is prone to oxidation.
- Decarburize steel.
- Control the surface chemistry of steel which means the elements must not be oxidized or reduced during heating.
- Produce “blueing” effect in steel. The blueing effect imparts a wear-resistant and oxidation-resistant surface finish.
- reduce oxides formed on the surface.
- Make the surface hard by allowing carburizing or nitriding.
Gases and their behavior:

1. Nitrogen is the primary component of atmospheric air (78.1%). Oxygen is 20.9%. Rest 1% could be other gases, which is of very little significance. Nitrogen is considered to be chemically inert and is used as a carrier gas for reactive furnace atmosphere, for purging etc. At high temperatures, nitrogen may show reaction with Mo, Ti, Cr and Co.

2. Hydrogen is a reducing gas and is used where reducing atmosphere is required. It may be used to prevent oxidation of iron

   \[ \text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O} \]
   \[ \text{Fe}_3\text{O}_4 + \text{H}_2 = \text{H}_2\text{O} + 3 \text{FeO} \]

   Hydrogen can also be used to decarburize the steel for certain applications. At the material temperature is greater than 973K, the following reaction occurs:

   \[ \text{C} + 2 \text{H}_2 = \text{CH}_4 \]

   Hydrogen may be absorbed by the metal at elevated temperatures and cause hydrogen embrittlement.

3. Carbon monoxide: it is also a reducing gas and is used to create a reducing atmosphere

4. Carbon dioxide: it is a mild oxidizing gas. It forms oxides with iron at elevated temperatures. At temperatures greater than 540°C, the following reaction may occur

   \[ \text{Fe} + \text{CO}_2 \rightleftharpoons \text{FeO} + \text{CO} \]

   and at temperatures lower than 540°C, the following reaction may occur

   \[ 3 \text{FeO} + \text{CO}_2 \rightleftharpoons \text{Fe}_3\text{O}_4 + 3 \text{CO} \]

   Decarburization may also result by the reaction like

   \[ \text{Fe}_3\text{C} + \text{CO}_2 \rightleftharpoons 3 \text{Fe} + 2 \text{CO} \]
   \[ \text{C} + \text{CO}_2 \rightleftharpoons 2 \text{CO} \]

5. Argon and Helium: Both are inert gases and are used to maintain inert atmosphere. In some applications argon is used for purging.
Steam: it is used to provide blueing effect in steel between 573K and 923K. Blueing effect is due to the formation of either Fe$_2$O$_3$, Fe$_3$O$_4$, or FeO. The formation of oxide of iron depends on temperature, and ratio by partial pressure of H$_2$O to partial pressure of H$_2$ in the atmosphere.

“Dew points” quantifies the concentration of H$_2$O vapor in the atmosphere. Dew point is a temperature at which gas is saturated with water vapour (100% relative humidity). In a furnace, water-gas reaction controls the concentration of H$_2$, H$_2$O, CO and CO$_2$ according to the following reaction:

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2. \]

Prepared atmospheres

For heal treatment and other purposes atmosphere comprising of gases is prepared according to the requirement. American Gas Association (AGA) has classified atmospheres in 6 groups, on the basis of method of preparation

a) **Exothermic base (AGA 100):** Prepared either by partial or by complete combustion of gaseous fuel with air. Water vapour may be removed to produce a desired dew point. The atmosphere is a mixture of CO + CO$_2$ + H$_2$ + H$_2$O +N$_2$. In a lean exothermic atmosphere the ratio of CO$_2$/CO is greater than a rich exothermic one. This atmosphere is prepared by burning a mixture of hydrocarbon fuel and air. The combustion products are passed to a condenser to remove water. The combustion products are further dried by using an absorbent such as activated alumina or activated silica. The dried atmosphere is then transferred to the furnace. Typical applications include bright annealing of steel, copper, sintering of non ferrous metal powders, and iron powders.

b) **Prepared nitrogen base (AGA200)**

They are exothermic atmospheres and produced by combustion of a mixture of air and fuel gas. Carbon dioxide and H$_2$O are removed from products of combustion.

They are used to heat treat low-carbon, medium-carbon and high carbon steels. N$_2$ atmosphere cannot be used for decarburization.

c) **Endothermic base atmospheres (AGA 300).**

Endothermic base atmospheres are prepared by using a lean mixture of hydrocarbon fuel with air, i.e. mass of air is less than stoichiometric (theoretical) amount required for complete combustion. The objective is to produce CO and H$_2$. 
As amount of air is less than stoichiometric, a catalyst and extra amount heat are required to facilitate combustion. The endogas is cooled immediately to prevent the following reaction:

$$2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$$

Typical applications include bright annealing of steel of any carbon content without decarburization or carburization, heat treatment of steel of any carbon content, bright copper brazing, and carrier gas for gas carburizing or carbonitriding.

Consider complete combustion of methane

$$\text{CH}_4 + 2(\text{O}_2 + 3.76 \text{ N}_2) = \text{CO}_2 + 7.52 \text{ N}_2 + 2\text{H}_2 \text{O}$$

For the ratio of \(\frac{\text{mole of air}}{\text{mole of CH}_4}\) = 9.52, the atmosphere consists of CO\(_2\), N\(_2\) and H\(_2\). However if the said ratio is less than 9.52 e.g. 1.88, then according to following, reaction,

$$2\text{CH}_4 + (\text{O}_2 + 3.76 \text{ N}_2) = 2\text{CO} + 4 \text{H}_2 + 3.76 \text{N}_2$$

the atmosphere comprises of CO, H\(_2\) and N\(_2\). The volume of atmosphere would increase by 3 mole volumes. The atmosphere would comprise of 20.4% CO, 40.8% H\(_2\) and 38.8% N\(_2\).

**d) Charcoal base atmospheres (AGA 400)**

It is produced by following reaction

$$2\text{C}+\text{O}_2 + 3.76 \text{ N}_2 = 2\text{CO} + 3.76 \text{N}_2.$$ 

Theoretically atmosphere would consist of 34% CO and 66% N\(_2\). Due to moisture and volatiles in charcoal and incomplete combustion of carbon, the reaction would produce CO\(_2\), CO, H\(_2\), CH\(_4\) and N\(_2\).

Normally the atmosphere is neutral to higher carbon steels but the carbon potential may be increased by adding natural gas.

The charcoal based atmosphere is used for hardening, annealing and normalizing high carbon steels without scale formation or decarburization.

**e) Exothermic-Endothermic base atmospheres (AGA500)**

They are prepared by combusting a mixture of air and fuel. POC is dehydrated, and a predetermined quantity of hydrocarbon fuel is added. The mixture is made to react in presence of a catalyst.

Typical application includes carburizing and carbonitriding. Due to the cost of production, these atmospheres are not very often used.
f) Ammonia base atmospheres (AGA 600)

Ammonia dissociation is used to prepare highest purity nitrogen which is free from oxygen.

Liquid ammonia is vaporized into a heat exchanger and is fed to dissociate in a reactor called as dissociater. The decomposition of ammonia to nitrogen and hydrogen begins at around 300-320°C. Rate of decomposition increases as temperature increases.

Its primary use is for bright annealing metals such as silicon to obtain electrical properties. Ferrous and non ferrous metals are bright annealed in ammonia atmosphere.

Bright silver brazing and copper brazing of steel are other applications.

Protective atmospheres applications

<table>
<thead>
<tr>
<th>Composition(vol%)</th>
<th>Applications.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>Bright annealing of Cu, sintering of ferrites</td>
</tr>
<tr>
<td>Lean exothermic</td>
<td>Bright annealing low C steel, silicon steels/Cu brazing, sintering</td>
</tr>
<tr>
<td>Rich exothermic</td>
<td>Brazing sintering bright annealing</td>
</tr>
<tr>
<td>Dissociated NH₃</td>
<td>Hardening, carburizing with CH₄, sintering brazing</td>
</tr>
<tr>
<td>Endothermic</td>
<td>Natural for annealing</td>
</tr>
<tr>
<td>Nitrogen H₂</td>
<td>Reducing, sintering</td>
</tr>
<tr>
<td>Ar or He</td>
<td>These are pure and inert gases and are used to prevent oxidation during welding of stainless steel, aluminum etc. and heat treatment of special steels.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>N₂</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂</th>
<th>CH₄</th>
<th>Dew point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td>86.8</td>
<td>10.5</td>
<td>1.5</td>
<td>1.2</td>
<td>-</td>
<td>4.5</td>
</tr>
<tr>
<td>Rich</td>
<td>71.5</td>
<td>5.0</td>
<td>10.5</td>
<td>12.5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Dissociated</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>75</td>
<td>-</td>
<td>-50 to +60</td>
</tr>
<tr>
<td>Endothermic</td>
<td>40-45</td>
<td>0-0.5</td>
<td>20</td>
<td>34-40</td>
<td>0.51</td>
<td>-10 to +10</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>99.9</td>
<td></td>
<td></td>
<td>99.9</td>
<td>-60</td>
<td>-68</td>
</tr>
</tbody>
</table>
Atmosphere volume requirements

It depends on

i) Type and size of furnace
ii) Environment and presence of draft.
iii) The nature and size of work pieces.
iv) Metallurgical process involved.
v) Presence or absence of curtains at entrance and exit.

Atmospheric sensors

It is important to measure the concentration of various components of the atmosphere during the treatment in the furnace. The constituents of atmosphere are CO, CO₂, H₂, H₂O, N₂ and hydrocarbon gases such as CH₄. The main objective of furnace atmosphere is to prevent decarburization, hydrogen embrittlement, oxidation, surface blueing and soot formation.

ORSAT analysis can be used to determine the composition of O₂, CO and CO₂. ORSAT analysis is described in lecture 10.

Among other techniques gas chromatography, thermal conductivity, oxygen sensors, dew point are also used. Details about the sensors can be obtained in references given at the end of the lecture.

References:


Furnace atmospheres and carbon control: ASM Committee on furnace atmospheres