

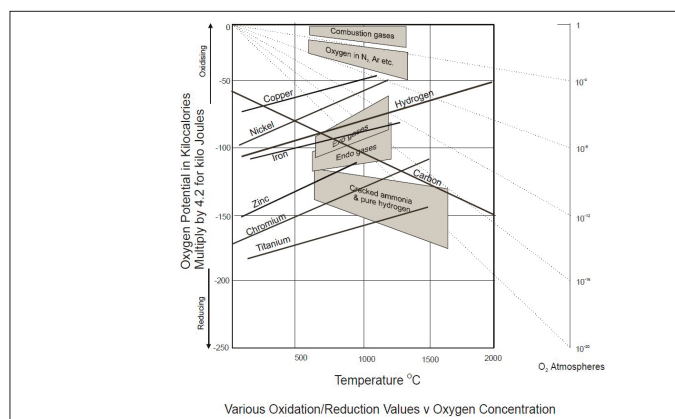
Oxygen Potential Measurements in Metal Heat Treatment Processes

For any particular metal or other oxidisable element a value of oxygen potential called the "free energy of formation" of the oxide exists. Above this value the metal will be oxidised but below no oxidation will take place.

This value is very much dependent upon temperature and usually increases with increasing temperature. The diagram on this page illustrates this for several elements. Nickel, for example, will undergo oxidation to nickel oxide (NiO) in an atmosphere with an oxygen potential greater than -60 kilocalories/mole at 1000°C, or -81 kilocalories/mole at 500°C. Chromium has a greater affinity for oxygen than nickel as shown by its lower line on the diagram. It would require an oxygen potential of less than -130 kilocalories/mole at 1000°C to prevent oxidation. Thus an atmosphere which is just adequate to prevent nickel from oxidising would not protect chromium from oxidation. Note that the lines on the diagram are for the lowest oxidation state of element.

Diagrams such as this enable the theoretical level of oxygen potential to be determined for a variety of conditions. For example if steel is to be decarburised by oxidising some of the carbon in the metal, and yet simultaneous oxidation of the metal is to be prevented, then at 1000°C this could be done at an oxygen potential of -100 kilocalories/mole. Below about 750°C however, it will not be possible to decarburise without simultaneously oxidising the iron in the steel, since the carbon line crosses the iron line on the free energy diagram at this temperature.

In the past the measurement of the oxidising/reducing power of a protective atmosphere, or the carbon potential of a carburising atmosphere, was achieved inferentially; either by the measurement of the CO₂ content, the CO/CO₂ ratio or the dew point (effectively the moisture content), depending upon the nature of the atmosphere. These measurements can however be directly related to the oxygen potential or the oxygen partial pressure. For example a rich exothermic gas having a CO/CO₂ ratio of 10 has an oxygen potential of -93 kilocalories/mole or an oxygen partial pressure of 10⁻¹⁶ atmospheres at 1000°C. Similarly a lean exothermic gas with a CO/CO₂ ratio of 0.1 has an oxygen potential of -70 kilocalories/mole or an oxygen partial pressure of 10⁻¹² atmospheres at 1000°C. Cracked ammonia, which is frequently used when bright annealing stainless steel, is usually monitored by dew point measurement. This is related to the water content in the gas from which the H₂/H₂O ratio can be calculated - assuming that the H₂ content is known and constant - which is in turn related to the oxygen potential.



This data only provides information on whether or not a particular metal etc. will oxidise or not under certain conditions; it says nothing about factors such as rate of oxidation etc. Factors such as these will sometimes mean that higher oxygen potentials can be permitted than theoretical considerations alone would indicate. Furthermore, a certain amount of surface oxidation of the metal may be quite acceptable. Factors such as these should be taken into account when determining the most economic way to operate a process.

A zirconia oxygen sensor/analyser can provide very valuable information for analysing the effect of various conditions, as well as for controlling at the optimum condition once this has been established.

Atmospheres

Exothermic atmospheres are produced by burning a gaseous fuel, typically natural gas or methane, in varying amounts of air. These atmospheres can vary widely in composition depending on the air/gas ratio. They are frequently referred to as either rich or lean. Rich atmospheres contain excess 'fuel' which can sometimes mean they are flammable themselves, whereas lean atmospheres do not. The atmosphere is used to protect metals from oxidation during heat treatment processes such as annealing. Rich atmospheres tend to be used for ferrous metals, which require a lower oxygen content than non-ferrous (copper bearing) metals, which tend to use lean atmospheres to protect them.

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Sometimes exothermic atmospheres are treated to remove water and/or carbon dioxide. Again these vary greatly in composition depending on the starting gas and the treatment it undergoes. They often contain high amounts of hydrogen and this can be used as a measure of the gas quality along with oxygen potential.

Endothermic atmospheres are also produced by reacting gas with air, except that these are so gas rich they need to be reacted in the presence of a heated catalyst. Their composition is mainly carbon monoxide, hydrogen and nitrogen. Because the mixture is so rich, sooting up of the reactor and catalyst can occur if the process is not controlled. Monitoring hydrogen and oxygen potential provides the means to do this.

Cracked ammonia is produced by catalytically decomposing ammonia (NH₃) into hydrogen and nitrogen. It is a convenient way of producing hydrogen and the process may be controlled by measuring the hydrogen content. It is sometimes required to provide a "percentage dissociation" figure and it is possible for a MTL K1550 analyser to be programmed to display this.

Burned ammonia is produced by doing just that, usually in the presence of a catalyst. An atmosphere consisting of hydrogen, nitrogen and water is generated, and this is frequently dried to some extent by using the evaporation of the ammonia to cool the gas. The monitoring of the hydrogen content is again important.

The processes that use these gases are mainly of three types.

Annealing where a metal is heated to soften it prior to some other process such as rolling or drawing. Depending on the atmosphere oxygen, hydrogen or both are usefully monitored.

Carburising where the surface of ferrous metals is reacted with carbon to form a "case" of harder or tougher metal. It is usual these days to use insitu zirconia oxygen probes for this application. The disadvantage of using an ex-situ approach would be the sooting that occurs with the very rich atmospheres employed. There is scope for the lower cost ex-situ type if the process is a so called "long cycle" type, where the atmospheres are not so sooty.

Cosmetic surface treatment such as the 'blueing' and bright annealing of steel. 'Blueing' is often done by atmospheres that are wet (steam is sometimes used, in fact), so it is often necessary to close-couple the sensor to the process to avoid condensation. The MTL Z1900 type of sensor is ideally suited to this.

Conversion factors

1) kiloJoule (kJ) = kilocalorie (kcal) x 4.187

2) * kJ = (17.6 x log % oxygen) - 34.72

* Only applies to MTL zirconia oxygen sensors operating at 45mV per decade (634°C)

Note: The MTL Z1110 analyser is used in this type of application.



Eaton Electric Limited,
Great Marlings, Butterfield, Luton
Beds, LU2 8DL, UK.
Tel: + 44 (0)1582 435600 Fax: + 44 (0)1582 422283
www.mtl-inst.com
E-mail: mtlgas@eaton.com

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EUROPE (EMEA):
+44 (0)1582 723633
mtlenquiry@eaton.com

THE AMERICAS:
+1 800 835 7075
mtl-us-info@eaton.com

ASIA-PACIFIC:
+65 6 645 9888
sales.mtlasing@eaton.com

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