Measuring the Dewpoint of Hydrogen Forming Gas with a Zirconia Oxygen Sensor

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1   Abstract

This paper describes the uses of hydrogen forming gas in reducing and oxidising industrial applications and explains why controlling the water content is so important in the metal heat treatment industry. Measuring water at elevated temperatures is extremely difficult to do with normal equipment. Cambridge Sensotec has developed a high temperature forming gas analyser capable of measuring the hydrogen dewpoint using a series of thermodynamic calculations, based on the signals from a modified Rapidox zirconia oxygen sensor.

2   Background

Forming gas is used in many heat treatment applications as a cheap way to remove oxygen and control water in an oven or heat treatment process. Forming gas is a mixture of hydrogen (H_2) and an inert gas which is nearly always nitrogen (N_2). It can be made chemically by cracking ammonia:

$$2NH_3 \;\rightarrow\; 3H_2 \;+\; N_2 \qquad\qquad\qquad 1$$

which produces a ratio of 3:1 hydrogen to nitrogen. This method is not generally used because it is chemically inefficient and costly. More commonly the hydrogen and nitrogen are either mixed together on site or purchased as a pre-mixed cylinder from the gas company. Any mix of hydrogen and nitrogen can refer to forming gas, but the most common blend is 5% H_2 in 95% N_2. This mix is always below the lower explosive limit (LEL)

of hydrogen and is therefore considered a safe gas which does not require any special equipment or handling.

3   Forming Gas Applications

Forming gas is used in specialist soldering applications as well as some photographic applications to clean long exposed film (e.g. in astronomy photography). Ceramic components containing precious metal electrodes (e.g. ceramic capacitors) are often sintered in kilns containing forming gas to prevent oxidation of the electrode. The main application however is in metal heat treatment processes where the properties of metals are modified and improved by applying heat over time.

4   Heat Treatment of Metals Using Forming Gas (REDUCTION)

These processes can be categorised as follows:
- **Annealing**: metals are heated to soften them or change their internal microstructure.
- **Bright annealing:** metals are heated in an inert atmosphere of forming gas or pure hydrogen to limit oxidation.
- **Brazing:** when done on copper and silver uses an atmosphere of forming gas or pure hydrogen or, in some cases, dissociated ammonia.
- **Carburizing:** this process adds a thin layer of carbon to the surface of steel to increase its hardenability and typically uses an endothermic atmosphere such as forming gas.
- **Nitriding:** heating metal in the presence of nitrogen (usually as forming gas or ammonia) to increase both corrosion resistance and hardness.
- **Hardening:** used to prevent oxidation and decarburization in tool steels by using an inert or protective atmosphere such as nitrogen or forming gas.

- **Sintering:** where powdered metals are fused together to produce solid shapes. Depending on the metallic compounds being sintered, uses either an inert/protective atmosphere or a forming gas atmosphere
- **Tempering**: After heat treatment metals are often oven tempered over time to increase grain size and ductility. This requires an inert atmosphere such as forming gas.
- **Hot isostatic pressing (HIP)**: Metal powders are pressed under very high pressures whilst heated, to produce high density sintered metal parts.

Forming gas produces an inert and protective atmosphere in an oven or kiln during these processes. However, the nitrogen element is not completely inert and can react and cause nitriding of certain materials. So occasionally nitrogen needs to be substituted for argon, or even pure hydrogen. Although pure hydrogen is non-flammable as it is above the Upper Explosive Limit (UEL), working with pure hydrogen is more risky as any leaks into the atmosphere can quickly create a potentially explosive atmosphere.

At elevated temperatures the hydrogen present in forming gas will quickly react with any oxygen present in the oven thus guaranteeing a very low oxygen partial pressure. The reaction produces water which is discussed later in this paper. It also aids thermal transfer in the oven since it has a very high thermal conductivity. It is particularly suitable for bright annealing of steel; annealing of stainless steel, alloy steel, and non-iron; neutral hardening; and metal sintering.

Figure 1: Example of a forming gas metal heat treatment oven

5   Heat Treatment of Metals using Steam (OXIDATION)

Steam treatment is a batch thermal process that creates a thin controlled oxide layer on the surface of iron and steel components. It improves corrosion resistance, increases hardness and density and modifies the magnetic properties. The process can also be used to seal the porosity of the steel and improve its wear characteristic. Steam heat treatment processes often use forming gas as the background atmosphere.

As in most thermal treatments, time, temperature and atmosphere are carefully controlled to provide the optimal conditions for the expected surface finish. During a typical steam treatment process, parts are placed in a steam treatment oven and heated to approximately 540°C. Once the component is at temperature, steam is introduced to the forming gas and the water vapor reacts with the surface of the iron to form a very thin oxide layer (magnetite - Fe_3O_4). After a designated period normally 30-60 minutes, the component is

removed from the unit and allowed to cool. The oxide appears on the component surface giving it a blue / black colour finish.
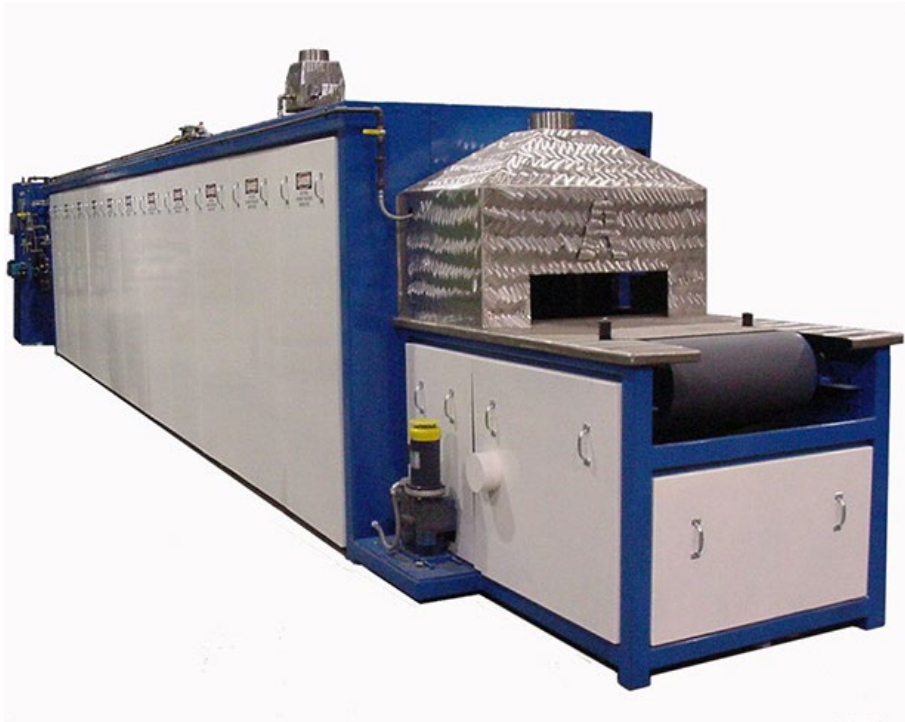

Figure 2: Example of a steam treatment oven

6   The Thermodynamics of Metal Heat Treatment Processes

The treatment of metals and oxides in atmospheres containing hydrogen relies on carefully controlling and monitoring the gases in the oven. Both reduction (e.g. bright annealing) and oxidation (e.g. corrosion resistance) processes are determined by temperature of the oven as well as the thermodynamic relationship between hydrogen, oxygen and water. This is commonly referred to as the dewpoint of hydrogen. The gas pressure is also an important variable but most metal teat treatment processes, except for HIP, are done at normal atmospheric pressure.

Figure 3 below shows the metal – metal oxide – hydrogen chart obtained by thermodynamic calculations taken from a paper published in the Welding Journal in May 1970 by Bredz and Tennenhouse [1]. This shows a selection of common metals plotted to show their equilibrium point between their oxide and their metal versus the hydrogen dewpoint. Passing through a point from top left to bottom right shows the transition point where oxidation stops and reduction begins. For practical purposes the most stable oxide is shown.
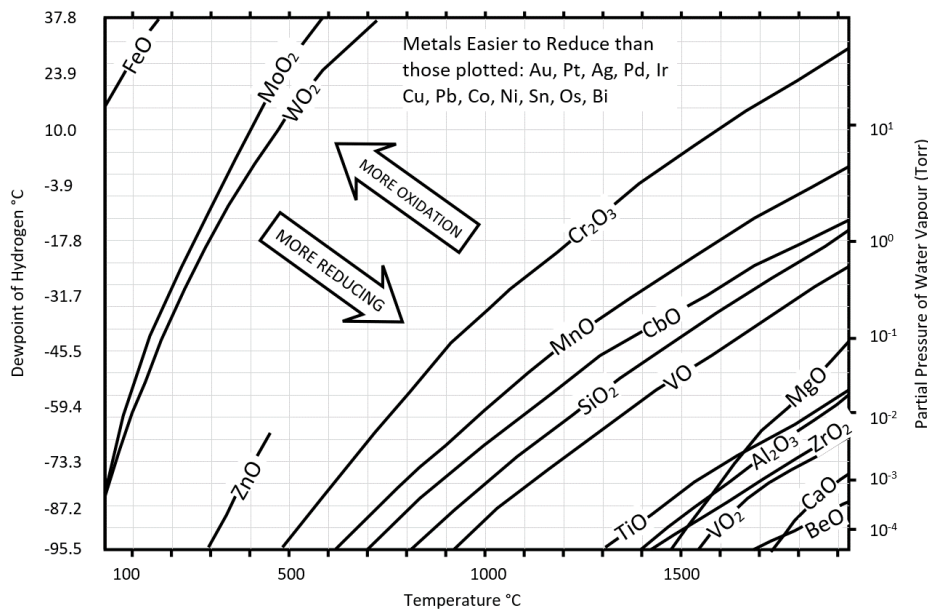

Figure 3: Plot of hydrogen dewpoint versus temperature for various metals showing the equilibrium position for the metal and their oxides.

Broadly speaking once the temperature is set then changing the hydrogen dewpoint of the forming gas by adding or removing steam will result in reducing or oxidizing conditions as defined in Figure 3 and the desired effect is produced.

7   Measuring Dewpoint in Heat Treatment Processes

The control of oxygen and water in forming gas applications is critical to ensure that the right conditions exist to achieve the desired effect on the product. For example, too much water in the oven will cause an unwanted dissociation reaction producing oxygen and hydrogen:

$$2H_2O \rightarrow 2H_2 + O_2 \hspace{4cm} 2$$

The resulting excess of oxygen can cause staining and scaling on the product which is highly undesirable.

Measuring oxygen at high temperatures is quite straight forward using a zirconia sensor since the sensor itself operates at elevated temperature. But measuring water with standard instrumentation is impossible much above 60°C as most sensors are based on polymers that will not withstand exposure to high temperature. Instead it is possible to determine the dewpoint in the oven using thermodynamic calculations based on oxygen measurements and the known level of hydrogen in the atmosphere. This method of analysis works because the hydrogen, oxygen and water are in a thermal equilibrium inside the oven and this can be written as a thermodynamic expression with Kp as the equilibrium constant:

$$Kp_{diss} = \frac{PH_2{}^2 \times PO_2}{PH_2O^2} \hspace{3cm} 3$$

and

$$Kp_{ass} = \frac{1}{Kp_{diss}} \hspace{4cm} 4$$

Where "diss" means dissociation (of H_2O) and "ass" means association (of O_2 and H_2) and.

There are well-known published formula for calculating Kp, but when using a zirconia sensor with platinum electrodes, one needs to first determine the percent dissociation of steam on a platinum electrode at any given temperature to accurately calculate Kp. The expression shown below developed empirically by Langmuir [2] gives the % dissociation "α" of steam at any temperature (in Kelvin) on a platinum surface. The constant "c" is 3.806 and is the average of 3 independent measurements, non of which varies by more than +/0.03. An initial pH_2O of 1 atmosphere is assumed in these sorts of calculations, but the theory applies to any initial pH_2O.

$$\log \alpha = c - \frac{8343}{T} + 0.88 \log \frac{T}{1000} - 0.00018(T - 1000) \qquad 5$$

At the operating temperature of the zirconia sensor of 664°C, α = 7.7361 x 10^{-06} and equation 3 can be solved:

$$Kp_{diss} = \frac{\alpha/100 \times \frac{\alpha/100}{2}}{1 - (\alpha/100)} \qquad 6$$

With this information, Kp_{ass} is solved by simply reciprocating Kp_{diss} as shown in equation 4 and the water partial pressure is determined using the following equation 7 using the oxygen partial pressure taken from the zirconia sensor signal and the hydrogen partial pressure as entered by the operator:

$$pH_2O = \sqrt{Kp_{ass} \times pO_2 \times pH_2{}^2} \qquad 7$$

Converting pH_2O into a dewpoint is done using a formula derived from Perry's Chemical Engineering handbook 8th edition [3]:

$$T_{dew} = 8.4543 \ln(H_2Oppm) - 82.665 \qquad 8$$

Equation 9 below is the standard Nernst equation written in terms of calculating oxygen from the zirconia oxygen sensor signal emf (E).

$$E = \frac{2.303RT}{zF} Log_{10} \left(\frac{pO2_{air}}{pO2_{sample}} \right) \qquad 9$$

where: EMF = Electro-motive force (V)
R = Molar gas constant (8.3144 J. mol^{-1}.K^{-1})
T= Absolute temperature (°K)
Z = Number of charge units transferred (z = 4 for oxygen)
F= Faraday's constant (9.6485 x 10^4 C. mol^{-1})
pO$_2$ (reference) = Partial pressure of oxygen in the air reference
pO$_2$ (measurement)= Partial pressure of oxygen in the measurement gas

Equation 9 can be re-written to calculate the PO$_2$ of the forming gas:

$$pO2_{sample} = \frac{pO2_{air}}{10^{\frac{EzF}{2.303RT}}} \qquad 10$$

With PO$_2$ calculated this is substituted back into equation 7 above and equation 7 is solved after the operator has dialled in the level of hydrogen present in the gas (Normally fixed and known); the default being 5%. As long as the operating conditions are stable and within the limits of the calculations the dewpoint is calculated from equation 8 above and the resulting chart is created from the data (the example shows 5% and 75% curves at 664°C).
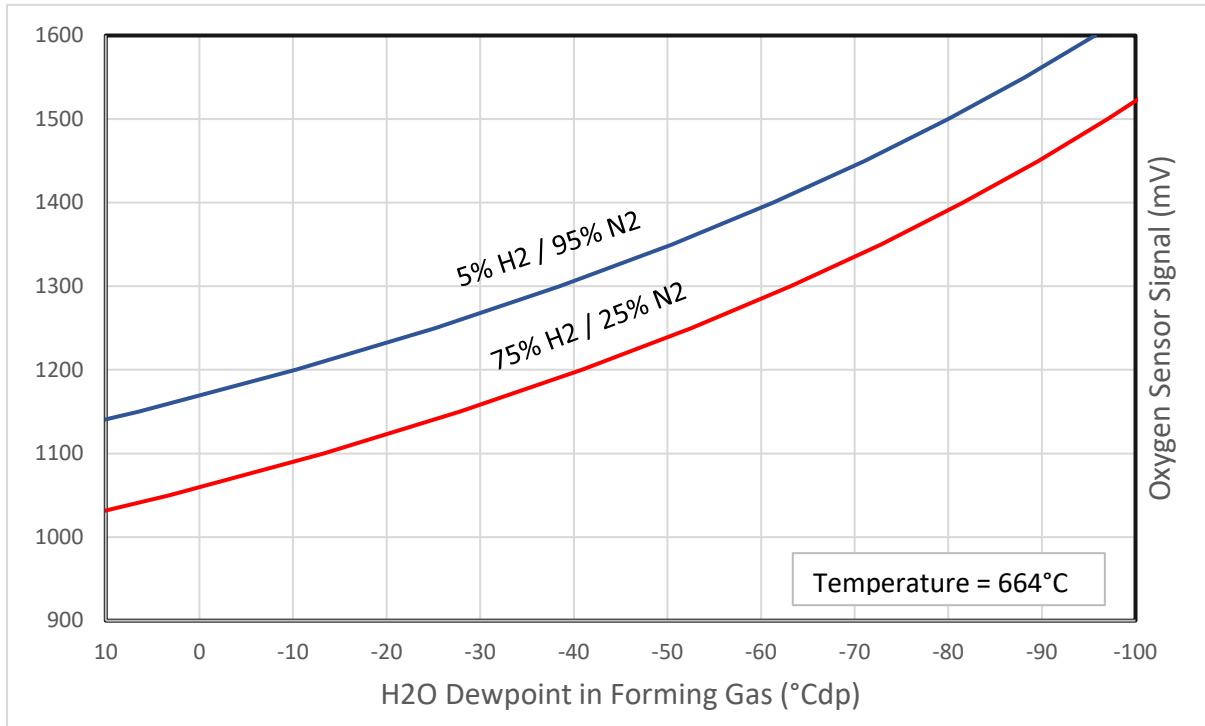
Figure 4: Plots of hydrogen dewpoint calculations based on a sensor temperature of 664°C at 5% and 75% hydrogen content.

Cambridge Sensotec has developed a special Forming Gas analyser (FGA) version of the existing Rapidox 2100 zirconia oxygen analyser. The analyser is programmed with all the above thermodynamic equations required to produce an accurate calculation of the water content in hydrogen forming gas. This calculation works because:

1) The hydrogen content is fixed and known in a standard gas mixture and is programmed into the Rapidox FGA analyser by the operator as a %H_2 amount.
2) The sensor temperature (and therefore the platinum electrode temperature) is known.
3) The oxygen partial pressure is calculated directly from the zirconia sensor signal voltage using the standard Nernst equation.

The Rapidox zirconia sensor operates at an average temperature of 664°C so for applications below this temperature the sensor temperature is used in the calculations for determining

the dewpoint. Above 664°C the type K thermocouple (included in the analyser package) is used to measure the operational temperature and calculate the dewpoint based on this measurement. Note that below 500°C kinetic hinderance would mean that hydrogen and oxygen would not re-associate back to steam so the system would no longer be in the assumed equilibrium. Therefore, the calculations are only accurate when operating at elevated temperatures greater than 500°C.

The Rapidox makes live-time calculations of the hydrogen dewpoint based on the formula presented above and shown in Figure 4. As long as the correct hydrogen value has been dialled in to the analyser by the operator, the display will show the oxygen reading as well as the dewpoint calculation, together with the operator entered hydrogen level:
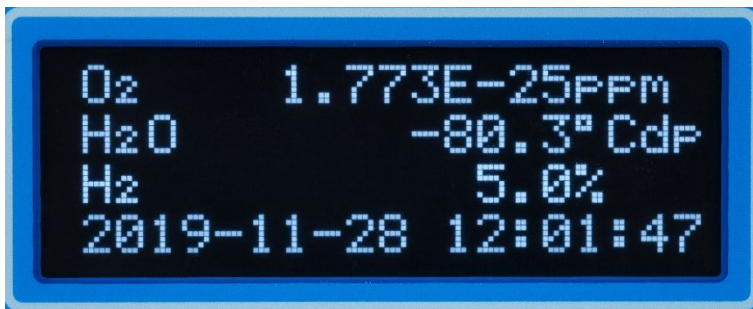

Figure 5: Example screen shot of the Rapidox FGA operating in 5% hydrogen forming gas and displaying a dewpoint of -80°Cdp based on the thermodynamic calculations in this paper.

8   References

1. N. Bredz and C. C. Tennenhouse, *Metal-metal Oxide-hydrogen Atmosphere Chart for Brazing or Bright Metal Processing*, Supplement to The Welding Journal, May 1970

2. http://oxygen.atomistry.com/dissociation_of_steam.html

3. Don W. Green & Robert H. Perry, *Perry's Chemical Engineers' Handbook, Eighth Edition (Chemical Engineers Handbook)*, 1934