Hot Zone Nitrogen-Hydrogen Atmosphere Monitoring with Gas Density Sensor

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Abstract

Nitrogen-Hydrogen atmosphere is the most popular hot zone atmosphere for continuous sintering furnace. It balances oxidizing gas components in the atmosphere, such as residual oxygen and moisture, to ensure the reducing potential of hot zone atmospheres to avoid oxidation and de-carb of sintered parts at high temperature. Dew point (DP) measurement is widely used help maintaining an ideal hot zone atmosphere. However, if the gas sampling system is not well designed, dew point sensors can be easily damaged after being exposed to toxic and 'dirty' sampled hot zone atmosphere. A secondary atmosphere monitoring sensor can always help to monitor the furnace atmosphere and the health of dew point sensor. Air Products invented a quartz based gas density sensor for this application. It has been successfully tested and installed in several sintering furnaces which run nitrogen-hydrogen blends as hot zone atmosphere.

Introduction

Since the late 1970's the use of Nitrogen/Hydrogen systems has become one of the atmosphere choices for sintering of iron and steel powder metal (PM) parts. The original motivation for the switch from conventional natural gas based endothermic atmosphere was due to natural gas shortages. With time, the additional benefits of inherent safety, higher properties, better economics and increased reliability became the reasons for the adoption and popularity of the nitrogen based atmospheres. [1-2]

With increasing demands on the properties of sintered components used in the automotive industry, it was not sufficient just to obtain better properties, but imperative to obtain the same properties consistently. The final properties of sintered components are determined by a multitude of processing variables such as powder particle size and size distribution, composition and purity, and carbon content. Additional variables that influence the end results include, type and amount of lubricants, compaction densities, and furnace parameters (temperature, time at temperature, cooling rates and belt loading.). Often overlooked is the sintering atmosphere as a variable. While most of the variables mentioned earlier are determined during the design stage of the component, it is the atmosphere that can change or can be made to change as a function of time, thereby influencing the final properties and their consistency. The sintering mechanisms and sub processes taking place inside the furnace in the presence of a controlled atmosphere include:

- reducing specific surface area and rounding of pores
- increasing number and strength of inter-metallic bonds
- decreasing pore volume/increasing density
- alloying and homogenization
- eliminating/reducing lattice defects

Sintering Atmosphere Control

In blended nitrogen-based sintering atmospheres, the incoming composition is relatively stable, but the gas chemistry within the furnace can vary depending on the integrity of the furnace and external factors such as room pressures and exhaust systems. It is also important to be aware that new species of gas are formed within the furnace, even though they were not part of the original supply system.

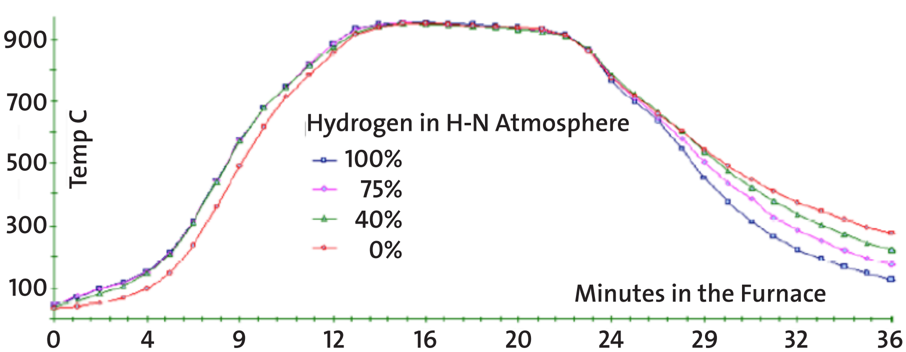
The key functions of atmosphere in the three main zones of the furnace are represented below in Table 1.

Table 1: Key functions of sintering atmosphere [1]

Preheat zone	Lubricant removal, i.e. CxHy + H_2O -> H_2 + CO,
Hot zone	Oxide removal, i.e. FexOy + H_2 ------> Fe + H2O,
Cooling zone	Heat transfer & oxidation prevention

In the pre-heating zone an oxidizing atmosphere is required to react with the hydrocarbon vapors, and prevent sooting or the formation of solid carbon. In the high heat zone the hydrogen to moisture ratio determines the reducing potential and one needs to maintain this ratio as high as possible at the lowest cost. The oxidation/reduction potential determines the rate at which the surface oxides of the powder particles are reduced, and this directly influences the sintering or bonding between the particles as well as hardenability and product performance, that is, strength and corrosion resistance. In the cooling zones the primary atmosphere function is to prevent oxidation and maximize cooling rates. Generally, nitrogen by itself does an effective job of keeping oxygen out of the furnace; however, with sinter hardening considerations, we can increase the cooling rates significantly by adding hydrogen in this zone. Bowe [3] examined the effect of hydrogen on the heating and cooling rates and the results are shown in Figure 1. [1]

Figure 1. Higher hydrogen content in sintering furnaces increases heating and cooling rate [3]



Since atmosphere plays a critical role in the final quality and properties of the sintered part, it is also important to be able to control the atmosphere through direct or indirect control of the variables of an atmosphere system. The primary variables in an atmosphere system are [1-2]:

- composition
- flow rates and distribution
- pressure inside the furnace
- exit velocity
- stability (external influences)
- door opening (part height)
- furnace curtain design

In most practices, a well-designed gas flow control panels are believed to be enough for furnace operators to precisely monitor and control the mixing of different gases that make up the required atmosphere system. Measurement of atmosphere DP is also widely used to provide meaningful data to help sintering furnace operators to monitor water vapor concentration in N_2/H_2 atmosphere and optimize other process parameters.

However, there are still many considerations in order to produce and maintain an ideal and consistent sintering furnace atmosphere to ensure better and consistent PM part quality. Firstly, most of the gas flow control panels for sintering furnace are using variable area flowmeters (rotameters). Before they are installed, they are normally calibrated at 70F and 14.7psia. Seasonal temperature changes could make a difference (~3% change in flow reading with 15F temperature change) when going from winter to summer. Secondly, the sintering furnace is not an ideal environment for DP measurement sensors and probes. The temperatures involved are beyond the operating limits of most sensors, and the furnace environment may contain chemical vapors and contaminants such as oils, salts, and particulates. Special sampling systems typically are required to enable the DP sensors to be used for furnace atmospheres, especially for continuous measurement. If the gas sampling system is not well designed for DP sensor, it can be easily damaged after being exposed to toxic and 'dirty' sintering furnace atmosphere, especially from the hot zone.

If a hydrogen sensor can be installed together with a DP sensor, the H_2/H_2O ratio, which measures the reducing capacity of furnace atmosphere, can be calculated directly. Additionally, the hydrogen sensor can act as a backup furnace atmosphere measurement and can indicate the health of the DP sensor.

Gas Density Sensor to Measure N_2/H_2

Rapid and accurate hydrogen gas concentration measurement is essential to alert to the formation of potentially explosive mixtures with air. There are lots of technologies that have been developed and demonstrated for the detection and measurement of hydrogen gas. [4] However, most of them are not used by customers because of high cost and intensive maintenance. Simpler and universal solutions are in many cases more desirable and often more straightforward to implement as a plug-in sensor system.

In this study, as shown in Figure 2, a quartz based gas density sensor is developed and evaluated in industrial practice.

Figure 2. Air Products gas density sensor

The Air Product gas density sensor comprises a pressure sensor, a density sensor and a temperature sensor. With the readings of these three sensors, the molecular weight of a binary gas mixture can be calculated with the following equation (1):

$$MW_{mixture}=\rho RT/P \qquad (1)$$

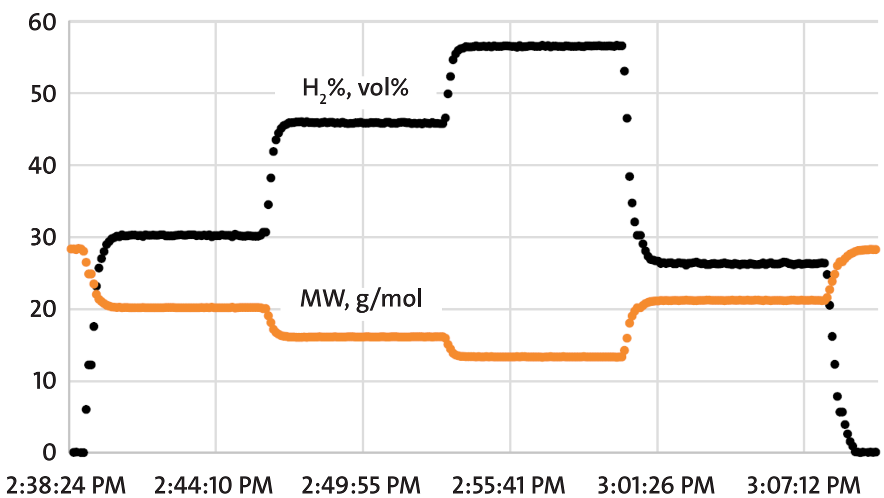
The molecular weight of nitrogen and hydrogen are well known as 28.013g/mol and 2.016g/mol respectively. So, the hydrogen concentration in nitrogen/hydrogen binary mixtures can be calculated with following equation (2):

$$H_2\_concentration=(28.013-MW_{mixture})/(28.013-2.016) \qquad (2)$$

Inside the sensor, there is an in-built micro-processor, which can run the calculations. The data and sensor parameters can be transferred between the sensor and a computer or other devices through RS-485 communication cable.

Because the sensor measures the gas density directly, the response time of this sensor to atmosphere composition change is very short. Fig.3 gives an example of using this gas density sensor for nitrogen-hydrogen mixture composition measurement. It registers any small composition fluctuation in a few seconds.

Figure 3. Quick response of Air Products gas density sensor to nitrogen-hydrogen atmopshere composition changes

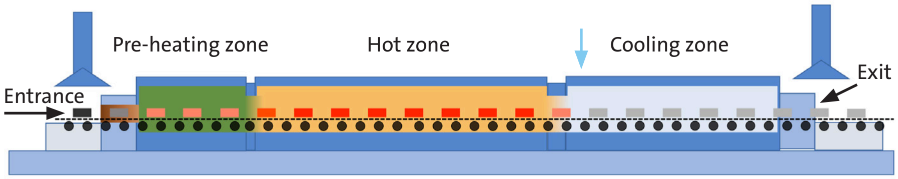


Case Study: Continuous Atmosphere Monitoring in a Sintering Furnace with Gas Density Sensor

Figure 4. shows a typical continuous sintering furnace design. Atmosphere quality plays a key role in the final properties of a sintered part. As we discussed before, different furnace zones require varying degrees of oxidizing or reducing potential to develop optimum final sintered part properties. Generally, a reducing and carbon-neutral atmosphere is desired in the hot zone for ferrous parts.

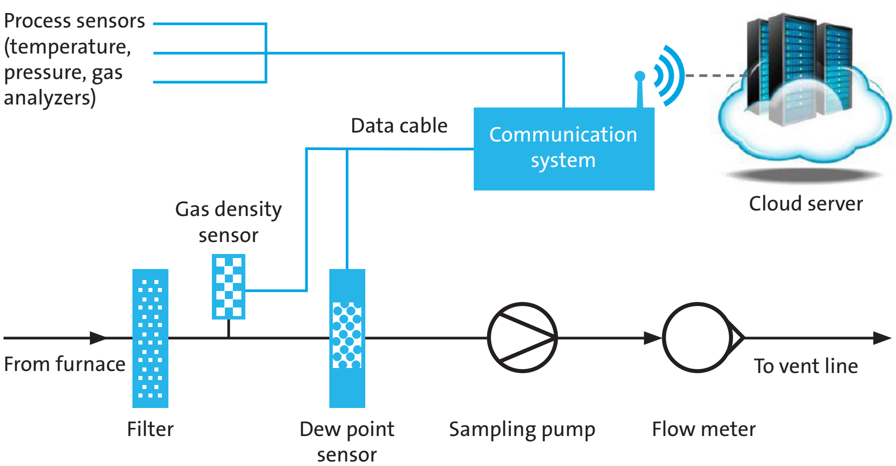
In the hot zone, the hydrogen-to-moisture ratio determines reducing potential of the hot zone atmosphere. Moisture is simply a product of powder oxides reduced by hydrogen introduced into the furnace, as well as belt reduction and air ingress. Properties of sintered parts, such as surface hardness and strength, are affected if uncontrolled carburizing or de-carburizing occurs. For example, in nitrogen and hydrogen sintering atmospheres, a hot zone an atmosphere DP below –30°F is ideal for common steel grades used in gear manufacturing. Thus, monitoring and controlling hot-zone atmosphere DP is necessary for better sintering process control and production cost control. [5] In this case, other than the DP sensor, a gas density sensor is also installed to continuously measure the hydrogen percentage inside the hot zone.

Figure 4. Typical design of continuous sintering furnace [5]



Unlike most other hydrogen analyzers, the Air Products gas density sensor can be easily installed in the current sampling line of the sintering furnace. As Figure 5 shows, this installation also features a wireless/cloud-server data storage function.

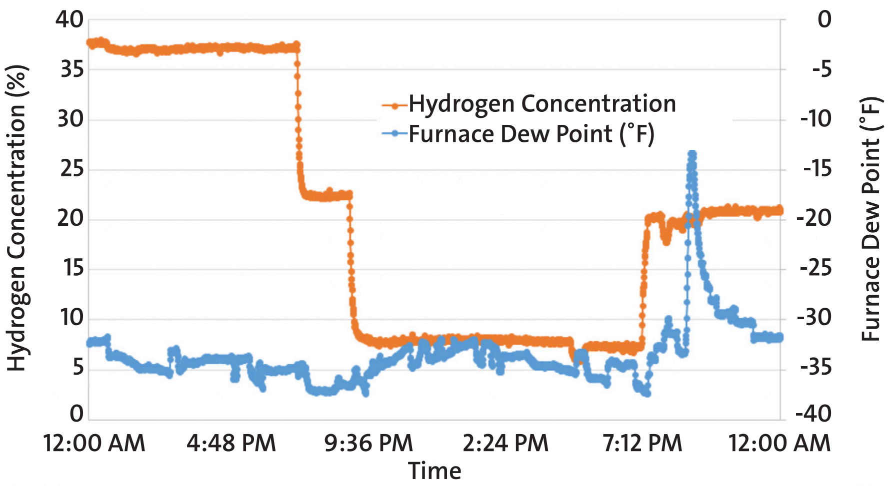
Figure 5. Schematic of hot zone atmosphere monitoring system



Readings of dew point sensors and gas density sensors and other furnace operating parameters can be recorded and sent to a local or cloud server continuously. Process engineers can observe the current furnace atmosphere and furnace operation locally on the screen of the unit or review historical data archived on the cloud server and accessible in the form of customized reports. Stored historical data can help furnace operators or process engineers to identify and address furnace operation issues quickly and proactively. Analysis of sensor readings could also help to facilitate planning furnace shutdowns and scheduling preventive maintenance, which saves the cost of unnecessary maintenance work and reduces the possibility of unexpected downtime.

In the experiments at Ames Reese, it was found that monitoring only dew point may not be enough to ensure a quick and accurate response to changes in furnace atmosphere, especially a hydrogen flow change. For example, Figure 6 shows how the dew point and hydrogen concentration changed in one test.

Figure 6. Measurement results of dew point (°F) and hydrogen concentration (%) in one-day experiment



In this one-day test, the hydrogen concentration inside the hot zone is increased from 8% to 38% on purpose by adjusting the hydrogen flow rate. However, the dew point measurement results cannot tell the furnace operator that the hot zone atmosphere is experiencing such a big hydrogen flow change: 1) the dew point reading shows minimal change when we lower the hydrogen concentration from 38% to 8%; 2) when the hydrogen concentration is increased from 8% to 22% after 10 hours of stability of hot zone atmosphere, the dew point sensor shows a slight increase and an abnormal peak about two hours later after the flow meter adjustment; 3) after another three hours, the dew point sensor starts to show a relatively stable dew point reading, around -32 °F, which is very close to what it was showing when hydrogen concentration was only 8% in hot zone. So, if the furnace operator watches the dew point sensor only, it is hard to identify the changes coming from abnormal hydrogen flow changes.

As discussed previously, in the hot zone, moisture is simply a product of powder oxides reduced by hydrogen introduced into the furnace, as well as belt reduction and air ingress. So, even if the hydrogen flow rate changes, the amount of moisture that is produced from the chemical reactions will not change because the amount of oxygen does not change. Therefore, dew point does not change when hydrogen concentration decreases. When the hydrogen concentration goes up suddenly, the balance among all chemical reactions and the balance of inside atmosphere flow pattern is upset. Then, the abnormal dew point changes and re-stabilization of hydrogen concentration are observed. So, it is very important if the hydrogen concentration inside hot zone can be measured or monitored continuously.

Conclusions

In sintering furnaces, continuous measurement and control of furnace atmosphere is increasingly important to improve quality control, reduce costs and comply with regulatory requirements. Continuously measuring dew point and hydrogen concentration together gives the furnace operator an opportunity to know the furnace atmosphere composition and furnace flow pattern better. Air Products has developed a novel gas density sensor and successfully implemented it for hydrogen concentration measurement of hot zone nitrogen-hydrogen atmosphere. The first Air Products gas density sensor has been running at Ames Reese for more than eighteen months without any technical issue and calibration drift.

Air Products' continuous furnace atmosphere measurement system is designed to overcome common obstacles to analyzing heat treating atmospheres. The system can also be upgraded with an atmosphere control function to automatically adjust flow rates of process gases.

Acknowledgments

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References

[1] Thomas Philips, John J. Dwyer, Jr. and Zbigniew Zurecki. Controlling properties of sintered steel powder metal components using atmosphere composition as a variable. http://www.airproducts.com. 2017

[2] Thomas Philips, John J. Dwyer, Jr. and Zbigniew Zurecki. Techniques and tips to optimize, control and stabilize the atmosphere inside a continuous sintering furnace. http://www.airproducts.com. 2017

[3] Donald J. Bowe, Air Products & Chemicals Inc. MPIF Sinter Hardening Seminar, Cleveland, OH April 13, 1999

[4] T Hübert, L. Boon-Brett, G. Black and U. Banach. Hydrogen sensors – A review. Sensors and Actuators B, 157 (2011). Page 329-352

[5] Liang He, Donald Bowe, Philips Thomas and Ranajit Ghosh. Improved Reliability of Dew Point Measurements of Furnace Atmosphere on a Continuous Basis. Heat Treating 2017, Columbus, OH.

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