Advanced Atmosphere Control System for Improving Annealing of Steel Components

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Abstract

Carbon steel components have been routinely annealed or heat treated in nitrogen-hydrogen atmospheres to relieve stress, alter microstructure and/or improve surface appearance for a number of years. The flow rate and composition of nitrogen-hydrogen atmosphere to be used for annealing components in furnaces are usually determined by a trial and error approach. Once the atmosphere flow rate and composition that produces parts with acceptable quality have been determined, they are generally fixed for future annealing operations. Although the composition of nitrogen-hydrogen atmosphere introduced into a furnace does not change with time, the true reducing or oxidizing potential of the atmosphere inside the furnace changes continuously with time due to leaks and drafts in the furnace, desorption of impurities such as moisture from the surface of components or decomposition of lubricant present on the surface of components being annealed. This continuous change in reducing or oxidizing potential of the atmosphere inside the furnace provides a great difficulty to commercial heat treaters and parts producers to produce annealed components with good and consistent quality and compete effectively in the global market. Therefore, to provide operational flexibility to commercial heat treaters and parts producers in terms of (1) controlling the true reducing or oxidizing potential of the atmosphere inside the furnace and (2) improving quality of annealed components, Air Products has developed an advanced control system currently being marketed under the trade name Purifire®AN. This paper will describe in detail design and operation of the system for monitoring and regulating the true reducing or oxidizing potential of the atmosphere inside a continuous furnace to produce annealed carbon steel components with good and consistent quality.

Introduction

Low- and high- carbon steel components are routinely annealed or heat treated after machining or mechanical fabrication to relieve stress, alter microstructure and/or improve surface appearance. They are typically annealed either in batch furnaces such as bell furnaces or continuous furnaces such as mesh-belt and roller hearth-furnaces in the presence of an atmosphere that is non-oxidizing or reducing in nature to components. These atmospheres are either produced on-site using exothermic generators or supplied by blending nitrogen and hydrogen. Since exothermic atmospheres are produced by partial oxidation of a hydrocarbon gas in air and the composition of both air and a hydrocarbon gas change continuously with time, it is difficult to produce and supply exothermic atmospheres with consistent quality and composition. This is the prime reason that a number of manufacturers have switched to blended nitrogen-hydrogen atmospheres from exothermically generated atmospheres.

Although it is preferred to anneal carbon steel components in continuous furnaces to increase throughput and productivity, large components such as coils of steel wires and strips are still being annealed in batch furnaces. In many cases, the operators of these batch furnaces have opted to use pure hydrogen for annealing these large components to utilize superior thermal or heat transfer properties of hydrogen and improve productivity by shortening heating and cooling times. Since the thrust of this paper is annealing in nitrogen-hydrogen atmospheres, batch annealing of steel components in pure hydrogen atmosphere will not be addressed anymore.

A typical annealing process involves heating components to a pre-determined temperature, holding them at this temperature for a pre-determined time, and thereafter cooling them. Since carbon steel components are exposed to elevated temperatures, it is important to select the right atmosphere flow rate and composition both in batch and continuous furnaces to avoid surface oxidation and decarburization. The right atmosphere flow rate and composition are usually determined by a trial and error approach because of a lack of set standards for designing annealing furnaces. Once the right atmosphere flow rate and composition are determined, they are generally fixed for future annealing operations.

Although the composition of nitrogen-hydrogen atmosphere introduced into the furnace does not change with time, the true reducing or oxidizing potential of the atmosphere inside the furnace changes continuously with time due to leaks and drafts in the furnace, desorption of impurities such as moisture from the surface of components or decomposition of lubricant present on the surface of components being annealed. Therefore, an advanced control system has been developed for monitoring and regulating the true reducing or oxidizing potential of the atmosphere inside the furnace. This paper will describe in detail design and operation of the system for monitoring and regulating the reducing or oxidizing potential of the atmosphere inside a continuous furnace while annealing carbon steel components.

Reducing or Oxidizing Potential of Atmosphere

The effectiveness of a nitrogen-hydrogen atmosphere is generally determined by its reducing or oxidizing potential, which is commonly determined by the ratio of partial pressure of moisture to partial pressure of hydrogen present in the atmosphere. Since the nitrogen-hydrogen atmospheres is produced by blending pure nitrogen with pure hydrogen with specifications shown in Table 1, the blended atmosphere contains very low levels of impurities in the form of residual oxygen and moisture and is non-oxidizing and non-decarburizing to steel components.

Although the flow rate and composition of nitrogen-hydrogen atmosphere introduced into the furnace is fixed, the true atmosphere composition inside the furnace changes continuously with time due to leaks and drafts in the furnace, desorption of impurities such as moisture from the surface of components or decomposition of lubricant present on the surface of components being annealed. These undesirable factors change the effective moisture level or dewpoint of the atmosphere inside the furnace, sometimes making the atmosphere oxidizing to iron and alloying elements present in the carbon steel components. The oxidation of iron and alloying elements by moisture can be represented by the following reactions:

$$3\,Fe + 4\,H_2O \rightarrow Fe_3O_4 + 4\,H_2 \qquad (1)$$

$$Fe + H_2O \rightarrow FeO + H_2 \qquad (2)$$

$$x\,Me + y\,H_2O \rightarrow Me_xO_y + y\,H_2 \qquad (3)$$

Where, Me represents an alloying element.

In reality, however, the oxidizing potential of the moisture is counterbalanced by the reducing potential of hydrogen present in the atmosphere. Therefore, the true reducing or oxidizing potential of the atmosphere present inside the furnace is determined by the ratio of partial pressure of moisture to partial pressure of hydrogen (Kp), as represented by the following expression:

$$Kp = pH_2O/pH_2 \qquad (4)$$

Numerous studies have been carried out by researchers in the past to (1) establish relationship between Kp and the furnace operating temperature and (2) identify the safe furnace operating conditions, i.e., the operating conditions that would anneal carbon steel components with a non-oxidized surface finish. These relationships for iron and alloying elements that could be present in the carbon steel components have been shown in Figures 1a and 1b, respectively. These figures indicate that a low Kp value (or a low moisture content) is required for the atmosphere present in the furnace to be reducing to iron and alloying elements. They also show that a slightly higher level of Kp (or moisture content) can be tolerated while maintaining reducing potential of the atmosphere in the furnace but only at higher operating temperatures. This relationship between Kp and operating temperature has been used as a basis to design and build an advanced atmosphere monitoring and control system.

Reducing or Oxidizing Potential of Atmosphere Present Inside a Continuous Furnace

The observed values of Kp inside a continuous furnace is plotted in Figure 2 to show the impact of atmosphere composition (or more specifically Kp) on the quality of annealed carbon steel components. The required values of Kp to produce non-oxidized annealed components in this furnace are also plotted in this figure. The furnace consisted of a pre-heating zone, an annealing zone operated at a temperature greater than 900°C, and a water cooled cooling zone. A fixed flow rate of nitrogen-hydrogen atmosphere with a known composition was introduced into the furnace through a transition zone located between the heating and cooling zones, as shown in Figure 2. A part of the fresh atmosphere traversed through the cooling zone and exited the furnace through the exit end. The remaining part traversed through the heating and pre-heating zones and exited the furnace through the feed end.

Low values of Kp, even lower than required to produce annealed components with a reduced or bright surface finish, were noted in the high heating and cooling zones of one of the furnaces (see Figure 2). However, the Kp value in the pre-heating zone was considerably higher than the value required for the atmosphere to be reducing in nature. The presence of high Kp value (or high level of moisture) in the pre-heating zone of the furnace was caused by desorption of moisture from the surface of components. This condition could have not been judged or identified by the composition of the fresh nitrogen-hydrogen atmosphere introduced into the furnace. Consequently, the carbon steel components annealed in this furnace had a matte surface finish instead of a bright surface finish – they were oxidized in the pre-heating zone and reduced in the high heating zone. Besides producing annealed components with a matte surface finish, the presence of high moisture content in the pre-heating zone of the furnace resulted in partially decarburizing annealed components. Although there are better and more cost-effective solutions for the problem observed in this furnace, it was nonetheless solved by significantly increasing the overall atmosphere flow rate.

Advanced Atmosphere Monitoring and Control System

The problem describes above could have been identified very early on and resolved without producing any poor quality components had there been a system to continuously monitor and control the reducing or oxidizing potential of the atmosphere inside the furnace. The system could have identified the presence of high moisture content or high value of Kp in the pre-heating zone of the furnace and counterbalanced it by adding additional amount of hydrogen in the pre-heating zone rather than significantly increasing the overall atmosphere flow rate. Problems similar to that discussed above were the driving force for Air Products to develop and commercialize an advanced atmosphere monitoring and control system.

The advanced atmosphere monitoring and control system consists of a nitrogen and hydrogen gas flow panel, a dedicated oxygen probe and a PLC-based control panel to regulate flow rates of nitrogen and hydrogen introduced into a furnace (see Figure 3). The gas flow panel is also equipped with a flow line to introduce an oxidizing component into certain sections of the furnace for operations that require maintaining a desired level of an oxidizing potential in the atmosphere such as annealing of electrical laminations. The oxygen probe is used to determine or calculate value of Kp in the atmosphere present inside the furnace.

The oxygen probe was selected to calculate Kp value in the furnace atmosphere because it (1) is more reliable than an instrument used to measure moisture content, (2) has a very short response time, (3) can be programmed to provide a direct value of Kp without measuring hydrogen content, and (4) can be used to provide close to a continuous measurement. The Kp value was calculated directly from an electromotive force (emf) output of the oxygen probe using the procedure described in detail below.

The emf output from the oxygen probe is used to determine equilibrium partial pressure of oxygen in the atmosphere using the following equation:

$$E = 2.303 * \frac{R * T}{4 F} * \log \frac{P_{O2}}{P'_{O2}} \quad (5)$$

Where,

E is emf output from the oxygen probe,

T is probe operating temperature,

R is gas constant,

F is Faraday's constant,

Po_2 is partial pressure of oxygen in the furnace atmosphere, and

$P'o_2$ is partial pressure of oxygen in reference air.

It is well known that any oxygen present in the furnace atmosphere is in equilibrium with hydrogen as per the following reaction:

$$2 H_2O \leftrightarrow 2 H_2 + O_2 \quad (6)$$

Since the equilibrium constant (K) value for reaction (6) is well known at various oxygen probe operating temperatures, it can be used to correlate partial pressure of oxygen in the furnace atmosphere to Kp value according to the following equation:

$$K = \frac{p^2H_2 * pO_2}{p^2H_2O} \quad (7)$$

or

$$Kp = pH_2O/pH_2 \quad Kp = (pO_2/K)^{1/2} \quad (8)$$

The calculated value of Kp is compared to the value of Kp that is required to maintain a reducing potential inside the furnace. The system then automatically regulates the flow rate of a reducing gas such as hydrogen or an oxidizing gas to bring the calculated value of Kp close to the required value of Kp. In case the calculated value of Kp is close to the required value of Kp the system optimizes the overall atmosphere consumption by regulating the total atmosphere flow rate. The system provides an alarm if the atmosphere composition drifts to a range that is not desirable from the safety point of view. Finally, the system automatically saves information about processing parameters for future reference.

The performance of a proto-type system was tested in a continuos mesh belt furnace shown in Figure 3. A two step approach was used to verify the performance of the system. In the first step the applicability of the oxygen probe to reliably determine Kp value of the atmosphere present in the furnace was tested. In the second and last step the ability of the proto-type system to maintain the desired value of Kp in the furnace was tested by allowing the system to regulate flow rates of hydrogen and an oxidizing gas such as humidified nitrogen. Since it was not possible to directly measure Kp in the furnace atmosphere, it was decided to measured directly moisture content in the furnace atmosphere using a highly reliable chilled mirror moisture analyzer and compare it to moisture content calculated indirectly using Kp value from an oxygen probe. The moisture content was calculated by measuring hydrogen concentration in the furnace atmosphere and plugging in hydrogen partial pressure and Kp values in Equation 8. The calculated and measured values of moisture content plotted in

Figure 4 show a linear relationship between them, indicating that an oxygen probe can be used reliably to calculate moisture content or determine Kp value present in the furnace atmosphere. The proto-type system was then tested to maintain the desired Kp value in the furnace atmosphere by automatically regulating flow rate of hydrogen or humidified nitrogen. It was found to react very quickly to maintain the desired Kp value in the furnace atmosphere.

The scope of the proto-type advanced atmosphere monitoring and control system shown in Figure 3 was expanded to design a commercial system shown in Figure 5. This system is capable of monitoring and controlling reducing or oxidizing potential of atmosphere present in a number of furnaces simultaneously.

Conclusions

This paper describes the design and operation of an advanced atmosphere monitoring and control system to continuously monitor and regulate the true reducing or oxidizing potential of the atmosphere present inside a furnace used for annealing carbon steel components. The system was developed with objectives to (1) provide a reliable and consistent reducing or oxidizing potential of the atmosphere inside annealing furnaces and (2) improve quality and consistency of annealed carbon steel components. The system utilizes a gas flow panel, an oxygen probe and a PLC based control panel to monitor and regulate reducing or oxidizing potential of atmosphere present inside a number of continuous annealing furnaces simultaneously. The system appears to be very promising in terms of reducing overall operating cost by improving quality of annealed components and reducing rejects and reworks.

Table 1. Impurities Present in the Pure Nitrogen and Hydrogen Gases and Nitrogen-Hydrogen Atmosphere

Atmosphere Component	Impurities	
	Residual Oxygen, ppm	Moisture Content or Dew Point, °C
Nitrogen	< 5 ppm	< -65°C
Hydrogen	< 5 ppm	< -65°C
Nitrogen-Hydrogen	< 5 ppm	< -65°C

Figure 1a. Equilibrium Phase Diagram (Kp vs. Temperature) for Iron

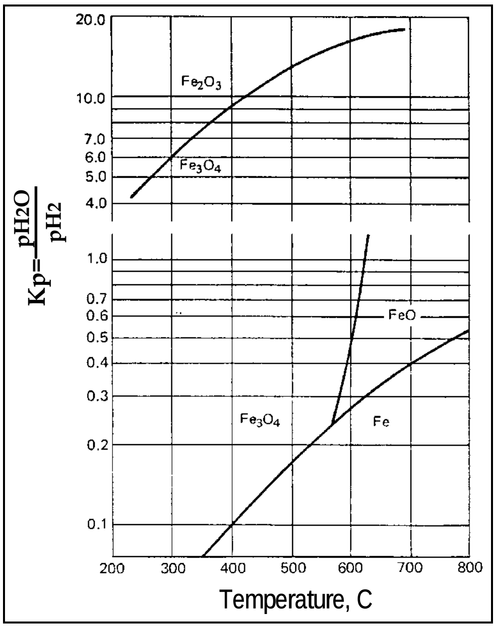

Figure 1b. Equilibrium Phase Diagram (Kp vs. Temperature) for Alloying Elements

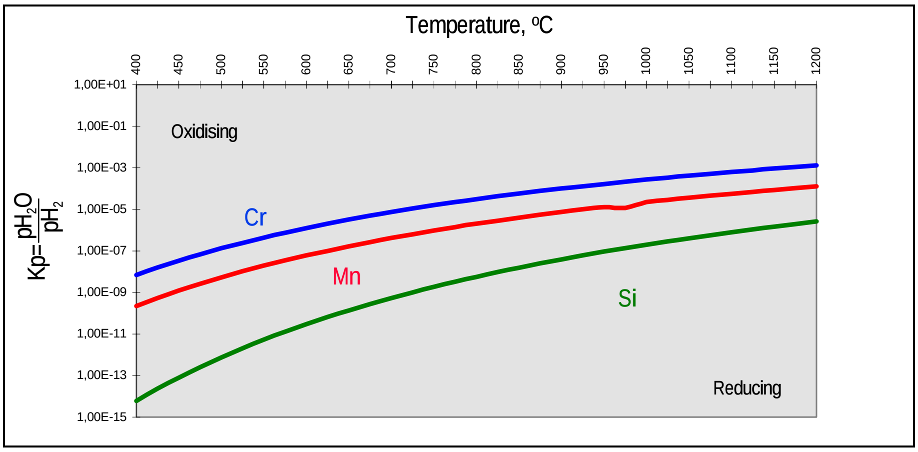

Figure 2. Reducing and Oxidizing Potential of Atmosphere Present Inside a Continuous Furnace

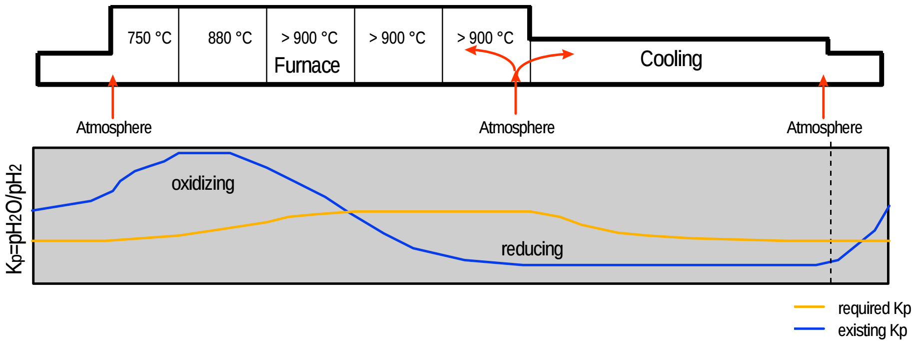

Figure 3. Schematic of the Advanced Atmosphere Monitoring and Control System

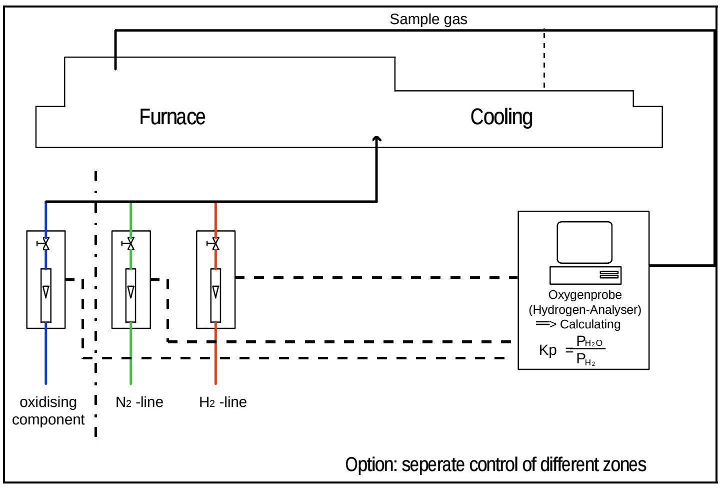

Figure 4. Comparison of Calculated vs. Measured Dew Point in the Furnace Atmosphere

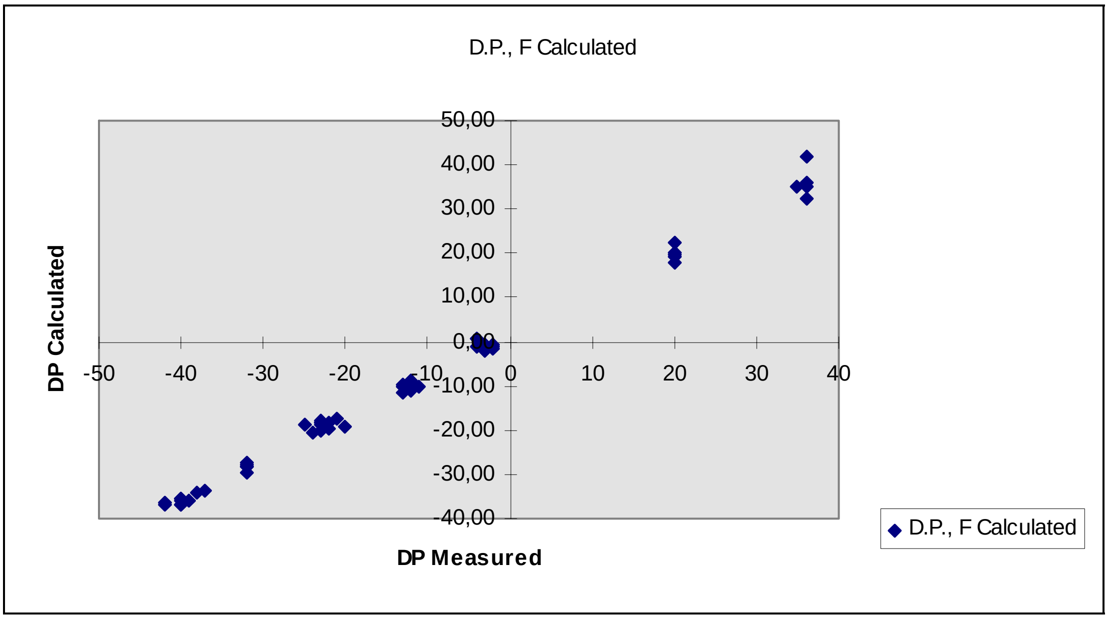

Figure 5 Schematic of a Commercial Advanced Atmosphere Monitoring and Control System